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# ТОНКИЕ ХИМИЧЕСКИЕ ТЕХНОЛОГИИ

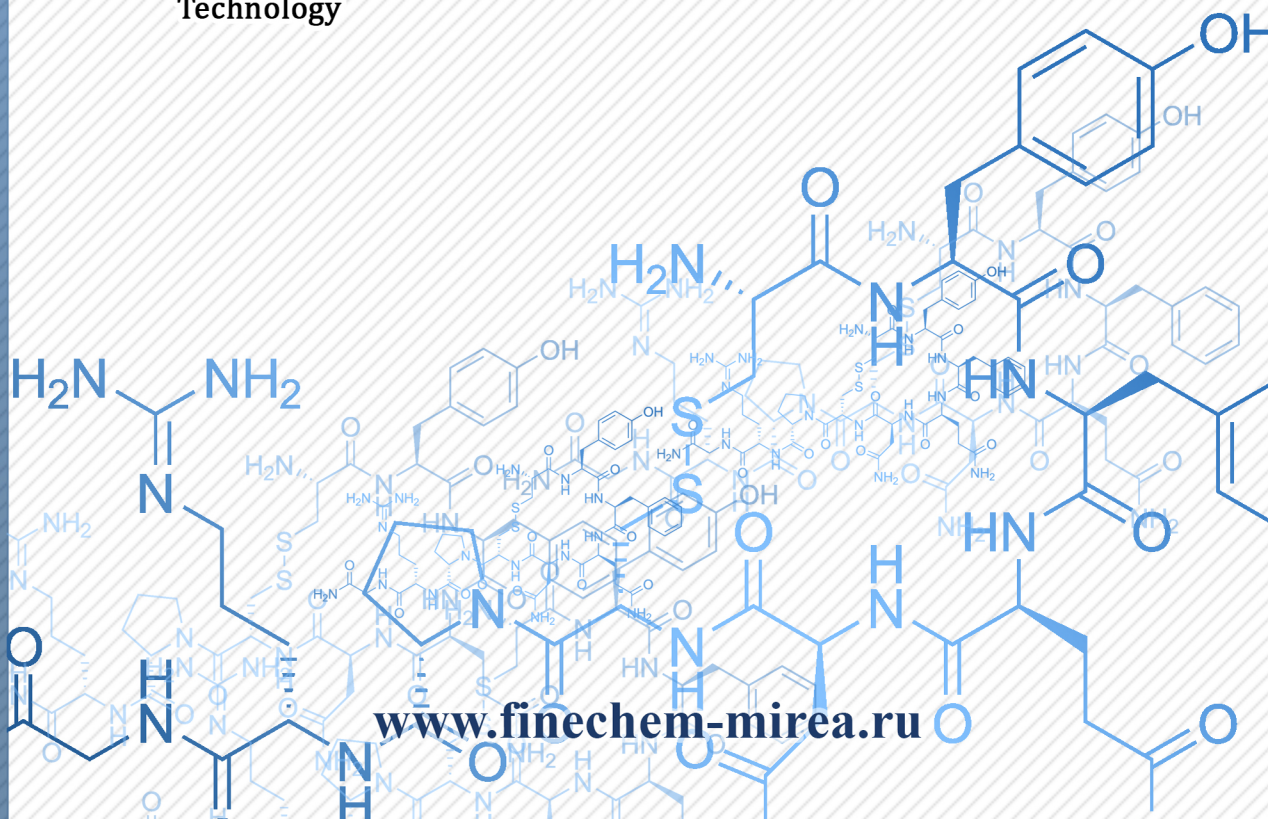
## Fine Chemical Technologies

- | Theoretical Basis of Chemical Technology
- | Chemistry and Technology of Organic Substances
- | Chemistry and Technology of Medicinal Compounds and Biologically Active Substances
- | Biochemistry and Biotechnology
- | Synthesis and Processing of Polymers and Polymeric Composites
- | Chemistry and Technology of Inorganic Materials
- | Analytical Methods in Chemistry and Chemical Technology
- | Mathematical Methods and Information Systems in Chemical Technology

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Theoretical basis of chemical technology  
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RESEARCH ARTICLE

## Liquid–liquid phase equilibrium for the *tert*-butanol–methyl *tert*-butyl ether system with choline chloride-based deep eutectic solvents

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### Abstract

**Objectives.** In comparison with methyl *tert*-butyl ether (MTBE) and methanol mixtures, the separation of MTBE and *tert*-butanol (*tert*-butyl alcohol, TBA) mixtures represents a relevant challenge in chemical technology due to limited research in this area. Our aim was to evaluate the potential and efficiency of using choline chloride-based deep eutectic solvents (DESs) as green extractants for the separation of the MTBE–TBA system via liquid–liquid extraction (LLE).

**Methods.** DESs were prepared by mixing and heating a hydrogen bond acceptor (choline chloride, ChCl) with hydrogen bond donors (HBDs) as follows: malonic acid (1 : 1 molar ratio), glutaric acid (1 : 1), urea (1 : 2), and glycerol (1 : 2). Liquid–liquid phase equilibrium was experimentally studied in four ternary systems containing MTBE, TBA, and DES at temperatures of 293.15 and 313.15 K and atmospheric pressure. The compositions of the equilibrium liquid phases were determined using <sup>1</sup>H nuclear magnetic resonance spectroscopy (500 MHz, dimethyl sulfoxide-*d*<sub>6</sub>).

**Results.** The experimental data allowed the key extraction parameters to be calculated: distribution coefficients for TBA and selectivity for MTBE–TBA separation for each investigated DES. A comparative analysis of the extraction capacity of the synthesized solvents toward the separated components was performed. The experimental phase equilibrium data confirm the fundamental possibility of using the ChCl-based DESs under study as extractants for separating the MTBE–TBA system. The calculated selectivity and distribution coefficient values allow the efficiency of various HBDs within the DES composition to be evaluated for solving this separation task. The comparative analysis of the DES extraction capacity showed a dependence of selectivity on the HBD and a slight dependence of selectivity on temperature. The highest selectivity values were observed for DESs based on ChCl/glycerol (1 : 2) and ChCl/urea (1 : 2) systems.

**Conclusions.** The feasibility of using DESs based on choline chloride with malonic acid, glutaric acid, urea, and glycerol as extractants for separating the MTBE–TBA mixture by LLE method has been experimentally confirmed. The calculated distribution coefficients and selectivity values enable a quantitative assessment and comparison of the efficiency of different DESs for this task, identifying the most promising compositions. The results obtained can be used as the basis for further development and optimization of the LLE process for MTBE and TBA using promising green solvents.

### Keywords

liquid–liquid equilibrium, deep eutectic solvents, methyl *tert*-butyl ether, *tert*-butanol, extraction, selectivity

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#### НАУЧНАЯ СТАТЬЯ

## Фазовое равновесие в системах трет-бутанол – метил-трет-бутиловый эфир с глубокими эвтектическими растворителями на основе хлорида холина

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#### Аннотация

**Цели.** Разделение смеси метил-трет-бутилового эфира (МТБЭ) и трет-бутанола или трет-бутилового спирта (ТБС) представляет собой актуальную задачу химической технологии из-за ограниченных исследований в этой области по сравнению со смесью МТБЭ–метанол. Целью данной работы является оценка возможности и эффективности использования глубоких эвтектических растворителей (ГЭР) на основе хлорида холина в качестве «зеленых» экстрагентов для разделения смеси МТБЭ–ТБС методом жидкостно-жидкостной экстракции (ЖЖЭ).

**Методы.** ГЭР были приготовлены методом смешения и нагревания акцептора водородной связи с соответствующими донорами водородной связи в определенных молярных соотношениях. Экспериментально изучено фазовое равновесие жидкость–жидкость в четырех трехкомпонентных системах, содержащих МТБЭ, ТБС и ГЭР на основе хлорида холина в сочетании с малоновой кислотой (1 : 1), глутаровой кислотой (1 : 1), мочевиной (1 : 2) и глицерином (1 : 2). Эксперименты проведены при температурах 293.15 и 315.15 К и атмосферном давлении. Определены составы равновесных жидких фаз методом спектроскопии ядерного магнитного резонанса  $^1\text{H}$  (500 МГц, диметилсульфоксид- $d_6$ ).

**Результаты.** На основе экспериментальных данных рассчитаны ключевые параметры экстракции: коэффициенты распределения для ТБС и селективность разделения МТБЭ–ТБС для каждого из исследованных ГЭР. Проведен сравнительный анализ экстракционной способности исследуемых ГЭР по отношению к разделяемым компонентам. Экспериментальные данные по фазовому равновесию подтверждают принципиальную возможность использования исследованных ГЭР на основе хлорида холина в качестве экстрагентов для разделения смеси МТБЭ–ТБС. Рассчитанные значения селективности и коэффициентов распределения позволяют оценить относительную эффективность различных доноров водородной связи в составе ГЭР для данной задачи разделения. Сравнительный анализ экстракционной способности ГЭР показал сильную зависимость селективности от природы донора водородной связи и ее незначительную зависимость от температуры. Наибольшие значения селективности наблюдались для ГЭР на основе систем хлорида холина с глицерином (1 : 2) и хлорида холина с мочевиной (1 : 2).

**Выводы.** Экспериментально подтверждена возможность использования ГЭР на основе хлорида холина в комбинации с малоновой кислотой, глутаровой кислотой, мочевиной и глицерином в качестве эффективных экстрагентов для разделения смеси МТБЭ–ТБС методом ЖЖЭ. Рассчитанные коэффициенты распределения и селективности позволили количественно оценить и сравнить эффективность различных ГЭР для данной задачи, выявив наиболее перспективные составы. Полученные результаты представляют собой необходимую основу для дальнейшей разработки и оптимизации процесса ЖЖЭ МТБЭ и ТБС с использованием перспективных «зеленых» растворителей.

#### Ключевые слова

равновесие жидкость–жидкость, глубокие эвтектические растворители, метил-трет-бутиловый эфир, трет-бутанол, экстракция, селективность

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## INTRODUCTION

Methyl *tert*-butyl ether (MTBE) and *tert*-butanol (*tert*-butyl alcohol, TBA) are important components in various chemical processes. Despite some recent environmental concerns, MTBE has long been used as a high-octane additive to motor fuels to improve the knock resistance of internal combustion engines and to reduce greenhouse gas emissions [1, 2]. TBA is a valuable intermediate in organic synthesis, capable of acting as a reagent in the synthesis of MTBE from TBA and methanol [3] or in alkylation reactions [4].

The key challenge in separating MTBE and TBA stems from their similar physicochemical properties, such as low polarity and comparable boiling points, which makes conventional methods, e.g., distillation, insufficiently effective for obtaining high-purity products. To address such challenges in industrial conditions, alternative approaches can be employed, including extractive distillation or liquid–liquid extraction (LLE) using selective extractants [5].

It should be noted that various methods for separating the MTBE–methanol binary system, including such techniques as pervaporation using polymer membranes [6, 7] and LLE employing deep eutectic solvents (DES) [8], have already been the subject of a number of studies. However, the separation of the MTBE and TBA system remains a significantly less studied area, which constitutes a current challenge in chemical technology. Therefore, the development of effective methods for separating MTBE–TBA mixtures is of significant practical interest for ensuring high product purity, reagent recycling, and process optimization.

In recent years, significant attention has been focused on the search for and application of green solvents characterized by low volatility, low toxicity, and high potential for regeneration. DESs are among such promising solvents [9, 10]. DESs are mixtures of two or more components (a hydrogen bond acceptor and hydrogen bond donors) with a melting point significantly lower than that of the individual components. Due to their low cost, ease of preparation, low volatility, potential biodegradability, and a wide tunability of properties through component selection [9], DESs are actively used in various fields, including extraction processes [11], organic synthesis [12], catalysis [13], and electrochemistry [14]. The ability of DESs to selectively dissolve various compounds makes them potentially effective extractants for separating complex mixtures, including azeotropic ones.

The task of assessing the feasibility of separating the MTBE–TBA system using DESs as extractants requires knowledge of the phase equilibrium in the corresponding multicomponent systems. Liquid–liquid

equilibrium data are essential, in particular, for selecting a suitable extractant. Despite the growing interest in DESs, experimental data on phase equilibria in ternary systems comprising DES–simple ether–alcohol remain extremely limited in the literature.

This paper presents the results of an investigation into the liquid–liquid phase equilibrium in ternary systems of MTBE–TBA and choline chloride-based DESs. Malonic acid, glutaric acid, urea, and glycerol are used as hydrogen bond donors for the DESs. We set out to evaluate the potential of using these DESs as selective extractants for the separation of the MTBE–TBA system.

## MATERIALS AND METHODS

### Reagents

The following reagents were used in this work: TBA, MTBE, choline chloride, malonic acid, glutaric acid, urea, glycerol. Choline chloride, purchased from *AppliChem* (Germany), was used as the hydrogen bond acceptor. Due to its high hygroscopicity, choline chloride was dried under vacuum for 5 h at 313.15 K prior to use. Malonic acid, glutaric acid, urea, and glycerol (*Vekton*, Russia) were used as hydrogen bond donors. MTBE and TBA were also of commercial origin (*Vekton*, Russia). The sources and purity of all reagents used are presented in Table 1.

### DES preparation

Pre-dried choline chloride and the respective hydrogen bond donors were mixed in 10 mL vials in molar ratios of 1 : 1 for choline chloride with malonic acid and glutaric acid, and 1 : 2 for choline chloride with urea and glycerol [15]. The components were weighed on a Pioneer PA-214C analytical balance (*Ohaus*, USA) with an accuracy of  $\pm 0.1$  mg. The mixtures were vigorously stirred on a magnetic stirrer upon heating using a magnetic stir bar at 323 K (a stirring speed of 300 rpm) until a clear, homogeneous solution was formed (typically 30–60 min), indicating the formation of a DES. The formation of deep eutectic mixtures for all compositions was confirmed by  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy [16]. The synthesized DESs were stored in tightly sealed glass vials at room temperature.

### Phase equilibrium study

Liquid–liquid phase equilibrium experiments were conducted in glass vials (10 mL). Ternary mixtures were prepared by adding precise amounts of MTBE and TBA to a pre-synthesized DES. The mixtures were vigorously stirred on a magnetic stirrer (900 rpm) for

**Table 1.** Purification methods and reagent purity

| Chemical name    | Source           | Purity | Purification method | Analysis method |
|------------------|------------------|--------|---------------------|-----------------|
| MTBE             | <i>Vekton</i>    | 0.990  | No                  | GC              |
| TBA              | <i>Vekton</i>    | 0.990  | No                  | GC              |
| Glutaric acid    | <i>Vekton</i>    | 0.990  | No                  | NMR             |
| Malonic acid     | <i>Vekton</i>    | 0.990  | No                  | NMR             |
| Urea             | <i>Vekton</i>    | 0.990  | No                  | NMR             |
| Glycerol         | <i>Vekton</i>    | 0.980  | No                  | NMR             |
| Choline chloride | <i>AppliChem</i> | 0.960  | Drying              | NMR             |

Note: GC—gas chromatography; NMR—nuclear magnetic resonance.

4–6 h at a specified temperature, maintained using a thermostated water bath (accuracy  $\pm 0.1$  K), to achieve effective mass transfer and establish equilibrium. After stirring, the mixtures were allowed to settle for at least 10 h to ensure complete phase separation. The presence of a clear interface between the upper organic phase and the lower DES phase was visually confirmed. The composition of each coexisting phase was determined by  $^1\text{H}$  NMR spectroscopy. Measurements were performed at 298.15 K in dimethyl sulfoxide- $d_6$  on an AVANCE III spectrometer (500 MHz, *Bruker*, Germany). Spectra were processed using the TopSpin 4.0 software. Quantitative analysis was carried out by integrating the characteristic proton signals of each component in both phases.

## RESULTS AND DISCUSSION

In this study, experimental liquid–liquid phase equilibrium data for the ternary systems of TBA–MTBE–DES were obtained at temperatures of 293.15 and 313.15 K and atmospheric pressure. The following DES systems were used: choline chloride/malonic acid (1 : 1), choline chloride/glutaric acid (1 : 1),

choline chloride/urea (1 : 2), and choline chloride/glycerol (1 : 2). The separation efficiency of the DES for the investigated mixtures was evaluated using the distribution coefficient of a component ( $\beta_i$ ) and selectivity ( $S$ ), calculated according to equations (1) and (2):

$$\beta_i = \frac{\omega_i^{\text{II}}}{\omega_i^{\text{I}}}, \quad (1)$$

$$S = \frac{\omega_i^{\text{I}} \omega_j^{\text{II}}}{\omega_i^{\text{II}} \omega_j^{\text{I}}}, \quad (2)$$

wherein  $\omega_i$  is the mass fraction; I and II are the organic phase and DES phase, respectively;  $i$  and  $j$  are indices corresponding to the system components. The results are presented in Tables 2–7, where  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  are the mass fractions of TBA, MTBE, and choline chloride, respectively;  $\beta_1$  is the distribution coefficient of the alcohol;  $\beta_2$  is the distribution coefficient of the simple ether;  $S$  is the selectivity. In all experiments, the standard uncertainty of the experimental temperature determination was 0.05 K; the standard uncertainty of atmospheric pressure measurement was 1.5 kPa; and the standard uncertainty of concentration determination was 0.005 mass fractions.

**Table 2.** Experimental data on the liquid–liquid phase equilibrium in the TBA–MTBE–DES (choline chloride/malonic acid) system at 293.15 K and atmospheric pressure

| Organic phase |            |            | DES phase  |            |            | $\beta_1$ | $\beta_2$ | $S$ |
|---------------|------------|------------|------------|------------|------------|-----------|-----------|-----|
| $\omega_1$    | $\omega_2$ | $\omega_3$ | $\omega_1$ | $\omega_2$ | $\omega_3$ |           |           |     |
| 0.000         | 1.000      | 0.000      | 0.000      | 0.004      | 0.570      | –         | –         | –   |
| 0.077         | 0.855      | 0.000      | 0.005      | 0.005      | 0.576      | 0.060     | 0.006     | 9.8 |
| 0.114         | 0.818      | 0.000      | 0.011      | 0.009      | 0.564      | 0.097     | 0.011     | 8.8 |
| 0.162         | 0.766      | 0.000      | 0.015      | 0.015      | 0.557      | 0.093     | 0.019     | 4.9 |
| 0.230         | 0.698      | 0.000      | 0.017      | 0.013      | 0.560      | 0.072     | 0.018     | 4.0 |
| 0.320         | 0.580      | 0.000      | 0.023      | 0.013      | 0.562      | 0.070     | 0.023     | 3.1 |
| 0.379         | 0.527      | 0.000      | 0.025      | 0.016      | 0.574      | 0.066     | 0.030     | 2.2 |
| 0.433         | 0.472      | 0.000      | 0.030      | 0.016      | 0.596      | 0.070     | 0.033     | 2.1 |
| 0.503         | 0.372      | 0.000      | 0.031      | 0.014      | 0.572      | 0.062     | 0.037     | 1.7 |

*Note.* Notations in Tables 2–7:  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  are the mass fractions of TBA, MTBE, and choline chloride, respectively;  $\beta_1$  is the distribution coefficient of alcohol;  $\beta_2$  is the distribution coefficient of ether;  $S$  is the selectivity. Standard uncertainty of the experimental temperature is 0.05 K. Standard uncertainty of atmospheric pressure measurement is 1.5 kPa. Standard uncertainty of concentration is 0.005.

**Table 3.** Experimental data on the liquid–liquid phase equilibrium in the TBA–MTBE–DES (choline chloride/malonic acid) system at 313.15 K and atmospheric pressure

| Organic phase |            |            | DES phase  |            |            | $\beta_1$ | $\beta_2$ | $S$ |
|---------------|------------|------------|------------|------------|------------|-----------|-----------|-----|
| $\omega_1$    | $\omega_2$ | $\omega_3$ | $\omega_1$ | $\omega_2$ | $\omega_3$ |           |           |     |
| 0.000         | 0.936      | 0.000      | 0.000      | 0.008      | 0.568      | –         | –         | –   |
| 0.068         | 0.860      | 0.000      | 0.005      | 0.007      | 0.575      | 0.070     | 0.008     | 8.4 |
| 0.118         | 0.809      | 0.000      | 0.007      | 0.008      | 0.578      | 0.058     | 0.010     | 6.0 |
| 0.167         | 0.745      | 0.000      | 0.013      | 0.012      | 0.575      | 0.080     | 0.016     | 4.9 |
| 0.217         | 0.693      | 0.000      | 0.017      | 0.013      | 0.573      | 0.079     | 0.018     | 4.4 |
| 0.297         | 0.614      | 0.000      | 0.025      | 0.014      | 0.573      | 0.082     | 0.023     | 3.6 |
| 0.367         | 0.546      | 0.000      | 0.025      | 0.012      | 0.589      | 0.069     | 0.023     | 3.0 |
| 0.439         | 0.479      | 0.000      | 0.037      | 0.013      | 0.595      | 0.083     | 0.028     | 3.0 |
| 0.480         | 0.393      | 0.000      | 0.056      | 0.016      | 0.627      | 0.118     | 0.041     | 2.9 |

**Table 4.** Experimental data on the liquid–liquid phase equilibrium in the TBA–MTBE–DES (choline chloride/glutaric acid) system at 313.15 K and atmospheric pressure

| Organic phase |            |            | DES phase  |            |            | $\beta_1$ | $\beta_2$ | $S$ |
|---------------|------------|------------|------------|------------|------------|-----------|-----------|-----|
| $\omega_1$    | $\omega_2$ | $\omega_3$ | $\omega_1$ | $\omega_2$ | $\omega_3$ |           |           |     |
| 0.000         | 0.949      | 0.000      | 0.000      | 0.014      | 0.503      | –         | –         | –   |
| 0.057         | 0.887      | 0.000      | 0.007      | 0.011      | 0.505      | 0.125     | 0.013     | 9.6 |
| 0.117         | 0.793      | 0.000      | 0.015      | 0.011      | 0.526      | 0.127     | 0.014     | 9.3 |
| 0.166         | 0.738      | 0.000      | 0.027      | 0.014      | 0.505      | 0.162     | 0.020     | 8.3 |
| 0.234         | 0.653      | 0.000      | 0.039      | 0.016      | 0.522      | 0.165     | 0.025     | 6.7 |
| 0.303         | 0.576      | 0.000      | 0.048      | 0.017      | 0.515      | 0.159     | 0.030     | 5.3 |
| 0.379         | 0.508      | 0.000      | 0.055      | 0.016      | 0.509      | 0.144     | 0.031     | 4.7 |
| 0.435         | 0.452      | 0.000      | 0.075      | 0.022      | 0.537      | 0.172     | 0.049     | 3.5 |
| 0.491         | 0.394      | 0.000      | 0.089      | 0.022      | 0.534      | 0.181     | 0.055     | 3.3 |
| 0.523         | 0.367      | 0.000      | 0.101      | 0.024      | 0.534      | 0.193     | 0.064     | 3.0 |
| 0.564         | 0.314      | 0.000      | 0.113      | 0.025      | 0.555      | 0.200     | 0.080     | 2.5 |

**Table 5.** Experimental data on the liquid–liquid phase equilibrium in the TBA–MTBE–DES (choline chloride/urea) system at 313.15 K and atmospheric pressure

| Organic phase |            |            | DES phase  |            |            | $\beta_1$ | $\beta_2$ | $S$  |
|---------------|------------|------------|------------|------------|------------|-----------|-----------|------|
| $\omega_1$    | $\omega_2$ | $\omega_3$ | $\omega_1$ | $\omega_2$ | $\omega_3$ |           |           |      |
| 0.000         | 1.000      | 0.000      | 0.000      | 0.000      | 0.527      | –         | –         | –    |
| 0.053         | 0.947      | 0.000      | 0.004      | 0.004      | 0.525      | 0.072     | 0.004     | 18.9 |
| 0.140         | 0.860      | 0.000      | 0.008      | 0.004      | 0.532      | 0.054     | 0.005     | 10.5 |
| 0.233         | 0.767      | 0.000      | 0.010      | 0.005      | 0.530      | 0.044     | 0.007     | 6.5  |
| 0.305         | 0.695      | 0.000      | 0.014      | 0.006      | 0.530      | 0.047     | 0.008     | 5.8  |
| 0.348         | 0.648      | 0.000      | 0.017      | 0.006      | 0.514      | 0.050     | 0.009     | 5.6  |
| 0.390         | 0.607      | 0.000      | 0.026      | 0.008      | 0.532      | 0.068     | 0.013     | 5.3  |
| 0.435         | 0.561      | 0.000      | 0.041      | 0.011      | 0.549      | 0.094     | 0.019     | 5.0  |
| 0.536         | 0.451      | 0.000      | 0.068      | 0.012      | 0.520      | 0.127     | 0.026     | 4.9  |
| 0.609         | 0.373      | 0.000      | 0.097      | 0.013      | 0.498      | 0.159     | 0.034     | 4.7  |
| 0.654         | 0.333      | 0.000      | 0.144      | 0.021      | 0.456      | 0.221     | 0.063     | 3.5  |
| 0.709         | 0.274      | 0.000      | 0.158      | 0.023      | 0.466      | 0.222     | 0.083     | 2.7  |
| 0.777         | 0.200      | 0.000      | 0.174      | 0.021      | 0.464      | 0.224     | 0.107     | 2.1  |

**Table 6.** Experimental data on the liquid–liquid phase equilibrium in the TBA–MTBE–DES (choline chloride/glycerol) system at 293.15 K and atmospheric pressure

| Organic phase |            |            | DES phase  |            |            | $\beta_1$ | $\beta_2$ | $S$  |
|---------------|------------|------------|------------|------------|------------|-----------|-----------|------|
| $\omega_1$    | $\omega_2$ | $\omega_3$ | $\omega_1$ | $\omega_2$ | $\omega_3$ |           |           |      |
| 0.000         | 1.000      | 0.000      | 0.000      | 0.002      | 0.425      | –         | –         | –    |
| 0.053         | 0.947      | 0.000      | 0.004      | 0.002      | 0.421      | 0.070     | 0.002     | 28.5 |
| 0.105         | 0.895      | 0.000      | 0.007      | 0.002      | 0.418      | 0.066     | 0.003     | 24.0 |
| 0.134         | 0.866      | 0.000      | 0.008      | 0.004      | 0.419      | 0.062     | 0.005     | 13.1 |
| 0.207         | 0.793      | 0.000      | 0.013      | 0.006      | 0.416      | 0.061     | 0.007     | 8.4  |
| 0.283         | 0.702      | 0.000      | 0.018      | 0.005      | 0.414      | 0.062     | 0.008     | 8.1  |
| 0.351         | 0.634      | 0.000      | 0.020      | 0.005      | 0.414      | 0.056     | 0.008     | 7.1  |
| 0.412         | 0.571      | 0.000      | 0.022      | 0.005      | 0.416      | 0.053     | 0.009     | 5.8  |
| 0.481         | 0.498      | 0.000      | 0.025      | 0.007      | 0.411      | 0.051     | 0.014     | 3.7  |
| 0.556         | 0.412      | 0.000      | 0.035      | 0.008      | 0.421      | 0.062     | 0.020     | 3.1  |

**Table 7.** Experimental data on the liquid–liquid phase equilibrium in the TBA–MTBE–DES (choline chloride/glycerol) system at 313.15 K and atmospheric pressure

| Organic phase |            |            | DES phase  |            |            | $\beta_1$ | $\beta_2$ | $S$  |
|---------------|------------|------------|------------|------------|------------|-----------|-----------|------|
| $\omega_1$    | $\omega_2$ | $\omega_3$ | $\omega_1$ | $\omega_2$ | $\omega_3$ |           |           |      |
| 0.000         | 1.000      | 0.000      | 0.000      | 0.002      | 0.425      | –         | –         | –    |
| 0.043         | 0.957      | 0.000      | 0.007      | 0.005      | 0.419      | 0.172     | 0.005     | 33.6 |
| 0.105         | 0.895      | 0.000      | 0.009      | 0.003      | 0.420      | 0.090     | 0.003     | 26.0 |
| 0.132         | 0.855      | 0.000      | 0.012      | 0.006      | 0.417      | 0.090     | 0.007     | 13.7 |
| 0.206         | 0.780      | 0.000      | 0.015      | 0.004      | 0.411      | 0.073     | 0.006     | 13.2 |
| 0.309         | 0.675      | 0.000      | 0.015      | 0.007      | 0.408      | 0.050     | 0.011     | 4.7  |
| 0.362         | 0.624      | 0.000      | 0.018      | 0.007      | 0.415      | 0.049     | 0.011     | 4.5  |
| 0.399         | 0.580      | 0.000      | 0.023      | 0.008      | 0.414      | 0.057     | 0.013     | 4.4  |
| 0.480         | 0.494      | 0.000      | 0.027      | 0.009      | 0.417      | 0.057     | 0.017     | 3.2  |
| 0.570         | 0.400      | 0.000      | 0.032      | 0.009      | 0.418      | 0.056     | 0.022     | 2.6  |

The experimental data presented in Tables 2–6 were plotted as triangular Gibbs–Roozeboom diagrams (Figs. 1–4). An analysis of the diagrams revealed that all investigated systems are characterized by the presence of significant heterogeneous regions. In all cases, extremely low mutual solubility is observed between the

organic phase (rich in MTBE and TBA) and the DES phase. The concentration of DES in the equilibrium organic phase ( $\omega_3$ ) is minimal (close to zero) across all experimental points, which minimizes extractant loss and simplifies the subsequent purification of the final products.

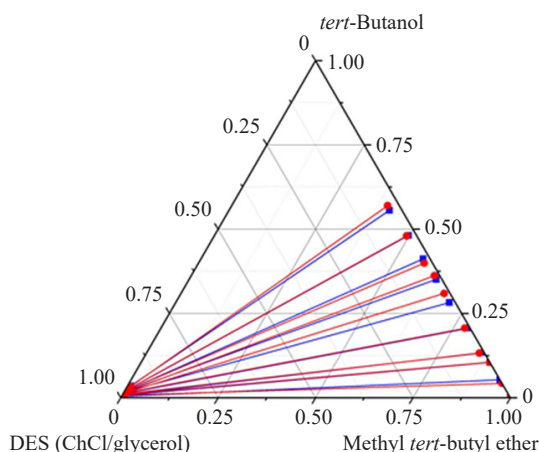


**Fig. 1.** Phase diagram of the TBA–MTBE–DES system based on choline chloride and glycerol at temperatures of 293.15 K (■) and 313.15 K (●) and atmospheric pressure

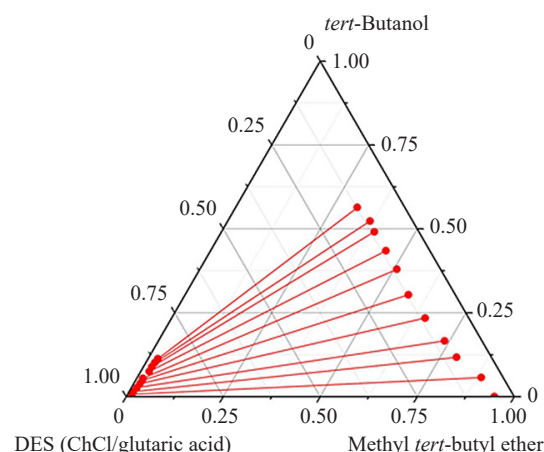


**Fig. 2.** Phase diagram of the TBA–MTBE–DES system based on choline chloride and glutaric acid at a temperature of 313.15 K and atmospheric pressure

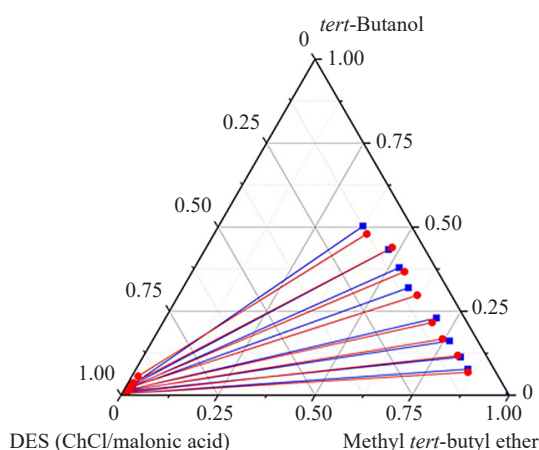


**Fig. 3.** Phase diagram of the TBA–MTBE–DES system based on choline chloride and malonic acid at temperatures of 293.15 K (■) and 313.15 K (●) and atmospheric pressure

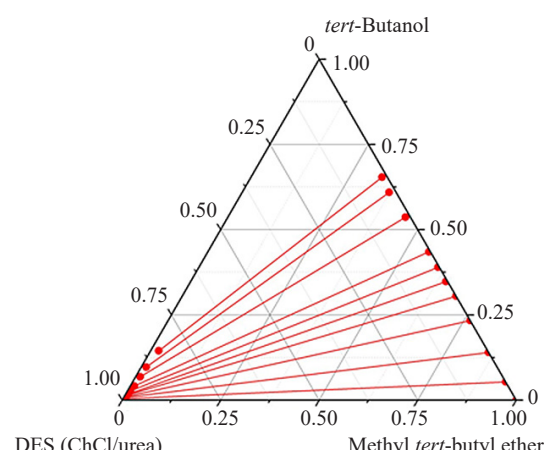


**Fig. 4.** Phase diagram of the TBA–MTBE–DES system based on choline chloride and urea at a temperature of 313.15 K (●) and atmospheric pressure

The efficiency of TBA extraction from its mixture with MTBE was evaluated using TBA distribution coefficients ( $\beta_1$ ) and selectivity ( $S$ ). The TBA distribution coefficients calculated for all systems (Tables 2–7) are less than unity in most cases, indicating that the equilibrium concentration of TBA is higher in the organic phase than that in the DES phase. Nevertheless, for assessing the suitability of DESs as extractants, selectivity is the key parameter, which reflects the ability of the DES to preferentially extract TBA compared to MTBE. The selectivity values for all studied DESs significantly exceed unity, confirming their capacity for selective extraction of TBA from its mixture with MTBE. The highest selectivity values are observed at low TBA concentrations in the organic phase and gradually decrease with increasing TBA content (Fig. 5). A power function was used to approximate the selectivity values. The specific

expression of this function for each investigated system is presented in Fig. 5.

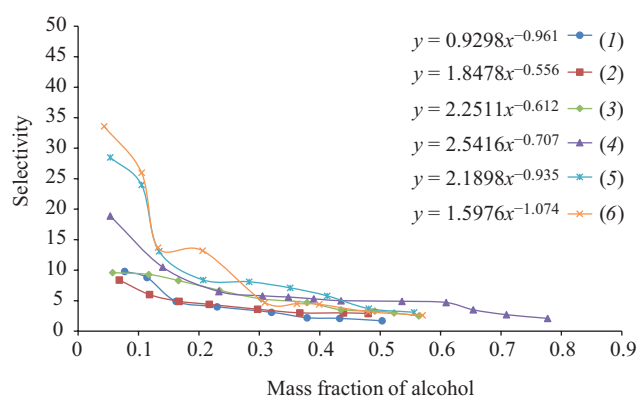


**Fig. 5.** Selectivity values vs alcohol mass fraction: (1) malonic acid at 293.15 K; (2) malonic acid at 313.15 K; (3) glutaric acid at 313.15 K; (4) urea at 313.15 K; (5) glycerol at 293.15 K; (6) glycerol at 313.15 K

A comparative analysis of the efficiency of different DESs reveals a dependence of selectivity on the nature of the hydrogen bond donor. The highest selectivity values are demonstrated by systems with DESs based on glycerol and urea. Thus, at 313.15 K, the maximum selectivity for the DES with the composition of choline chloride/glycerol reaches 33.6, while that for the DES with the composition of choline chloride/urea at 313.15 K equals 18.9. Systems with DESs based on dicarboxylic acids (malonic and glutaric) show a significantly lower selectivity, with maximum values that are comparable to one another, at 9.8 and 9.6, respectively. The differences in selectivity are attributed to variations in the strength and nature of hydrogen bonds formed between the DES components and the extracted TBA. Glycerol and urea are capable of forming a more extensive and stable network of hydrogen bonds with TBA compared to dicarboxylic acids, which significantly increases their selectivity toward TBA.

The effect of temperature on phase equilibrium and selectivity was studied using the DES systems—choline chloride/malonic acid and choline chloride/glycerol—as examples. In both cases, a negligible effect of temperature on separation selectivity was observed between 293.15 and 313.15 K. Therefore, the extraction process can be carried out at room temperature without a significant loss of efficiency.

The experimental data obtained demonstrate the high selectivity of glycerol- and urea-based DESs toward TBA, rendering them promising green solvents for separating this mixture via LLE, particularly in regions of low alcohol concentration.

## CONCLUSIONS

We investigated the liquid–liquid phase equilibrium in ternary MTBE–TBA–DES systems. New experimental data on the compositions of coexisting liquid phases were obtained using four DESs based on choline chloride with hydrogen bond donors, including malonic acid, glutaric acid, urea, and glycerol, at temperatures of 293.15 and 313.15 K and atmospheric pressure.

The experimental data obtained allowed us to calculate TBA distribution coefficients and TBA–MTBE separation selectivity values, confirming the suitability of the studied DESs for the extractive separation of such mixtures. A comparative analysis showed that glycerol- and urea-based DESs exhibits the highest selectivity. A negligible influence of temperature on separation selectivity within the studied range was established.

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## Authors' contributions

**A.A. Samarov**—research concept, analysis of the results, writing the text of the manuscript.

**N.Y. Volodina**—conducting the experiments, design of the experiments, analysis of the results, writing the text of the manuscript.

**I.V. Prikhodko**—writing the text of the manuscript.

**A.M. Toikka**—research concept, analysis of the results, writing the text of the manuscript.

*The authors declare no conflicts of interest.*

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RESEARCH ARTICLE

## Hydrolysis of tetraethoxysilane in various associated media of diols

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### Abstract

**Objectives.** To investigate the specific features of tetraethoxysilane (TEOS) hydrolysis in associated media of saturated diols and their esters in acidic media. Propylene- and butylene glycols and ethylcarbitol were selected as associated systems.

**Methods.** Association, hydrolysis, and condensation processes in the TEOS–diol system were studied by potentiometry, infrared spectroscopy, and dynamic light scattering in liquid media. The acidic environment was created by adding HCl in the amount not exceeding 0.3 wt %.

**Results.** The hydrolysis of TEOS in associated alcohol media is limited by the reaction that yields silanol  $(\text{RO})_3\text{SiOH}$ , which further interacts with the associated diol. This results in the incorporation of  $(\text{RO})_3\text{SiO}$  groups into the hydrogen bond network of diols. This is confirmed by a decrease in the self-association of diols with a decrease in size in the diol– $(\text{RO})_3\text{SiO}$  domains of up to 1–7  $\mu\text{m}$ .

**Conclusions.** The use of diols as a reaction medium for TEOS with a low content of  $\text{H}_2\text{O}$  in acidic media limits the depth of hydrolysis and condensation, which increases the possibility of esterification reactions of diol with alkoxy derivatives of silanols. The decreased number of hydroxyl groups during the transition from diols to their esters has a significant effect on the degree of association.

### Keywords

association, diffusion coefficient, diols, IR spectroscopy, hydrodynamic radius, hydrolysis, laser diffraction, tetraethoxysilane

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НАУЧНАЯ СТАТЬЯ

# Гидролиз тетраэтоксисилана в ассоциированных средах предельных диолов и их эфиров

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## Аннотация

**Цели.** Исследование особенностей процесса гидролиза тетраэтоксисилана (ТЭОС) в ассоциированных средах предельных диолов и их эфиров в кислых условиях. В качестве ассоциированных систем были выбраны пропилен- и бутиленгликоль, а также этилкарбитол.

**Методы.** Исследование процессов ассоциации, гидролиза и конденсации в системе ТЭОС–диолы проводили методами потенциометрии, инфракрасной спектроскопии и динамического рассеяния света в жидких средах. Кислотность среды обеспечивалась добавлением не более 0.3 мас. % HCl.

**Результаты.** Гидролиз ТЭОС в ассоциированных спиртовых средах лимитируется протеканием реакции образования силанол  $(\text{RO})_3\text{SiOH}$ , который в дальнейшем взаимодействует с ассоциированным диолом, что приводит к встраиванию групп  $(\text{RO})_3\text{SiO}$  в сетку водородных связей диолов. Это подтверждается снижением самоассоциации диолов с уменьшением размера в доменах диол– $(\text{RO})_3\text{SiO}$  до 1–7 мкм.

**Выводы.** Использование в качестве реакционной среды диолов для ТЭОС при малом содержании  $\text{H}_2\text{O}$  в кислых средах ограничивает глубину гидролиза и конденсации, что увеличивает возможность протекания реакций этерификации диола алкокси-производными силанолов. Большой эффект на степень ассоциации оказывает уменьшение числа гидроксильных групп при переходе от диолов к их эфирам.

## Ключевые слова

ассоциация, гидродинамический радиус, гидролиз, диолы, ИК-спектроскопия, коэффициент диффузии, лазерная дифракция, тетраэтоксисилан

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## Для цитирования

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## INTRODUCTION

Currently, sol–gel technology is widely used for producing transparent, shape-stable hybrid materials (HMs). The as-obtained materials enable the incorporation of organic groups into inorganic systems [1]. When optimizing synthesis conditions, HMs with unique, synergetic characteristics can be obtained, with their properties outperforming those of each individual component [2, 3].

The sol–gel process also enables the production of improved materials with high purity and homogeneity under relatively mild conditions. The exceptional properties of such materials are explained by the extended polymer-nanofiller interfacial area and are determined by the strength of interfacial interactions. Furthermore, polymer hybrids exhibit optical transparency due to the small area of heterogeneity domains [4, 5].

The main advantage of sol–gel technology, which encompasses hydrolysis and condensation processes,

lies in its capacity to tailor the synthesis by varying and monitoring the reaction parameters (e.g., pH, catalyst nature, temperature, and/or reagent ratios) [3]. The formation of gels with controlled nanoscale architecture, unique morphology, and properties under mild reaction conditions [6] accounts for their wide range of applications, e.g., as hybrid coatings [7], biohybrids [8], and materials for medicinal purposes [9].

Gels based on silicic acid occupy a significant place among gel materials. These are porous, elastic materials with a 3D polymer network, the pores of which are primarily filled with solvent molecules or, in the case of hydrogels, with water, typically up to 70–99% [10].

The number of biomedical applications for hydrogels is rapidly increasing due to their outstanding physical, structural, and mechanical properties. The silicic acid polymer network, filled with water, imparts unique characteristics to hydrogels, rendering them particularly attractive for applications in biomedical engineering [10–13].

The formation of a 3D siloxane network during the synthesis of hybrid sol–gel materials and the subsequent polymerization of the resulting dispersed silicic acid particles lead to the capillary-porous structure of the elastic gel [14].

The strategy for synthesizing hybrid sol–gel materials is represented mainly by two synthetic pathways [3, 14–15]:

- one-stage synthesis in an alkaline medium (condensation);
- two-stage synthesis, where the first hydrolysis stage primarily occurs under acidic conditions, while the second stage of alkaline condensation is conducted separately (silylation).

The key difference between these two strategies consists in the degree of incorporation of organic groups, which attach to the internal and external pore walls during their formation.

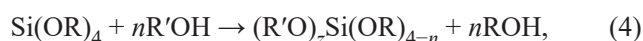
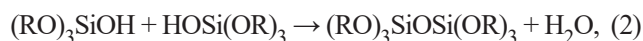
In the two-stage synthesis, after pore formation, the organic modifier in the silylation stage attaches only to the external pore walls. This increases the limit of organic solvent incorporation to 40% or greater [9]. In these systems, interfacial properties play an essential role in determining the functional properties of the material. Depending on the type of interface, the sol–gel process enables the formation of two main classes of HMs.

In the first class of materials, inorganic and organic components are connected by weak (non-covalent) bonds, including ionic interactions, hydrogen bonds (H-bonds), van der Waals forces, and  $\pi$ – $\pi$  interactions [1]. The cases in point include rhodamine 6G [16] or enzymes [17] formed through encapsulation of an organic molecule within the formed cavities of an inorganic matrix. In the second class of materials, the embedded phase is firmly bound by chemical bonds to the silicon matrix of the gel.

The sol–gel process can be managed by a known method involving the use of organic components as templates [18–21] to obtain final products whose properties are determined by the organic–inorganic interface. Depending on the intended use of the product, the template or sacrificial spacer can be chemically removed, leaving voids with a specific pore size [20].

Various methods for optimizing synthesis using a wide range of solvents, surfactants, and natural products have been discussed in the literature [22, 23]. In this regard, highly associated alcohols [24] and polyols [25], which possess a strong internal network of hydrogen bonds, can be of interest as solvents. Alkoxysilanes, including tetraethoxysilane (TEOS), are predominantly used for obtaining inorganic structures. TEOS is one of the most common precursors for forming a silica network *in situ* within an organic matrix.

The synthesis of silicic acid gels comprises a stage involving the hydrolysis of silicon alkoxides dissolved in various alcohols, ROH, in the presence of mineral acid or base catalyst (Eq. 1), and subsequent condensation reactions involving silanol groups, resulting in the formation of siloxane bonds and byproducts, which are water molecules (Eq. 2) or alcohol (Eq. 3):



The sol–gel process is sensitive to the nature of the catalyst. Acidic catalysts primarily promote the hydrolysis process, while basic catalysts are capable of facilitating the polycondensation process [3]. The choice of a catalyst determines the growth mechanism of silica domains, thus being an important factor for filler dispersion. In most cases, the morphology of the final product is controlled by the type of the catalyst used. Acid-catalyzed reactions lead to the formation of a 3D gel or network structure [26, 27], while base-catalyzed reactions result in the formation of condensed spherical particles [28, 29].

Previous research showed the hydrolysis stage (Eq. 1) to be the limiting step for particle formation not only in alkaline media [30–32] but also in acid-catalyzed systems [33, 34].

In comparison with other components in sol–gel systems, the alcohol solvent plays a rather complex role. The nature and content of the alcohol are significant from the standpoint of the solubility of intermediates containing polar and charged groups [34]. Alongside regulating the system miscibility, the alcohol used in the synthesis process can act as a reagent in transesterification reactions (Eq. 4). According to the study [34], for low-molecular-weight alcohols, such as methanol and ethanol, transesterification of TEOS is negligible and largely determined by the water/alcohol ratio.

During the synthesis of silicic acid gels in an alcohol solvent medium, stages of silylation of ROH by alkoxysilanols (Eq. 5) can also occur.

Previously, the use of  $^{29}\text{Si}$  and  $^{13}\text{C}$  nuclear magnetic resonance and small-angle X-ray scattering methods [35, 36] established that the rates of condensation stages decrease in an alkaline medium when transitioning from the initial TEOS monomer to a dimer with a siloxane bond. When the reaction proceeds in methanol or ethanol, transesterification between methanol and TEOS was found to occur (Eq. 4),

although being negligible compared to the formation of hydrolyzed intermediates (Eq. 1). The authors believe that the differences in the sizes of silicon-containing particles in the reactions conducted in methanol or ethanol are due to thermodynamic interactions between the solvent and the hydrolyzed intermediates of a silanol nature.

In the study [37], the influence of the solvent on the kinetics of the initial hydrolysis stage was investigated from the perspective of solvent polarity and hydrogen bond formation. It was shown that the initial hydrolysis rate and the average particle size increase with an increase in the molecular weight of primary alcohols. For secondary alcohols, the hydrolysis rate decreases while particle size increases.

The study [38] investigated the influence of various alcohols on the reaction rates and particle sizes of silica synthesized via TEOS hydrolysis and condensation. Silica particles ranging in size from 100 nm to 2  $\mu\text{m}$  were obtained by varying the ROH composition, where  $R = C_nH_{2n+1}$  with  $n$  values from 1 to 15. The reactions proceed fastest in an ethanol/decanol mixture at a ratio of about 1 : 1 and slowest in pure ethanol. The authors established that both the hydrolysis rate and the condensation rate increase with a decrease in solvent polarity. At the same time, no correlation between polarity and rate constants was observed.

A number of studies have shown that alkoxy exchange is activated in an acidic medium, while it cannot be detected in basic media [33, 39]. However, in a work by Lima *et al.* [40], the possibility of rapid exchange of alkoxy groups at an early stage of TEOS hydrolysis in a basic medium was established. Under these conditions, both the reaction rate and the size of the resulting silica particles undergo a significant change.

Knowledge of the phase interface structure in organic–inorganic hybrid materials obtained via sol–gel processes makes it possible to tailor the structure and properties of silicic acid gels, which is extremely important for the synthesis of new, promising materials.

Associated media are characterized by strong intermolecular binding through hydrogen bonds or dipole and ion–dipole interactions, e.g., in polyvinylpyrrolidone. Systems with strong hydrogen bonds include saturated 1,2- and 1,3-diols, triols, polyols, and their ethers.

This paper presents the results of TEOS hydrolysis in diols: 1,3-propylene glycol (PG), 1,3-butylene glycol (BG), and the monoethyl ether of diethylene glycol, i.e., ethyl carbitol (EC), using infrared (IR) spectroscopy

and dynamic light scattering (DLS) methods in an acidic medium. The acidic medium was ensured by the addition of HCl. The  $H_2O$  concentration was determined solely by the water content in the initial diols and/or the water introduced with HCl, not exceeding 0.3 wt %.

## EXPERIMENTAL

In this work, the following chemical compounds were used:

- 1,3-Butylene glycol (*KhimFarm*, Russia) (CAS No. 107-88-0), main substance content not less than 99.5%;
- 1,3-Propylene glycol (*NOVATORKHIM*, Russia) (CAS No. 504-63-2), 99.95%;
- Ethyl carbitol (2-(2-ethoxyethoxy)ethanol) (*BIOAMIN-RUS*, Russia) (CAS No. 111-90-0), Technical Specification TU 2422-125-05766801-2003, premium grade, main substance content not less than 99%, ethylene glycol content is 0.8%;
- Tetraethoxysilane (tetraethyl silicate) (*EKOS-I*, Russia) (CAS No. 78-10-4), Technical Specification TU 2435-419-05763441-2003, main substance content not less than 99.5%, ethyl alcohol content is no more than 0.10%;
- HCl (*KHIMMED*, Russia);
- Distilled water  $H_2O$  (Russia, RTU MIREA, M.V. Lomonosov Institute of Fine Chemical Technology, Ya.K. Syrkin Department of Physical Chemistry), GOST R 58144-2018<sup>1</sup>.

IR spectra of samples in liquid and solid forms were recorded on a Cary 630 FTIR spectrometer (*Agilent Technologies*, USA) using a single-bounce diamond attenuated total reflectance accessory in the range of 4000–350  $\text{cm}^{-1}$  with a spectral resolution of  $<2 \text{ cm}^{-1}$ . Processing of the IR spectra was performed using the Agilent MicroLab software (*Agilent Technologies*, USA).

DLS spectra were recorded using a Photocor Compact-Z instrument (*Photocor*, Russia). The power of the thermostabilized semiconductor laser (638 nm) was 25 mW. Particle size measurements were conducted at angles of 90° and 160° at a constant temperature of 25°C. Measurements in concentrated and opaque systems were performed using the backscattering method at an angle of 160°. Signal analysis was carried out by the built-in Photocor FC correlator for auto- and cross-correlation measurements. Processing of DLS spectra was performed using the DynaLS software package by Photocor.

<sup>1</sup> GOST R 58144-2018. National Standard of the Russian Federation. Distilled water. Specifications. Moscow: Standartinform; 2018. URL: <https://cdn.termexlab.ru/files/4385340a/f801/428e/9766/de94c9e1741c.pdf>. Accessed July 01, 2019 (in Russ.).

Potentiometric pH determination was carried out using an Expert-001 ionometer (*Ekoniks-Expert*, Russia) with a measurement range of pH 0–14, using a combined glass electrode IT ESK 10601 7. The limit of permissible basic absolute measurement error was  $\Delta\text{pH}$  0.03.

## Preparation of reaction mixtures

Reaction mixtures with a volume of 50 mL were prepared by direct mixing of glycols or EC (94–95 wt %) with a constant amount of TEOS (5 wt %) under vigorous stirring at room temperature (25°C). An HCl solution was added as an acid catalyst. The pH value of the reaction mixture was maintained constant (pH 2.1–2.5). The total water content in the reaction mixture was determined by the amount of water in the initial glycols and the amount of water introduced with the HCl solution, not exceeding 1–2 wt %.

The solutions were transparent and similar in viscosity to the diols.

For reaction mixtures based on EC in the EC–TEOS system, solution opalescence with a whitish tint was observed.

The obtained reaction mixtures were analyzed using IR spectroscopy and DLS methods over a time interval of up to 48 days.

## RESULTS AND DISCUSSION

In the IR spectrum of PG diol (Fig. 1), alcohol association is manifested by the broadening of the bands of O–H bond stretching vibrations  $\nu(\text{OH}) = 3320\text{ cm}^{-1}$ , as well as C–H bonds in  $\text{CH}_2$ ,  $\text{CH}_2\text{--O}$  groups in the region

$\nu = 2867\text{--}2969\text{ cm}^{-1}$  and deformation vibrations of these groups in the region  $\delta = 1457\text{--}1260\text{ cm}^{-1}$ . This agrees with data on the formation of a hydrogen bond network in diols [41]. C–O bond stretching vibrations appear in the region of  $1125\text{--}1000\text{ cm}^{-1}$  in the form of two sets: a broadened band at  $1036\text{ cm}^{-1}$  for the associated form of diols and two narrow bands at 1135 and  $1075\text{ cm}^{-1}$ . Similar results are observed for BG, although with a slight difference.

Diols always contain a residual amount of water, with a band of O–H bond stretching vibrations  $\nu(\text{OH}) = 3430\text{ cm}^{-1}$  overlapping with the  $\nu(\text{OH})$  band of the diols and water deformation vibrations at  $1645\text{ cm}^{-1}$ .

In the IR spectrum of EC, due to the increased content of  $\text{CH}_2\text{--O}$  groups compared to PG, the intensity and width of the hydroxyl  $\text{OH}^-$  group vibration band at  $3320\text{ cm}^{-1}$  is significantly reduced, and the intensity of the C–H bond stretching vibration bands at  $\nu = 2867\text{ cm}^{-1}$  increases. This confirms a decrease in the degree of association of EC compared to diols. It should also be noted that instead of two narrow bands at 1135 and  $1075\text{ cm}^{-1}$ , a single combined band at  $1105\text{ cm}^{-1}$  is observed.

The presence of different forms of diol associates and silicon-containing products is confirmed by the obtained DLS spectra.

In the DLS spectrum of PG (Fig. 2a), two signals are observed: a fast mode (F1) and a slow mode (S1), with an average hydrodynamic radius for S1 of  $r_g = 11\text{ }\mu\text{m}$  and a ratio of F1 : S1 = 1 : 3. Thus, it can be assumed that the two forms of CO stretching vibrations correspond to the fast (F1,  $\nu = 1135\text{ cm}^{-1}$ ) and slow (S1,  $\nu = 1075\text{ cm}^{-1}$ ) modes of motion.

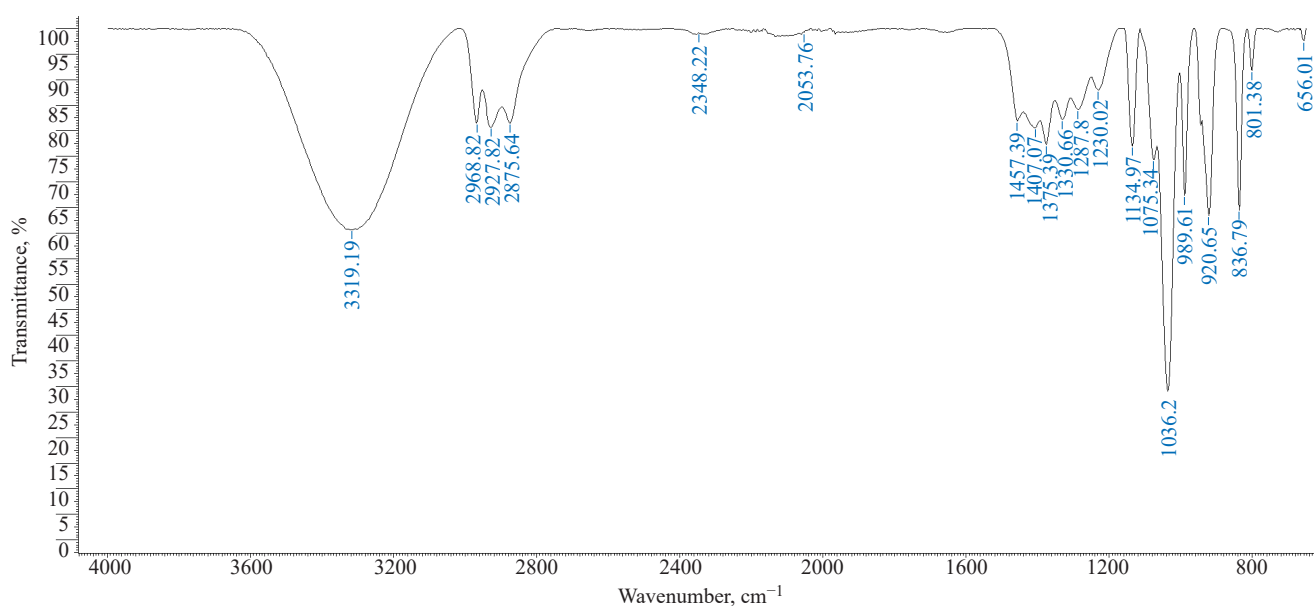


Fig. 1. Infrared spectrum of PG

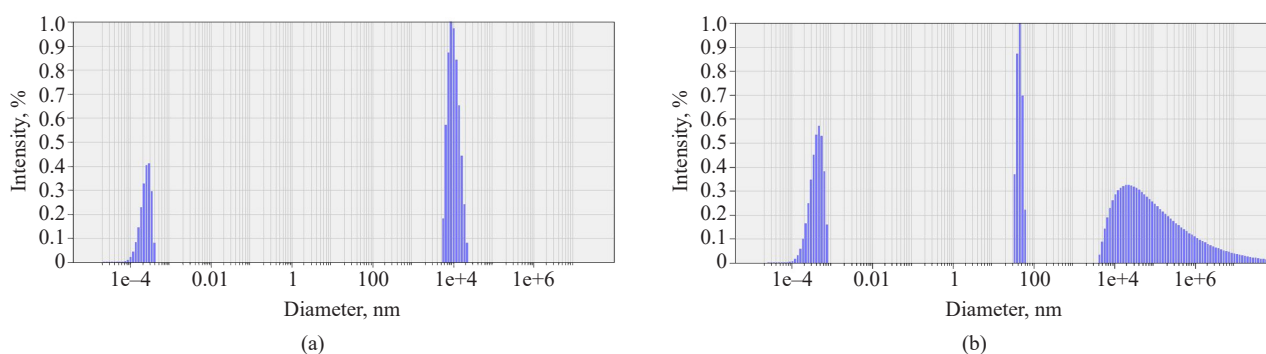


**Fig. 2.** DLS spectra of (a) PG, (b) EC

The substitution of PG with EC affects the appearance of the entire spectrum. The decrease in the degree of association for EC (Fig. 2b) leads to an increase in the contribution of the fast mode F1 and a decrease in the contribution of the slow modes S. At the same time, the slow mode splits into two components: S1 ( $\nu = 1105 \text{ cm}^{-1}$ ) and S2 ( $\nu = 1062 \text{ cm}^{-1}$ ) with diffusion coefficients of  $D_{S1} = 5.3 \cdot 10^{-8} \text{ cm}^2/\text{s}$  and  $D_{S2} = 8.1 \cdot 10^{-11} \text{ cm}^2/\text{s}$ .

In this work, the process of TEOS hydrolysis and condensation was monitored by changes in viscosity, IR spectra, and phase composition, as assessed by DLS spectra of the reaction system.

### PG + TEOS system

The structures of TEOS and diols are largely similar due to the presence of the C–O bond. This is confirmed by the appearance of bands corresponding to C–H bond stretching vibrations in the  $\text{CH}_2$  and  $\text{CH}_3$  alkoxy groups and deformation vibrations of the  $-\text{CH}_2-\text{O}$  groups in the regions similar to those for diols (Fig. 1). The absence of associations between TEOS molecules results in noticeably narrower vibration bands compared to PG. A distinctive feature of the alkoxy groups in TEOS is the presence of Si–O bond stretching and deformation vibration bands at  $1072$ ,  $958$ , and  $785 \text{ cm}^{-1}$  of comparable intensity. Furthermore, similar to diols, the presence of two sets of silicon alkoxide derivatives is observed: a broadened band at  $1072 \text{ cm}^{-1}$  and two narrow bands at  $1167$  and  $1100 \text{ cm}^{-1}$ . It can be seen from Fig. 3 that the IR spectrum at the onset of the experiment represents the sum of the glycol and TEOS spectra. Thus, the difference in the alkoxy groups of diols and TEOS is observed in the shift of the wavenumbers of the vibration bands:  $1135 \rightarrow 1167 \text{ cm}^{-1}$ ,  $1075 \rightarrow 1100 \text{ cm}^{-1}$ , and  $1038 \rightarrow 1072 \text{ cm}^{-1}$ .

In the DLS spectrum of TEOS (Fig. 4), a small number of oxysilicon particles with  $r_g = 93 \text{ nm}$ , dissolved in TEOS, is observed, along with a broadened signal of the slow mode S. This can be explained by an impurity

of a partially hydrolyzed product (due to atmospheric moisture) with  $D_S = 5.8 \cdot 10^{-10} \text{ cm}^2/\text{s}$ .

The addition of 3 to 5 wt % TEOS to diols at pH 2.5 leads to a noticeable change in the IR and DLS spectra. First of all, practically immediately after mixing, a narrowing of the C–H bond stretching vibration bands in the  $\text{CH}_3$ ,  $\text{CH}_2-\text{O}$  groups in the region  $\nu = 2867\text{--}2969 \text{ cm}^{-1}$  and the bands of deformation vibrations of these groups in the region  $\delta = 1457\text{--}1260 \text{ cm}^{-1}$  is observed in the IR spectrum for PG (Fig. 3). This indicates a decrease in the degree of association of the initial diol.

Following aging for 48 days, the reaction mixture remains close to homogeneous, and the IR spectrum shows a noticeable decrease in the intensity of the TEOS vibration bands at  $958$  and  $785 \text{ cm}^{-1}$ , indicating hydrolysis of the alkoxy silane.

For BG, replacing the H atom with a methyl radical in the  $\text{CH}_2\text{OH}$  group of PG increases the hydrophobicity of the diol and reduces its self-association. This is manifested in the narrowing of the bandwidth of the O–H stretching vibration at  $\nu(\text{OH}) = 3320 \text{ cm}^{-1}$ . At the same time, broadening of the C–H bond stretching vibration band in the  $\text{CH}_3$ ,  $\text{CH}_2-\text{O}$  groups in the region  $\nu = 2867\text{--}2969 \text{ cm}^{-1}$  is maintained. The persistence of the stretching vibration bands for TEOS confirms a decreased hydrolysis rate compared to PG.

### EC + TEOS

A different picture is observed for the less associated EC. The addition of TEOS to EC at pH 2.5 produces a negligible effect on the appearance of the IR spectrum (Fig. 5). It is only after aging the EC + TEOS reaction mixture for 48 days that a narrowing of the C–H bond stretching vibration bands in the  $\text{CH}_3$ ,  $\text{CH}_2-\text{O}$  groups in the region  $\nu = 2867\text{--}2969 \text{ cm}^{-1}$ , and the bands of deformation vibrations of these groups in the region  $\delta = 1457\text{--}1260 \text{ cm}^{-1}$  are observed. At the same time, the intensity of the bands characteristic of TEOS remains

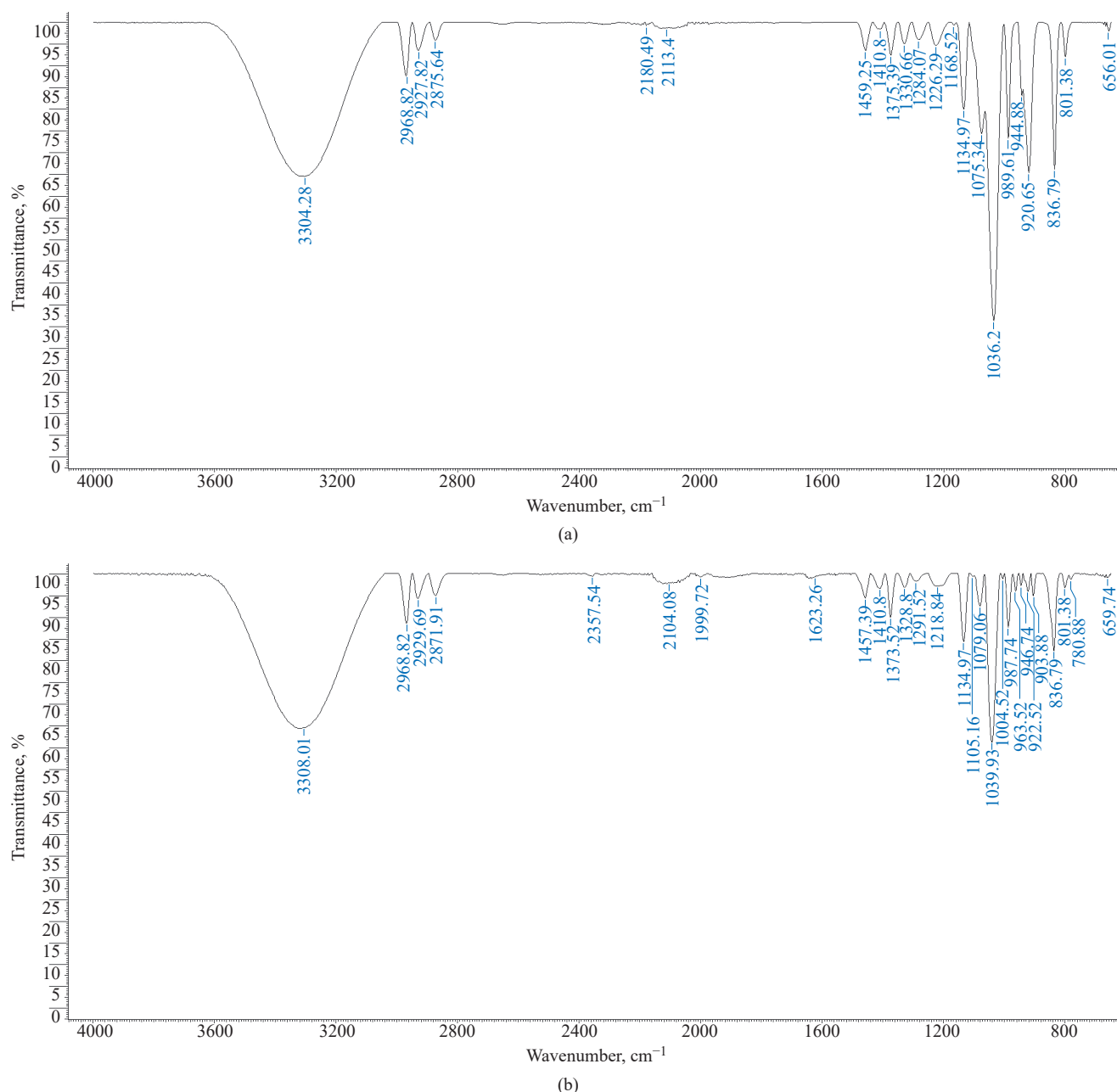


**Fig. 3.** IR spectra of PG + TEOS mixture: (a) immediately after mixing, (b) after 48 days

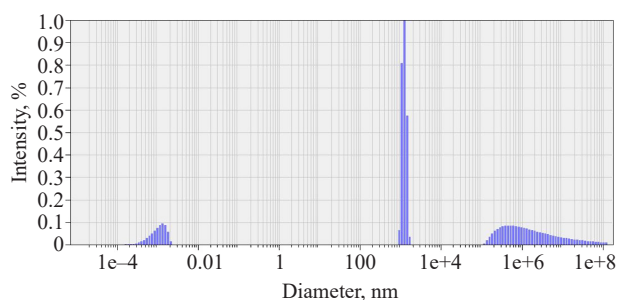
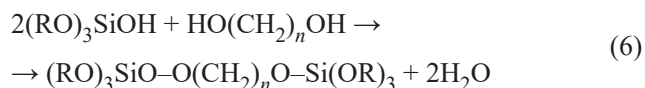


**Fig. 4.** DLS spectrum of TEOS

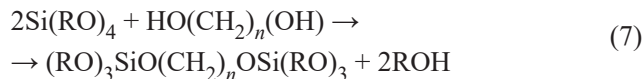
almost unchanged, indicating a decreased rate of hydrolysis and condensation for the EC ether compared to the saturated diols.

For all studied diols, the reaction mixture generally remains homogeneous. However, the onset of its phase separation is observed. The H–O–H deformation vibration band at  $1645\text{ cm}^{-1}$  splits into two bands at 1623 and  $1649\text{ cm}^{-1}$ . According to the authors [34], bands corresponding to Si–OH group vibrations may also appear in this region, which is consistent with the slower TEOS hydrolysis process in EC.

The studies [1, 6] reported that the formation of the primary silanol  $(\text{RO})_3\text{SiOH}$  remains the limiting stage of hydrolysis even under an excess of water in an acidic medium. Given the extremely low water content in the system, the obtained results can be explained not only by the condensation reaction with the formation of a siloxane bond (Eqs. 2 and 3) but also by a significant contribution from the esterification reaction of the resulting silanol derivatives of diols. This leads to the incorporation of alkoxy silanolic groups into the hydrogen bond network of the diols:



The possibility of transesterification of the initial TEOS in a 95–97% diol medium cannot be ruled out. This should also lead to the incorporation of alkoxy silanols into the hydrogen bond network of the diols:



Thus, the reactions according to Eqs. (6) and (7) proceed for diols, being unlikely for monohydric alcohols. The result of silylation of diols should lead to a decrease in their association (Fig. 6), forming smaller domains, which we observe in the DLS spectra.

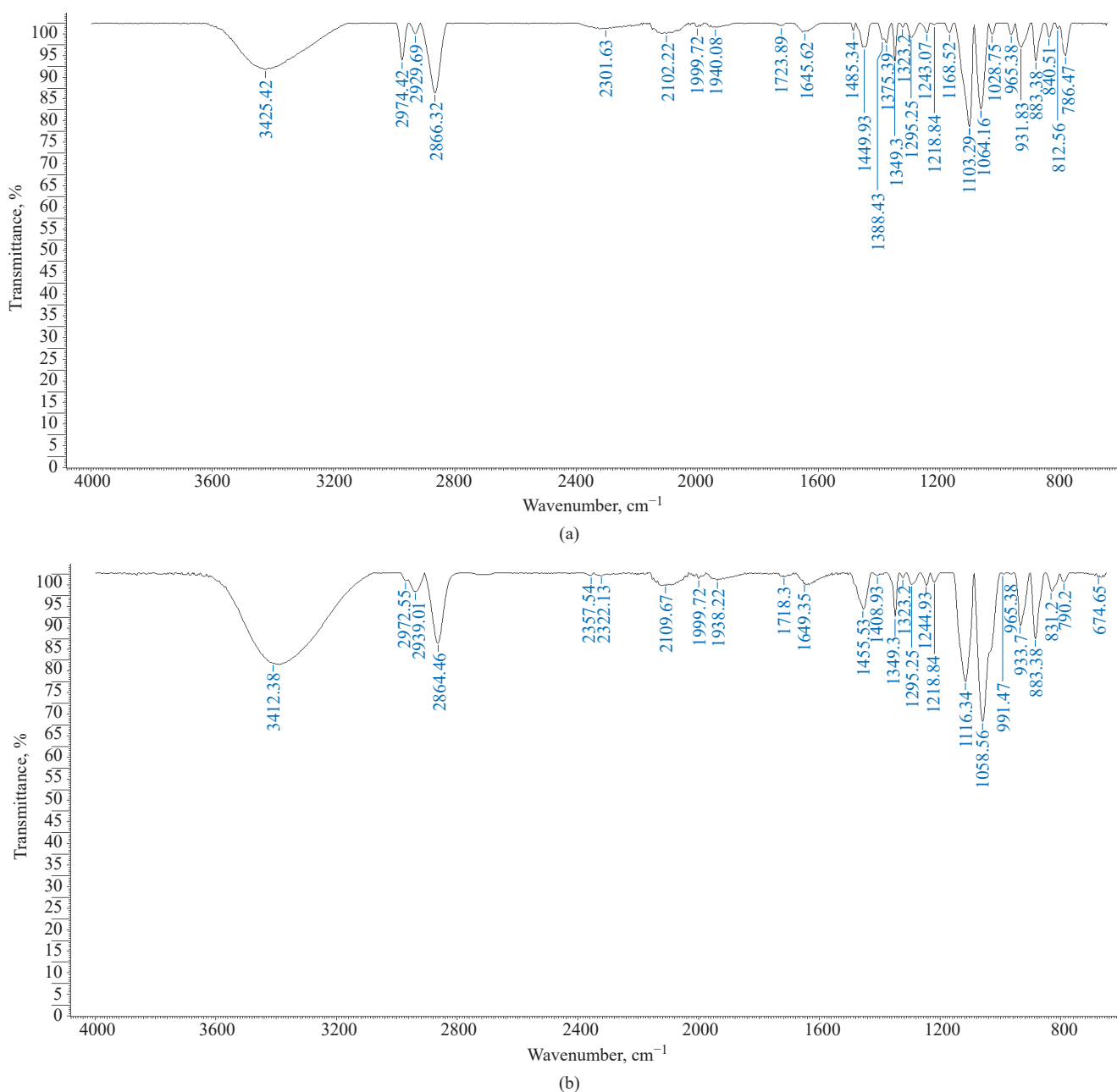


Fig. 5. IR spectra of EC + TEOS mixture: (a) immediately after mixing, (b) after 48 days

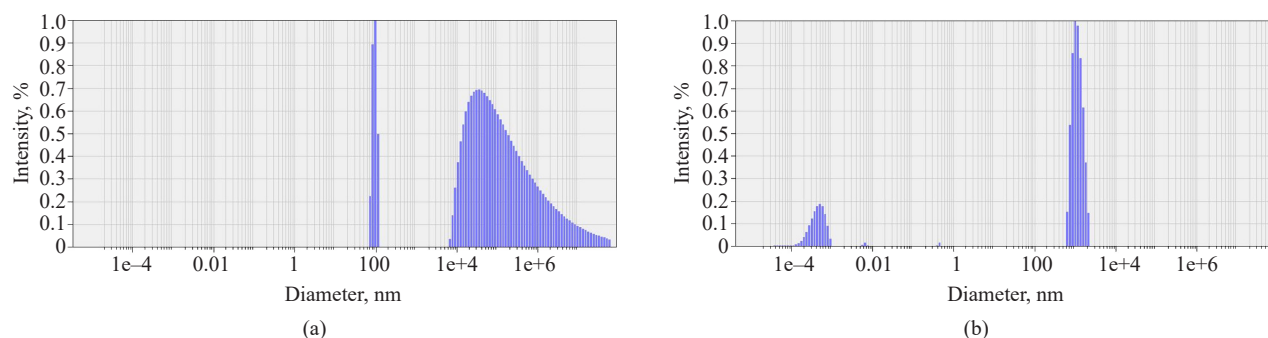


**Fig. 6.** DLS spectra of a mixture of PG + 5% TEOS: (a) immediately after mixing, (b) 48 days after mixing

Immediately after mixing saturated diol PG with 5 wt% TEOS (Fig. 6a), the fast mode F1 was not observed, while the slow mode signal split into two, S1 and S2, with diffusion coefficients  $D_{S1} = 2.2 \cdot 10^{-8} \text{ cm}^2/\text{s}$  and  $D_{S2} = 4.4 \cdot 10^{-11} \text{ cm}^2/\text{s}$ .

After the period of 48 days, the DLS spectrum of the system (Fig. 6b) showed signals for the fast mode F1 (19%) and a narrow monomodal signal of the slow mode S ( $r_g = 1.17 \text{ }\mu\text{m}$ ;  $D_S = 2.3 \cdot 10^{-9} \text{ cm}^2/\text{s}$ ). The significant reduction in the size of the associates and the diffusion coefficients fully confirms the aforementioned statement.

A similar result with a narrow monomodal signal of the slow mode S is observed for BG after 48 days, confirming the incorporation of alkoxysilanol into the hydrogen bond network. At the same time, larger domains with a smaller diffusion coefficient for the slow mode S ( $r_g = 7.18 \text{ }\mu\text{m}$ ;  $D_S = 3.7 \cdot 10^{-10} \text{ cm}^2/\text{s}$ ) are observed compared to S for PG ( $r_g = 1.17 \text{ }\mu\text{m}$ ;  $D_S = 2.3 \cdot 10^{-9} \text{ cm}^2/\text{s}$ ). However, this does not contradict the previous conclusion.

In comparison with PG diol, the decrease in the number of hydroxyl groups when moving to EC has a negligible effect on the appearance of the IR spectrum (Fig. 5).

The rate of hydrolysis/condensation in the EC–TEOS system substantially differs from the rate of reactions involving diols. After aging the EC–TEOS mixture for 48 days (Fig. 7), an increase in the viscosity of the reaction mixture is observed, producing bands characteristic of siloxane bonds in the IR spectra (Fig. 5). The intensity of the fast mode F1 signal is 19.9%. The diffusion coefficients of the two slow modes have practically remained unchanged: 9.3% S1,  $D_{S1} = 3.0 \cdot 10^{-9} \text{ cm}^2/\text{s}$  and 70.3% S2,  $D_{S2} = 4.5 \cdot 10^{-11} \text{ cm}^2/\text{s}$ . However, the size of the associate involving alkoxysilicon components of the slow mode S1 increased almost tenfold (to  $r_g = 840 \text{ nm}$ ) compared to PG ( $r_g = 93 \text{ nm}$ ) at the initial moment of contact. Thus, the decrease in diol association leads to two processes: less active

incorporation into the hydrogen bond network and the growth of agglomerates of siloxane condensation products of TEOS.

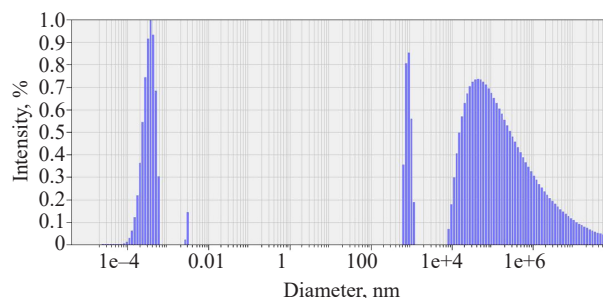


**Fig. 7.** DLS spectrum 48 days after mixing EC + 5% TEOS

## CONCLUSIONS

The use of diols as a reaction medium for TEOS hydrolysis, under conditions of low  $\text{H}_2\text{O}$  content in acidic media, limits the extent of hydrolysis and condensation, while increasing the possibility of esterification reactions between the diols and alkoxy derivatives of silanols. The incorporation of  $(\text{RO})_3\text{SiO}$  groups into the hydrogen bond network of the diols reduces diol association and decreases domain sizes to 1–7  $\mu\text{m}$ . The decrease in the number of hydroxyl groups in diol ethers has a significant effect on the degree of association. The results obtained demonstrate the possibility of creating a siloxane network through managing the hydrolysis and subsequent condensation processes when developing technologies for flexible, transparent, and shape-stable gels.

### Authors' contributions

**A.M. Bondareva**—conducting the experiments, discussion of the results.

**I.I. Pashkin**—discussion of the results.

**A.V. Krylov**—setting the task, discussing the results.

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REVIEW ARTICLE

## Features of oil disperse systems and changes in their properties under low-energy wave action

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### Abstract

**Objectives.** To analyze the properties, dispersion structure, and intermolecular interactions in oil disperse systems (ODSs) of various component compositions, and to consider the possibilities of controlling phase transitions in an ODS to achieve the most favorable dispersion properties for carrying out technological processes of refining hydrocarbons, upgrading petroleum products, or recycling oil waste. Phase transitions are proposed to be controlled by low-energy wave action (low-frequency ultrasound, constant magnetic field with low induction).

**Results.** The following features of oil disperse systems are considered and substantiated with literature data and the results of our own research: multiplicity of phases; diversity of hydrocarbon components and heteroatomic compounds contained in them; the nature of intermolecular interactions (the absence of charge interactions and the presence of charge–polarization and exchange spin-spin interactions); spin activity or paramagnetism of oil, petroleum products, and their various components; homolytic dissociation of high-molecular-weight and heteroatomic organic compounds, resulting in an increase in paramagnetism; as well as the presence of trace elements contained in organometallic compounds and in salts dissolved in emulsified water. An equation is presented for intermolecular interactions in ODSs, in which a decisive role is played by the exchange interactions caused by the presence of spin and spin-polarized molecules. Two-component models are described for the shells of complex structural units of the oil disperse system, their structure, and their interaction with the dispersion medium. Methods for controlling phase transitions and dispersity of ODSs are shown. Special attention is paid to low-energy wave technologies (ultrasonic waves with a frequency of 20–100 kHz with an intensity of up to 0.4 W/cm<sup>2</sup> and a constant magnetic field with an induction of less than 0.4 T). Examples are given for the intensification of such technological processes as separation of water–oil emulsions, removal of mechanical impurities, atmospheric and vacuum distillation, selective purification of oil fractions, degassing of heavy fuel oil to remove hydrogen sulfide, visbreaking, and others. Positive results are demonstrated for the application of low-energy technologies for reduction of the viscosity and pour point of oil and petroleum products in oil refining equipment. The study proposes a mechanism of the influence of a constant magnetic field on the flow of petroleum product or hydrocarbon raw material.

**Conclusions.** The study of the features of ODSs is key to the qualified colloid-chemical approach to processes of production, transportation, and processing of hydrocarbon raw materials. They are seen from the standpoint of ODS theory on the basis of the consideration of the dispersion structure and phase transitions in ODSs. Low-energy technologies in the petroleum industry are an effective tool for resource saving in various processes and optimization of their parameters without significant material costs.

### Keywords

oil disperse systems, asphaltene paramagnetism, complex structural unit, dispersity of oil systems, low-energy wave action, magnetic field, ultrasound

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## ОБЗОРНАЯ СТАТЬЯ

# Особенности нефтяных дисперсных систем и изменение их свойств при низкоэнергетических волновых воздействиях

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## Аннотация

**Цели.** Проанализировать особенности свойств, дисперсного строения, межмолекулярных взаимодействий в нефтяных дисперсных системах (НДС) разнообразного компонентного состава, а также рассмотреть возможности управления фазовыми переходами в нефтяной системе для достижения наиболее благоприятных дисперсных свойств при проведении технологических процессов переработки углеводородного сырья, облагораживания нефтепродуктов или утилизации нефтяных отходов. В качестве инструмента регулирования фазовыми переходами используют низкоэнергетические волновые воздействия (низкочастотный ультразвук, постоянное магнитное поле с невысокой индукцией).

**Результаты.** Рассмотрены и аргументированы литературными данными и результатами собственных исследований такие особенности НДС, как мультidisперсность; многообразие углеводородных компонентов и гетероатомных соединений, входящих в них; природа межмолекулярных взаимодействий (отсутствие зарядовых взаимодействий, зарядово-поляризационные и обменные спин-спиновые взаимодействия); спиновая активность или парамагнетизм нефти, нефтепродуктов и различных их компонентов; гемолитическая диссоциация высокомолекулярных и гетероатомных органических соединений, приводящая к росту парамагнетизма; присутствие микроэлементов, входящих в состав металлоорганических соединений и в виде солей, растворенных в эмульгированной воде. Приведено уравнение межмолекулярных взаимодействий в НДС, решающую роль в которых играют обменные взаимодействия, обусловленные присутствием спиновых и спинполяризованных молекул. Представлены двухкомпонентные модели оболочек сложных структурных единиц НДС, их строение и взаимодействие с дисперсионной средой. Показаны способы управления фазовыми переходами и дисперсностью НДС; особое внимание уделено волновым низкоэнергетическим технологиям (с использованием ультразвуковых волн с частотой 20–100 кГц с интенсивностью до 0.4 Вт/см<sup>2</sup> и постоянного магнитного поля с индукцией меньше 0.4 Тл). Даны примеры интенсификации таких технологических процессов, как разделение водонефтяных эмульсий, очистка от механических примесей, атмосферная и вакуумная перегонка, селективная очистка масляных фракций, дегазация мазута от сероводорода, висбрекинг и др. Показаны положительные результаты применения низкоэнергетических технологий для снижения вязкости и температуры застывания нефти и нефтепродуктов в оборудовании нефтепереработки. Предложен механизм влияния постоянного магнитного поля на поток нефтепродукта или углеводородного сырья.

**Выводы.** Изучение и учет особенностей НДС позволяет реализовать квалифицированный коллоидно-химический подход к процессам добычи, транспортировки, переработки углеводородного сырья с позиций теории НДС, основанный на анализе дисперсной структуры и фазовых переходов в НДС. Применение низкоэнергетических технологий в нефтяной отрасли — эффективный инструмент для ресурсосбережения в различных процессах и оптимизации их параметров без существенных материальных затрат.

## Ключевые слова

нефтяные дисперсные системы, парамагнетизм асфальтенов, сложная структурная единица, дисперсность нефтяных систем, низкоэнергетические волновые воздействия, магнитное поле, ультразвук

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## INTRODUCTION

Hydrocarbons are an invaluable resource for producing fuels, lubricants, construction and road materials, electrical insulating materials, and solvents. They are also a source for the production of a variety of petrochemical products. It is difficult to overestimate the importance of petroleum products as a source of energy for a wide variety of industries, household needs, and transportation. Over the past 150 years, a colossal infrastructure has been created focused on the consumption of oil as a fuel source. The number of vehicles on Earth powered solely by internal combustion engines has reached 1.5–2 billion [1].

The deep refining of hydrocarbon feedstocks is performed using various physical and physicochemical processes, catalysts, high temperatures and pressures, complex process equipment, and so on. However, increasing the depth of oil refining remains a pressing issue, given that fossil hydrocarbons are a finite resource. This task is further complicated by the ongoing trend toward deteriorating hydrocarbon feedstock quality: increasing levels of sulfur and organometallic compounds, mechanical impurities, resins and asphaltenes; increasing density and viscosity; and decreasing potential for light fractions.

The Energy Strategy of the Russian Federation to 2050<sup>1</sup> defines the need to increase oil refining depth to 90% by 2030 and to fully meet the demand of the domestic market in petroleum products, and to produce motor fuels with the highest environmental standards. This requires the implementation of new technological solutions for hydrocarbon processing.

According to Academician P.A. Reh binder, the founder of the school of physicochemical mechanics of disperse systems: “Optimization of the parameters of technological processes should be based on the most favorable content of physicochemical, thermal, and mechanical factors—changes in the chemical composition, including the addition of active substances, temperature, and the effects of external forces; optimal processes should always be complex. The task of the new field of knowledge, combining a number of problems of rheology, colloid chemistry, molecular physics, mechanics of materials, and the technology of their production, consists, first of all, in establishing the mechanism and patterns of the process of formation, deformation, and destruction of structures in order to control these processes” [2].

A qualified colloid-chemical approach to the production, transportation, and processing of hydrocarbon raw materials from the standpoint of the theory of oil disperse systems (ODSs) considering the dispersion structure and phase transitions in ODSs opens up significant opportunities for improving the efficiency and resource saving of various processes. It will also optimize their parameters without significant material costs. Scientists from Professor Z.I. Sunyaev’s scientific school “Physicochemical Foundations and Technologies of Oil Disperse Systems” continue to study the non-linear behavior of mixtures of hydrocarbon raw materials and petroleum products, accompanied by synergistic and antagonistic effects, and to investigate nonadditive effects in hydrocarbon feedstock processing [3–7].

The theoretical concepts and applied research of this school are based on the postulate of the relationship between the chemical and structural-group composition of the dispersed phase and its dispersity and physicochemical properties. The dispersed phase is considered to be a supramolecular structure: a complex structural unit (CSU) with characteristic composition, structure, properties, and internal interactions [8].

The discovery of the paramagnetic activity of molecules containing unpaired electrons reveals the nature of intermolecular interactions in CSU, and determines many features of the behavior, structure, and properties of CSE and ODS [9].

R.Z. Safieva’s review presents a systematic analysis of concepts regarding ODSs. Various approaches to accumulating and analyzing knowledge about ODSs (analytical, colloid-chemical, modeling, and chemoinformatic) were demonstrated. Each of these allows for the acquisition of digital data for the development of an information-based approach—petroinformatics. Concepts of the structure and properties of ODSs are based on the modern view of phase transitions involving asphaltenes and the understanding of the processes occurring within them when their conditions of existence change. These concepts provide the key to controlling phase transitions during hydrocarbon processing or to improving the quality of petroleum products [10].

The methods for influencing ODSs to control their structure can be divided into two groups: the introduction of new components into the system (additives, solvents, dopants, etc.) and wave action (mechanical or electromagnetic) of varying intensity. Mechanical actions are exerted by acoustic waves (including ultrasonic), cavitation, vibrating jets, pulsed

<sup>1</sup> Order of the Government of the Russian Federation of April 12, 2025, No. 908-r. “Energy Strategy of the Russian Federation for the Period up to 2050.” <http://static.government.ru/media/files/LWYfSENa10uBrrBoyLQqAAOj5eJY1A60.pdf>. Accessed November 22, 2025 (in Russ.).

impacts, cavitation mills, and elastic low-frequency vibrations generated by the column of pumped liquid. Electromagnetic actions are performed by constant and alternating electromagnetic fields. An alternating magnetic field is characterized by its frequency (from infrared to microwave and radiation).

In terms of intensity, wave actions can be conditionally divided into weak actions, which change the balance of intermolecular interaction forces, dispersion composition, and structure of an ODS, but do not affect the structure of molecules, and strong actions, which lead to a change not only in the dispersion composition but also in the molecular composition, i.e., cause chemical reactions [11].

Among the wave actions of interest are weak, or low-energy, wave actions (LWAs), produced by ultrasonic and constant magnetic fields. Their energy, as a rule, is significantly lower than the bond energies in hydrocarbons and heteroatomic compounds in ODSs.

The aim of this paper is to analyze features of the structure, properties, and intermolecular interactions of ODSs of various compositions and the possibility of controlling them using low-energy wave actions. The characteristics of ODSs and their differences from classical colloids are discussed.

### **Multiplicity of phases in oil disperse systems**

One of the features of ODSs is the multiplicity of phases: the ability of two or more phases (solid, liquid, and gaseous) to coexist in a single system. Examples of such ODSs include crude oil and unstable gas condensate, which contain dissolved gases, mineralized water, mechanical impurities of rocks, etc. The gas content in reservoir oil can reach 300–500 m<sup>3</sup>/m<sup>3</sup> or more. Its typical value for most grades of oil is 30–100 m<sup>3</sup>/m<sup>3</sup>.<sup>2</sup> For gas condensate, this value can exceed 600 m<sup>3</sup>/m<sup>3</sup>. For example, the unstable gas condensate of the Astrakhan gas condensate field contains 55–75 vol % dissolved gases. The water content in oil and the content of mineral salts also vary widely: up to 90 wt % and up to 10 g/dm<sup>3</sup>, respectively [12].

An even greater variety of dispersed inclusions is typical of waste oils, oil-containing waste, and sludge, in which the concentration of dispersed impurities, both inorganic and organic, varies over wide ranges.

### **The variety of hydrocarbon components and heteroatomic compounds contained in ODSs**

Another characteristic of ODSs is the diversity of hydrocarbon components and the heteroatomic compounds which they contain. They differ in their properties, structure, shape, and molecular size. For example, more than 140 different hydrocarbons were detected using chromatography in the 28–180°C gasoline fraction obtained at the Astrakhan Gas Processing Plant.<sup>3</sup>

Oil contains over 1000 identified organic compounds, but a much larger number remains unknown. Fourier-transform ion cyclotron resonance mass spectrometry has demonstrated that oils contain tens of thousands of compounds. The data obtained was processed in the form of a two-dimensional diagram corrected to the Kendrick mass using a method based on the idea that the oil system is characterized by continuous distribution of the molecular weights of the original components. A similarly complex structure is characteristic of heavy fractions and residues of oil in which molecules are complex hybrid structures containing saturated and unsaturated bonds. They are heteroatoms of sulfur, nitrogen, oxygen, and other elements. It was reported [10, 12, 13] that approximately 30 metals have been found in the organic compounds of oil.

### **Intermolecular interactions in ODSs: the absence of charge interactions and the presence of charge–polarization and exchange spin–spin interactions**

Another feature of ODSs is the absence of charge interactions between molecules in them. Conventional colloid chemistry represents electric charge as force centers, the main reason for the formation of colloidal particles. These concepts of Coulomb interactions are erroneously transferred to hydrocarbon media. In ODSs, there are no charged molecules, cations, and anions, easily traced by measurements of electrophoresis and the permittivity of petroleum products [9]. Among the variety of organic compounds in raw hydrocarbon materials and petroleum products, there are molecules containing functional groups of an acidic or basic nature, which are more or less obvious dipoles. Organic acids contained in oil have weak polarity. According

<sup>2</sup> Gas content (gas saturation) of reservoir oil. URL: <https://neftegaz.ru/tech-library/ngk/148222-gazosoderzhanie-gazonasyschennost-plastovoy-nefti/>. Accessed February 08, 2019 (in Russ.).

<sup>3</sup> The analysis was conducted at the plant's central laboratory with the author's participation. The data have not been published.

to the results of potentiometric titration, the content of benzoic and humic acids in the studied high-paraffin oil was 0.14 mg KOH/g [14]. Petroleum acids, as well as phenols, were detected in the resinous oil of the Irkutsk oblast [15].

Organic acids were reported to participate in the sedimentation process [10]. The presence of high-molecular-weight tetrameric naphthenic acids ( $C_{80}$ ) leads to the formation of naphthenate deposits during oil production and transportation.

It is also known that asphaltenes and resins are polar [3, 7, 8, 16, 17]. For example, it was shown [17] that, depending on the structure, molecular weight, number of aromatic cycles, and the presence of heteroatoms, the dipole moment of asphaltenes can vary widely from practically zero to 3.12 D.

Polarity was indicated as one of the causes of the self-aggregation of asphaltenes, with the  $\pi$  interaction between aromatic rings and the electron transfer being noted [18]. The solubility of asphaltenes in aprotic solvents with a low ionization potential was associated with the formation of donor–acceptor complexes [19].

Asphaltenes are insoluble in alkanes but dissolve well in light aromatic hydrocarbons (benzene, toluene), carbon disulfide, and carbon tetrachloride. All of the above solvents have a dipole moment equal to or close to zero (only toluene has a dipole moment of up to 0.37 D). On the other hand, asphaltenes are also soluble in polar substances such as pyridine and chloroform (2.2 and 1.15 D, respectively), but are insoluble in polar ethyl alcohol and ethyl ether (1.74 and 1.18 D, respectively).

The solubility of resins is significantly higher: from individual low-molecular-weight solvents (*n*-alkanes  $C_5$ – $C_7$ ,  $C_8$ , and others), petroleum ether, benzene, and toluene, which have no dipole moment, to alcohols, ethers, and organic acids, which have a dipole moment of 1.15 D and higher. Of course, resins are soluble in all substances in which asphaltenes dissolve.

The ambiguous behavior of resins and asphaltenes indicates that polarity is not a determining property in the interactions of the components of ODSs, charge interactions are absent, and charge–polarization forces are limited.

## Paramagnetism of oil and petroleum products

A distinctive feature of ODSs is paramagnetism. According to F.G. Unger's theory [9, 20, 21], the intermolecular interactions in hydrocarbon environments are dominated by the exchange interactions caused by the presence of molecules with stable radicals (with uncompensated spin) and estimated by the number of paramagnetic centers (PMCs). This property is

characteristic of a wide range of petroleum products: from gasolines ( $10^{15}$  spin/g) to asphaltenes, carbenes, and carboids (up to  $10^{23}$  spin/g). The number of PMCs in oil residues was experimentally measured [22] to be  $3 \cdot 10^{18}$  spin/g PMCs in heavy fuel oil of the Astrakhan gas condensate field and  $4.2 \cdot 10^{19}$  spin/g PMCs in tar of the Syzran oil refinery. The content of free radicals in Venezuelan oils and residues was analyzed [23]. The results showed that, in heavy oils, the PMC content ranges from  $2.4 \cdot 10^{17}$  to  $1.31 \cdot 10^{19}$  spin/g, and in the vacuum residues of these oils, the PMC content increases by one to two orders of magnitude—up to  $9.12 \cdot 10^{19}$  to  $1.372 \cdot 10^{20}$  spin/g.

It follows that a dominant role in the formation of colloidal particles in ODSs is played by the exchange interactions of the spin origin. Along with spin-containing molecules with explicit spin moments, ODSs also contain spin-polarized molecules, which similar to charge dipoles contain electrons with opposite spins, but separated in space. This creates a spin dipole which plays a significant role in exchange interactions during the formation of the ODS structure [9].

## Homolytic dissociation of components of an oil system

The number of PMCs in ODSs changes under the action of external factors (temperature, solvent) due to homolytic dissociation. Molecules with the lowest energy of forbidden reversible singlet–triplet transitions are separated into fragments. Each receives one electron from the broken bond, which leads to an increase in the number of free radicals. The phenomenon of homolytic dissociation was explored [20] during the dissolution and heating of asphaltene precipitates obtained by different methods. The NMR spectra of the samples differed depending on the nature of the solvent, the degree of heating, and the rate of removal of the precipitate from the solvent, even with the same feedstock. During dissolution or heating, the molecule passes into an excited state or undergoes cleavage of a weak bond to form a radical pair. The molecule becomes a triplet. Due to the positive sign of the interaction energy with solvent molecules (alkanes), these newly formed paramagnetic species precipitate along with the other paramagnetic species. When the precipitate is removed from the solvent, i.e., when paramagnetic materials are concentrated, conditions arise for a reverse triplet–singlet transition, i.e., for the recombination of radical pairs. The energy of such transitions is low and comparable to the energies of intermolecular interactions.

Similar conclusions were reached by M.Yu. Dolomatov in a study of the effect of heating the asphaltene concentrate from the second stage of propane deasphalting on its paramagnetic, electrically conductive,

and viscous properties. It was shown that an increase in the number of PMCs in asphaltenes is associated with an intensification of the thermal decomposition of metastable compounds due to the rupture of weak carbon bonds [17, 23].

Heating of heavy Venezuelan oils to 160–170°C leads to an increase in the number of free radicals. For the vacuum residues of these oils, the process of homolytic dissociation continued until approximately 230°C [24].

Since a change in the number of PMCs affects the behavior of ODSs in various refining processes, B.P. Tumanyan proposed the introduction, along with other physical and chemical properties, of a new evaluation parameter: the paramagnetic activity factor of a system. This factor more comprehensively assesses the quality of oil systems for their competent preparation for refining [6].

### Presence of trace elements in ODSs

One of the features of ODSs is also the presence of trace elements contained in oil which contribute to the overall picture of interactions in ODSs. More than 60 trace elements have been found in oils of various origins, including more than 30 metals [3]. The presence of transition *d*-metals in oils and petroleum products predetermines the existence of PMCs. Paramagnetism is most noticeable in petroporphyrins, in particular, in vanadyl porphyrin complexes, concentrated mainly in asphaltenes [25]. According to S.N. Khadzhiev, the content of transition metals in oil varies widely [26]. For example, in West Siberian oils of the Shaimskoe field, their concentrations (g/t) vary in the following ranges: Fe, 5.03–52.20; Mn, 0.02–0.64; V, 0.18–11.63; Ni, 0.41–17.06; and Cr, 5.3–32.7; at lower concentrations, Zn, Ti, Mo, Co, etc. are found. A correlation was noted between the contents of vanadyl porphyrins ultraheavy oil V(IV), sulfur, and nitrogen and the number of PMCs. The largest portion is found in resins and asphaltenes. The correlation between the concentrations of sulfur and vanadium was confirmed [16], but the relationship between the concentration of vanadium and the content of asphaltenes in tars proved to be inverse.

The electron paramagnetic resonance spectra of the samples of heavy and extra heavy Venezuelan crude oil and its vacuum residues showed an intense central signal related to free radicals and a multiplet due to the presence of porphyrin  $V^{+4}$  [24].

It should be noted that paramagnetism was also detected in oil-associated hardness salts in emulsified water globules. For example, the number of PMCs in the sediments of waters isolated from oil ranged from  $9.59 \cdot 10^{19}$  to  $1.61 \cdot 10^{20}$  spin/g [9, 21].

### Equation of intermolecular interactions in ODSs

All the above features determine specific intermolecular interactions characteristic of ODSs, namely, the formation of stable associative combinations based on exchange interactions caused by the spin and spin-polarized properties of molecules. This approach to the formation of colloidal particles was proposed by F.G. Unger. The development of quantum-chemical concepts made it possible to define a pair interaction operator  $U$  as a set of expressions depending on the distance between the interacting particles and the nature of the bond [9]:

$$U(R) = \pm k e^{-k_0 R} \pm k_1 R^{-1} \pm k_2 R^{-2} \pm k_3 R^{-3} \pm k_4 R^{-4} \pm k_5 R^{-5} - k_6 R^{-6},$$

wherein  $k$  are coefficients that can be represented as constants or functions, not necessarily linear;  $R$  is the distance between particles; and  $e$  is the base of the natural logarithm.

In this equation, each term accounts for interactions of only a specific type. The contribution of each subsequent term to the overall balance of intermolecular interactions decreases as the absolute value of the exponent of the term increases. The first term is the operator of exchange interaction between radicals and/or triplet (or higher-order multiplet) paramagnetic molecules to form a homeopolar (covalent) bond. The second term is the operator of pair interaction between two ions and characterizes charge (Coulomb) interactions. The third term is the operator of interaction between a charge and a charge dipole, resulting in charge interaction and the formation of ordered associative combinations. The fourth term is the operator of resonant interaction, i.e., the interaction of a radical (a paramagnetic molecule, a spin-containing particle) with a spin-polarized diamagnetic molecule. As in the previous case, a free radical can form an ordered associative combination with a certain number of spin-polarized molecules based on exchange interactions. Exchange interactions can be transmitted throughout the volume of a liquid by analogy with charge interactions. The fifth term is multipole and reflects the charge nature of the dipole, quadrupole, and multipole moments. The sixth term is also multipole but determines the spin nature of the dipole, quadrupole, and multipole moments. The seventh term describes only the van der Waals attraction of particles; therefore, it has a negative sign and characterizes long-range forces. These forces are represented by various interactions: orientational, dispersion, and induction ones.

From the analysis of F.G. Unger's equation, it can be concluded that the first, fourth, and sixth terms describe exchange interactions in oil systems. Moreover,

the highest contribution is made by the potential of pair interaction between two free radicals. This is the energy of a covalent bond. It is such bonds that exist in hydrocarbon molecules. For example, the energies of carbon–carbon bonds in alkanes are known to reach 440 kJ/mol, while in molecules containing oxygen, sulfur, and nitrogen heteroatoms, they are somewhat lower, around 270–350 kJ/mol. Resonant interactions between a radical and a diamagnetic spin-polarized molecule determine their attraction or repulsion. In ODSs, such forces arise between the paramagnetic core (most often asphaltene) and the nearest layers consisting of diamagnetic molecules capable of spin multipole–multipole interactions of diamagnetic molecules. These molecules are located in the outermost layers of the solvation shell; i.e., they are furthest from the core.

It should also be noted that, in ODSs, there are donor–acceptor interactions in the form of hydrogen bonding. Strong hydrogen bonds (60–200 kJ/mol), intrinsic to water and aqueous solutions, are not typical of components of oil systems. Heteroatoms and arene fragments tend to form medium hydrogen bonds (4–6 kJ/mol). Weak hydrogen bonds (0.5–4.0 kJ/mol) are formed by almost all petroleum hydrocarbons. The contribution of hydrogen bonds to the potential energy of interaction of nonpolar and polar compounds can reach 99%. The energy of a hydrogen bond includes three components: the electrostatic energy of attraction, which prevails at large distances; the energy of polarization (orientation and induction interactions) and charge transfer, which manifests itself as the distance decreases and promotes the attraction of molecules; and the energy of repulsion. Thermal exposure favors the destruction of hydrogen bridges with a bond energy of up to 40 kJ/mol [9].

Quantum-chemical calculations and experimental studies by M.Yu. Dolomatov [27] showed that a significant contribution to the intermolecular interactions of molecules in ODSs with the participation of asphaltenes is made by hydrogen bonds. The formation of a charge-transfer complex, and the ionization potentials and electron affinity are consistent with the data on optical density, electron affinity, and electrical conductivity.

The second, third, and fifth terms of the equation describe Coulomb interactions. Since charged molecules are absent in oil systems, and charge dipoles are present in very small quantities, their role in the formation of an ODS according to the presented concepts [9, 21] can be neglected.

On the other hand, a study of the viscosity increase mechanism in crude oil using electrostatic potential analysis and molecular dynamics established electrostatic interactions between asphaltene fragments [28].

Asphaltenes were modeled as normal (neutral), acidic, and anionic and explain the interactions of the components in the system by the presence of positive and negative electrostatic potential on the surfaces of their molecules. The extensive nonpolar space on the surface of normal asphaltenes facilitates their interaction with crude oil molecules (non-Coulomb interactions).

Quantum-chemical calculations using density functional theory determined the energy of intermolecular interactions between fragments of asphaltene nanoparticles in the range from 33.85 to 113.42 kJ/mol [27]. The stability of nanocluster formation was explained by donor–acceptor interactions between naphthenic–aromatic fragments.

The complexity of the structure of asphaltenes and various approaches to their isolation from oil systems, instrumental and chemical analysis, and mathematical and quantum-chemical description give rise to different models of intermolecular interactions, each of which has its own limitations and disadvantages.

## Two-component models of complex structural units of ODSs

All of the above-mentioned features of the composition of ODSs and the intermolecular interactions within them determine a certain ordered organization of ODSs which consist of structural elements. According to Z.I. Sunyaev, structural elements of ODSs are defined as sets of interacting elements of ODSs which retain their physicochemical characteristics and composition in space and time. Particles of the dispersed phase of ODSs are characterized by a specific structural organization. They determine the properties of the entire system and its susceptibility to various external influences. A particle of the dispersed phase is called a complex structural unit (CSU) [8].

As mentioned earlier, ODSs are multiphase and polydisperse systems. To a first approximation, they can be represented as systems containing two-component CSUs representing various dispersed inclusions. Figure 1 presents examples of the most common two-component models of CSUs of liquid ODSs.

An ODS consisting solely of hydrocarbons and various organic heteroatomic compounds (Fig. 1a) is a dispersion medium (diamagnetic hydrocarbons) and a CSU containing the heaviest components with unpaired radicals and surrounding layers arranged according to the exchange interaction potential. The composition of the core and the number of layers depend on the nature of the ODS.

Studies of the composition of CSUs by I.R. Khairutdinov and F.G. Unger [9, 29] using radioactive tracers showed that the solvate shells isolated from

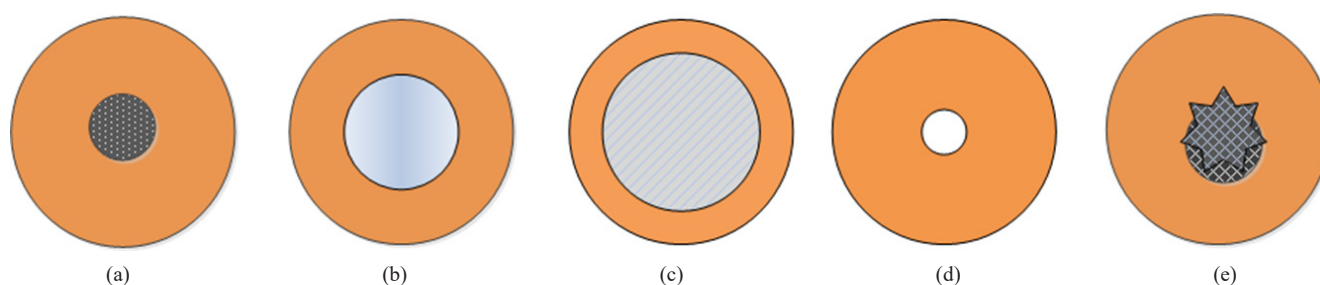


**Fig. 1.** Types of two-component models of complex structural units of oil disperse systems containing different dispersed phases in the dispersion environment:

- (a) high-molecular-weight condensed aromatic compounds;
- (b) water globule;
- (c) high-molecular-weight paraffins;
- (d) gas bubble;
- (e) inorganic particles, mechanical impurities

residual petroleum products contain low-molecular-weight maltenes, petroleum acids, thiols, phenols, and other heterocyclic compounds with weak paramagnetic properties. Along with them, high-molecular-weight aromatic compounds and resins are also present, with strongly manifested paramagnetism. The cores in liquid ODSs may also contain dense high-molecular-weight formations representing spin-containing particles.

For heavy distillates and residual petroleum products, the composition of the CSU can be described by a hypothetical model in which the core consists of highly condensed aromatic compounds with high paramagnetism (asphaltenes). The surrounding layers, in order of decreasing paramagnetism, contain aromatic and heteroatomic components with a smaller number of condensed rings, then condensed naphthenic–aromatic compounds and paraffin–naphthenic hydrocarbons with polycycles and with signs of spin polarization. The dispersion environment consists of paraffinic or paraffinic–naphthenic hydrocarbons without signs of spin polarization [9].

The photocolorimetrically determined sizes of CSUs vary depending on the nature of the petroleum product and range from tens of nanometers for light distillate fractions to hundreds of nanometers for vacuum distillates and residues [3, 30].

In emulsified oil systems (inverse (water-in-oil) emulsions), the dispersed phase is water (Fig. 1b). Water-in-oil emulsions have been an object of study for decades. Surfactants are adsorbed at the interface, and the surface layer differs sharply from the properties of the inner and outer parts of the adjoining phases. This is because the molecules comprising this layer have an excess of surface energy. The interaction energy of the solvation layer with molecules of the dispersed phase depends on the composition of the dispersed phase and determines the size and stability of the system.

A study of the interfacial layer of water-in-oil emulsions showed that it consists predominantly of asphaltenes [31, 32]. A more detailed analysis of structural-group composition revealed that the concentration of asphaltenes in the interfacial layers is 6.7–7.2 times higher than that in oil, and the content of resins is 2–3 times lower [33]. Figure 2 shows water globules enclosed in a complex shell consisting of a first layer of asphaltenes adsorbed directly at the interface and a second layer of resinous substances adjacent to the asphaltenes as a result of exchange interaction. The shells prevent the coalescence of the water globules.

The dispersion medium in a water-in-oil emulsion is inhomogeneous. It consists of hydrocarbons and organic heteroatomic compounds and, in turn, forms a dispersion environment with higher dispersity. Here intermolecular interactions form a CSU similar to that described in Fig. 1a. The dispersities of emulsified globules of water and the oil phase can differ from several to thousands of times, depending on the composition of the emulsion. The closer the dispersities of the water globules and the oil phase, the more stable the emulsion. This is a manifestation of such a property of the dispersion medium as polydispersity. The particle sizes of the aqueous dispersed phase in water-in-oil emulsions range from hundreds to nine thousand nanometers [34]. Figure 2 illustrates the structure of the disperse system of a water-in-oil emulsion.

The following two-component model of an ODS (Fig. 1c) contains a CSU, the core of which is high-melting paraffins [6, 14, 35–39]. The associative behavior of *n*-alkanes in ODSs and its change under different temperature conditions were investigated using dynamic light scattering methods, as well as optical, electron, and atomic force microscopy [35]. The associates of *n*-alkanes are shown to have a shell,

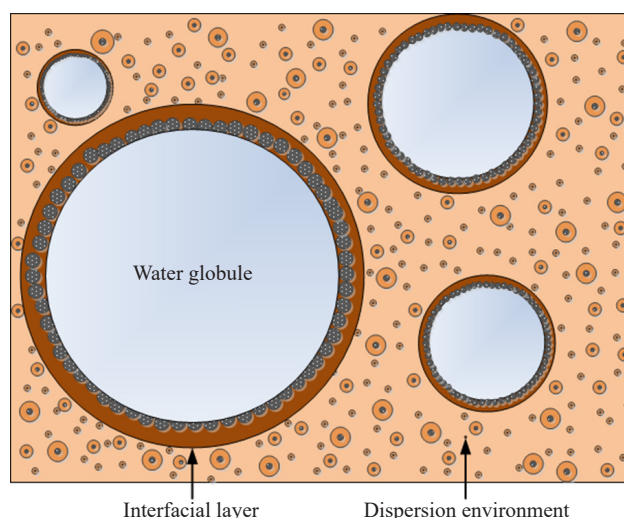


**Fig. 2.** Structure of the disperse system of a water-in-oil emulsion with the interface consisting of layers

a specific internal composition, and a structure. In the paraffinic oil system under investigation, the associates are preserved even at elevated temperatures. A study of the effect of paraffin concentration on the dispersed structure of hydrocarbon fluids at temperatures below the onset of crystallization established [38] that, at low concentrations (below 3 wt %), loose steric aggregates are formed. At higher concentrations, dense packings of gel-like structures of significant size are formed. The concentration of paraffins and resins and their ratio affect the process of coarsening of aggregates, the pour point, and the amount of asphalt–resin–paraffin deposits [39].

Using the example of the Tuymazy oil, it was shown [38] that asphaltenes and resins with a low content of paraffin fragments, high molecular weight, and polarity are adsorbed on paraffin crystals and form a dense packing of molecules.

A similar conclusion was made about the formation of stable associative complexes with an ordered structure in a mixture of resins and paraffin hydrocarbons and a decrease in the crystallization temperature of the system [36]. As in the case of water-in-oil emulsions, asphaltenes and resins are present at the interface, and the ODS containing paraffins in the CSU can be considered as a complex system with dispersity of different dimensions. Just as in the case of water-in-oil emulsions, where the oil medium acts as a dispersion environment for dispersed water globules, the ODS with the paraffin-containing CSU has an oil dispersion medium which is inhomogeneous and can itself be considered as an ODS with a dispersed phase particle size tens and thousands of times smaller.

Figure 1d presents the following two-component model of an ODS containing a gas bubble as the SCE

(gas-in-oil emulsion) which can be formed during the dissolution of gas or steam, as well as during the distillation of hydrocarbon feedstock. Gas-in-oil emulsions are characterized by very thick solvation layers, although the bubbles of the gas phase are small in size. If such an emulsion was formed by condensation, the dispersed phase (CSU cores) contains dissolved hydrocarbon vapors, and if it was formed by dispersing, the dispersed phase may contain gases insoluble in the hydrocarbon environment. The foaming capacity of gas-in-oil emulsions depends on the content of natural surfactants, such as naphthenic acids and their salts, sulfur compounds, and phenols. High-molecular-weight components, such as asphaltenes and resins, paraffins, and other poorly soluble compounds, have a stabilizing effect [3, 6, 7, 40, 41].

The particle size of the gas dispersed phase varies widely depending on the hydrocarbon composition of the dispersion environment, the nature of the gas in the CSU core, and the conditions in which the CSU is located. For a gas-in-oil emulsion such as fuel oil containing dissolved hydrogen sulfide, the photocolorimetrically determined particle size of the dispersed phase ranges from 350 to 600 nm [42]. However, the dispersity of heavy fuel oil after degassing increases significantly, while the average particle size of the dispersed phase decreases several times.

Figure 1e presents a two-component ODS containing a CSU in the form of mechanical impurities—solid inclusions of inorganic nature. The sources of mechanical impurities are sand, clay, fine iron particles, rust, salts, and dust, which primarily enter the oil during production, storage, transportation, and refining. At the interface between the solid particle and the oil dispersion environment, the same forces

determining the surface energy excess act leading to surfactant adsorption. The mechanisms of adsorption of asphaltenes at the interfaces between oil and silica-based nanofluid and oil and wetted sandstone were investigated [43]. The results of packet adsorption showed the emergence of a strong affinity of the silica nanofluid film. Thus, in this case, as in the previous ones, ODS is a complex system in which the particle of mechanical impurities is the core of the CSU with asphaltene shells, and the hydrocarbon phase is the dispersion medium. This hydrocarbon phase, in turn, is an ODS with higher dispersity, in which the particle size of the dispersed phase can vary by tens or hundreds of times depending on the oil composition, the nature of the impurities, and its extraction methods. For crude oil, the size of mechanical impurities varies from tens of nanometers to several millimeters.

### Redistribution of CSU components between layers and dispersion medium

Another feature of ODSs is the redistribution of SCU components between layers and the dispersion medium under external influences [3, 6–8].

According to Z.I. Sunyaev's theory of controlled phase transitions, the geometric dimensions of the CSU and, accordingly, the physicochemical and technological properties of the ODS change under the combined action of external factors. As the core size changes, hydrocarbons are continuously redistributed between the macrophases, i.e., between the dispersed phase and the dispersion environment. Moreover, the manifestations of this process undergo extreme or multiextremal changes [3].

It is precisely because of phase transitions in ODS that many of their properties are not additive ("anomalous"). The viscosity of mixed petroleum products is known not to be additive, since the mixing of petroleum products is already an external influence which alters the balance of intermolecular forces in the system, leading to a redistribution of components between the dispersed phase and the dispersion environment. Moreover, a study of the viscosity of oil from the Ashalchinskoye field and the light fractions, vacuum distillates, and residue isolated from it established the absence of additivity even in cases where the components of the original ODS were first separated by distillation and then combined again.

When adding 5 vol % gasoline fraction to the oil distillate, we observed nonadditive changes in kinematic viscosity. As expected, the kinematic viscosity decreased, but not according to the additivity rule. This parameter was determined at two temperatures, 40 and 100°C, and the results showed inconsistent changes.

For example, an increase in temperature decreases the viscosity of the original oil distillate by a factor of 6.9, while for the oil with gasoline additive, it decreased by a factor of 5.7. The activation energy for viscous flow of the oil with the additive was 13% lower than that of the original oil. A possible explanation is that, when the oil is diluted with gasoline, some of the solvation shells of the dispersed phase are transferred to the dispersion environment. Therefore, upon heating, the ability of such a system to further remove components from the CSU decreases when compared to the original ODS.

As already mentioned, the ability to control phase transformations in ODSs by changing the balance of intermolecular interaction forces and controlling the dispersity of ODSs allows the desired values of the macroproperties of hydrocarbon raw materials for efficient processing to be achieved, as well as those of petroleum products for improving their quality [3, 6, 7].

### Control of phase transitions and dispersity of ODSs

Another way to control the dispersity of ODSs is the introduction of solvents, additives, and dopants to hydrocarbon raw materials and petroleum products, and compounding to obtain specified dispersion properties that determine optimal physicochemical characteristics [3–8].

E.A. Chernysheva developed an index  $I_{hc}$  of hydrocarbon composition of oils: the ratio of the content of paraffinic hydrocarbons to the content of aromatic hydrocarbons and to the sum of the contents of resins and asphaltenes. This index is proposed as one of the criteria for assessing the stability of ODSs. It can be used in a set of parameters for assessing the stability and compatibility of oils sent for processing along with data on the group hydrocarbon composition, the stability factor indicator, and the ratio of physicochemical parameters of oil, reflecting the structural features of the oil system [5].

Another way to control phase transitions in ODSs is by wave actions. These include ultrasonic and electromagnetic actions of medium and low intensity. The effects of magnetic fields and ultrasound on oil, petroleum products, and hydrocarbons were initially studied in the middle of the last century [45–48], and the number of such studies is currently growing. Of significant interest are low-intensity wave actions (LWAs). These include ultrasonic waves with a frequency of 20–100 kHz and an intensity of up to 0.4 W/cm<sup>2</sup> and a constant magnetic field with an induction of less than 0.4 T.

The advantages of LWAs are low energy consumption, low environmental risks, technical simplicity, and low capital costs. The energy of this

type of wave actions is typically much lower than the bond energy in hydrocarbons and heteroatomic compounds of ODSs. This determines the range of their effect on the oil system, namely, on intermolecular interactions and phase transitions between the dispersed phase and the dispersion environment [3, 6, 11].

The ultrasonic action on oil systems has been explored in Russia and abroad [34, 47–49]. For many years, scientists at the Altai State University, under the direction of V.N. Khmelev, have been studying the effects of ultrasound on various phenomena and technological processes, as well as developing and creating ultrasonic devices [49–51].

At the Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, the effect of ultrasonic vibrations was experimentally and theoretically investigated under the direction of N.V. Yudina [14, 15, 36, 52, 53]. At this institute, the effect of magnetic fields on oil, petroleum products, and their components was also explored [54–57]. Scientists from the Ufa University of Science and Technology, headed by S.R. Alimbekova, proved that descaling of the surface of well equipment under the action of a constant magnetic field and an electromagnetic field is caused by the inhibition of the process of nucleation and growth of crystals, as well as by changes in their dispersity and polymorphism [58, 59].

Since 1995, a scientific school for exploring the effect of LWAs on oil systems in dynamic mode (on a liquid flow) has been formed at the Astrakhan State Technical University under the research leadership of the author of the article. The treatment with a constant magnetic field in dynamic mode was carried out in the range of induction of 0.1–0.4 T, and flow velocity in the active gap from 0.08 to 0.3 m/s. Ultrasound acting on the liquid flow had a frequency of 20–50 kHz and a power of 0.23–0.33 W/cm<sup>3</sup>. When testing various hydrocarbon raw materials, petroleum products, used oils, and oil waste, practical recommendations were obtained for the adaptation and implementation of the results in industry [11, 22, 30, 42, 46, 60–67].

During atmospheric and vacuum distillation of stable gas condensate, crude oil, and heavy fuel oil, all pretreated in a constant magnetic field, the yield of light fractions increased by 1–6 wt %. During visbreaking of magnetically pretreated heavy fuel oil, the coke and gas formation decreased by a factor of 1.2–2.3. The yield of light petroleum products increased by 4–8 wt %. Low-energy treatment of water-in-oil emulsion showed that the degree of its separation increased by 20–30%. The degree of removal of mechanical impurities from LWA-pretreated gas condensate increased by a factor

of 15. A significant, more than 80%, reduction in deposits from model mixtures on the heat exchange surface was also observed [11, 60, 61].

The purity reached 86% [42] after LWA during degassing of heavy fuel oil to remove hydrogen sulfide. The quality of LWA-pretreated diesel and marine fuel was improved, the fuel consumption decreased by 5%, and the carbon monoxide emissions in exhaust gases were lower [62, 63]. A positive effect of a magnetic field on the uniformity of the gas distribution in the adsorber for drying natural gas and an increase in the service life of zeolite were discovered [64]. The possibility of intensifying the selective purification of oils and the extraction of undesirable components from oil feedstock with *N*-methylpyrrolidone was demonstrated [65].

The treatment efficiency of magnetically pretreated oil-containing wastewater increased by a factor of 1.3–5.7 [66]. Laboratory and industrial tests of magnetic treatment of an amine solution showed a decrease in the foaming capacity of the absorbent, a decrease in foam stability, and more effective removal of mechanical impurities during filtration [67].

LWAs on a ODS lead to a change in its dispersity depending on the component composition of the system. If the ODS consists almost exclusively of hydrocarbons and various organic heteroatomic compounds, then a phase transition from the dispersed phase to the dispersion medium occurs, resulting in homogenization of the system. If the ODS is a more complex multiphase or polydisperse system, then the wave action influences different levels: homogenization in the hydrocarbon medium and the opposite effect for the coarse dispersed phase (water and gas emulsions, suspensions).

The effect of low-intensity and low-frequency ultrasound is exerted in both stationary and dynamic modes and leads to a change in the balance of intermolecular forces which organize the ODS. Even on prolonged exposure, a constant magnetic field of low induction under stationary conditions has virtually no effect. However, applying a magnetic field to a flow causes a noticeable change in its paramagnetic, dispersion, and physicochemical properties. In this case, it is possible that a synergistic effect of the energy of liquid motion and its structuring in a magnetic field is manifested. It was assumed [68] that shear stresses during liquid flow affect the viscosity of oil, the rate of paraffin deposit growth, and the rate of hardness salt deposit growth. They are a consequence of changes in the colloidal components of these systems, while the destruction of aggregates occurs even at low liquid velocity gradients, corresponding to low shear stresses.

We observed a 1.1–1.2-fold change in the number of PMCs in heavy fuel oil and its blends with tar when passing them at different flow rates through a setup consisting of a pump and transport tubes passing through a magnetic tunnel disconnected from the grid. When a magnetic field was applied, the number of PMCs increased 1.2–1.5 times [22]. Similar changes were observed for the dispersity of petroleum products of different compositions: diesel fraction, vacuum distillate, and heavy fuel oil [30].

### Constant magnetic field and ODSs

The mechanism of action of a constant magnetic field on an ODS consisting primarily of hydrocarbons and various organic heteroatomic compounds, some of which have spin properties, is as follows. Before exposure to a magnetic field, this system exhibits chaotically arranged spin dipoles, spin-containing particles and compactly organized CSUs, conventionally shown as two-layered (Fig. 3a). Under the action of a magnetic field, the paramagnetic nuclei are oriented along the field vector. During this movement, the shells are deformed, they move away from the core, partially detach, and pass into the dispersion medium (Fig. 3b). This leads to a decrease in the CSU size, i.e., an increase in the dispersity of the

system as a whole and an enrichment of the dispersion medium.

For more complex multiphase, polydisperse, multicomponent oil systems, the basic two-component models of which were discussed above, the magnetic field affects both the coarse dispersed phase and the inhomogeneous dispersion medium.

As already mentioned, in almost all ODSs, surfactants containing PMCs and associated shells are present at the interface.

The interlayer of paramagnetic molecules is also subject to the magnetic field, causing the molecules to align along the magnetic induction vector. It also deforms the interlayer, and detaches it, transferring into the dispersion oil environment. As a result, the surface of the dispersed particle is exposed and becomes accessible for coagulation or coalescence. This phenomenon facilitates the removal of mechanical impurities, the separation of emulsions, or the degassing of the liquid.

The combination of wave action and chemical methods increases the efficiency of technological processes [11, 42, 57, 60, 61, 65, 69–72]. For example, during the degassing of heavy fuel oil to remove hydrogen sulfide, the purity increases significantly under the sequential action of ultrasound and a constant magnetic field on the flow. Such treatment increases

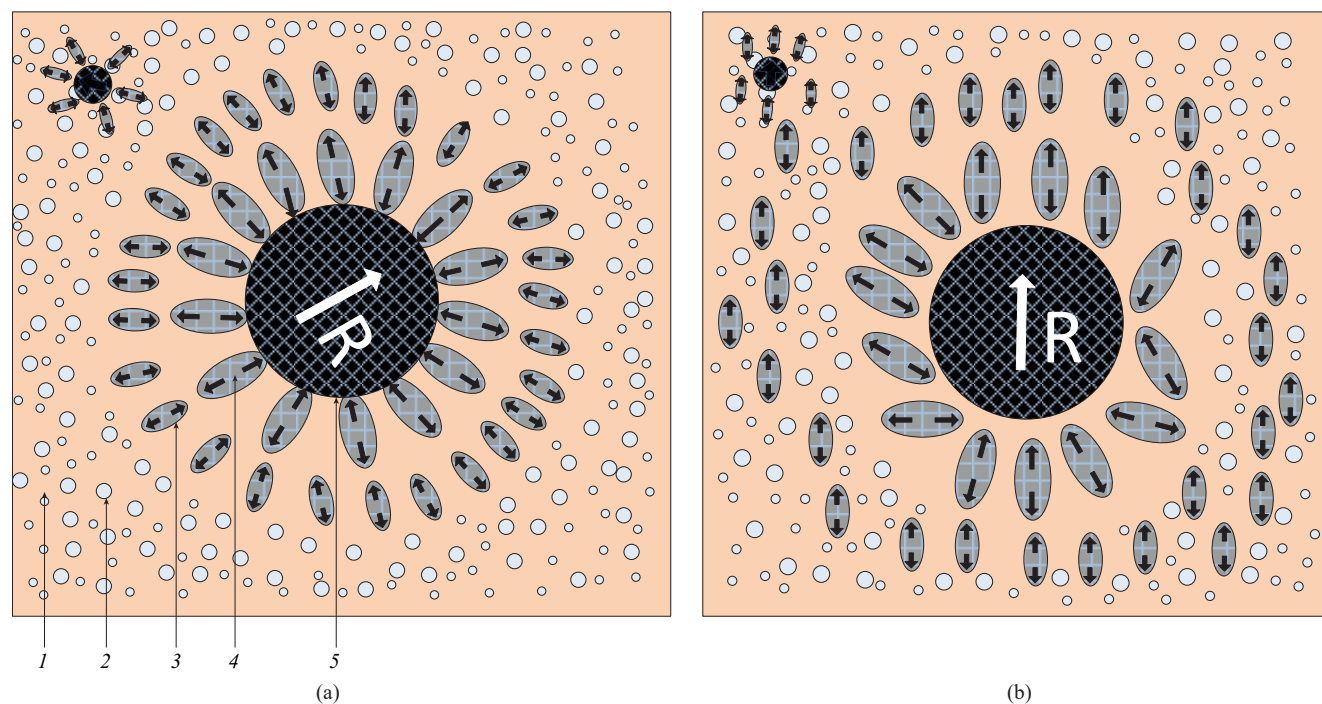


**Fig. 3.** Changes in the structure of an oil disperse system consisting of hydrocarbons and various organic heteroatomic compounds under the action of a constant magnetic field: (a) before and (b) after magnetic treatment. (1) Inhomogeneous neutral dispersion medium; (2) components of the dispersion environment from neutral molecules with compensated spins; (3) spin-polarized molecules with low paramagnetism; (4) spin-polarized molecules with increased paramagnetism; (5) the core consisting of spin-containing molecules with high paramagnetism

the yield of light fractions during the distillation of hydrocarbon feedstock, improves the separation of water and mechanical impurities from oil and gas condensate, and reduces the formation of deposits on heat exchange surfaces [11, 42, 60, 61].

Combined treatment has a more intensive effect on the viscosity and low-temperature properties of oil and the behavior of its components. The combination of wave action with reagent treatment increases the efficiency of oil preparation for refining. It decreases viscosity, and reduces the consumption of a demulsifier during oil dehydration, a hydrogen sulfide neutralizer during heavy fuel oil degassing, etc. [11, 57, 61, 65, 69–72].

## CONCLUSIONS

An analysis of accumulated knowledge about the characteristics of ODSs shows that they are characterized by multiplicity of phases, as well as a diversity of hydrocarbon components and heteroatomic compounds, mineral impurities, and trace elements. Intermolecular interactions in ODSs are dominated by exchange spin-spin interactions caused by the paramagnetism of resins and

asphaltenes, as well as the homolytic dissociation of high-molecular and heteroatomic organic compounds. Changes in the conditions of ODS existence and external influences lead to the redistribution of ODS components between the layers and the dispersion environment. Using two-component models of ODS shells, their interaction with the dispersion environment is explained, providing a key to understanding the possibility of controlling the structure, dispersity, stability, and other properties of oil systems.

Considering the specific features of ODSs is key to the efficient and optimal processing of hydrocarbon feedstock and the upgrading of petroleum products. Effective tools for controlling the dispersed state of oil systems include treatment in a constant magnetic field (magnetic induction no higher than 0.4 T), or ultrasonic treatment (20–50 kHz, 0.23–0.33 W/cm<sup>3</sup>). These wave actions are low-energy, and the equipment required does not necessitate significant capital or operating costs. As demonstrated above, LWAs considerably improve the technological and, consequently, economic performance of processes, promoting rational use of hydrocarbon feedstock and petroleum products.

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REVIEW ARTICLE

## Ionizable lipids as a promising platform for creating mRNA vaccines

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### Abstract

**Objectives.** Gene therapy involves the administration of various types of therapeutic nucleic acids into the organism, in order to treat severe hereditary diseases, as well as cancer. Furthermore, the COVID-19 pandemic demonstrated the possibility of rapid development and the effectiveness of both DNA and mRNA vaccines for the prevention of viral diseases. Numerous studies in the field of gene therapy have revealed that in most cases successful delivery of nucleic acids requires a special delivery system which protects nucleic acids from the effects of external and internal biological factors. Among the various types of such tools, non-viral delivery systems have proven to be the most versatile and safe ones. In the case of mRNA delivery, such systems are usually called mRNA vaccines, consisting of cationic or ionizable lipids. The purpose of this review is to justify the choice of the optimal structure of lipid components of mRNA vaccines and highlight the current prospects for their clinical use.

**Results.** In this review, we have considered the evolution of lipid structures, from cationic to ionizable, as the main components of mRNA delivery systems. Furthermore, the study demonstrated the necessity to use other types of lipids in mRNA vaccines. It also presents a review of clinical trials of mRNA vaccines against viral and oncological diseases, and provides recommendations for the design of the optimal structure of both cationic and ionizable lipids.

**Conclusions.** The most promising lipids for the development of mRNA vaccines are ionizable. They do not have a permanent positive charge which reduces their cytotoxicity and undesirable binding to components of the immune system. In general, mRNA vaccines can be universal and effective means for treating various types of diseases. However, their composition needs to be careful optimized.

### Keywords

gene therapy, mRNA vaccines, cationic liposomes, lipid nanoparticles, cationic lipids, ionizable lipids

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ОБЗОРНАЯ СТАТЬЯ

# Ионизируемые липиды как перспективная платформа для создания мРНК-вакцин

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## Аннотация

**Цели.** Генная терапия подразумевает введение в организм различных типов терапевтических нуклеиновых кислот для лечения тяжелых наследственных, а также онкологических заболеваний. Кроме того, пандемия COVID-19 показала возможность быстрой разработки и эффективность использования ДНК- и мРНК-вакцин для профилактики вирусных заболеваний. Многочисленные исследования в области генной терапии выявили, что в большинстве случаев успешная доставка нуклеиновых кислот требует наличия специальной системы доставки, защищающей нуклеиновые кислоты от действия внешних и внутренних биологических факторов. Среди различных типов таких инструментов наиболее универсальными и безопасными зарекомендовали себя невирусные системы доставки, такие как катионные липосомы и липидные наночастицы, формируемые из катионных или ионизируемых липидов соответственно. В случае доставки мРНК такие системы обычно называют мРНК-вакцинами. Целью данного обзора являлось обоснование выбора оптимальной структуры липидных компонентов мРНК-вакцин и освещение текущих перспектив их клинического применения.

**Результаты.** В данном обзоре мы рассмотрели эволюцию структур липидов, начиная с катионных и заканчивая ионизируемыми, как основных компонентов систем доставки мРНК. Кроме того, показана необходимость использования в составе мРНК-вакцин других типов липидов, проведен обзор клинических испытаний мРНК-вакцин против вирусных и онкологических заболеваний, даны рекомендации по дизайну оптимальной структуры катионных и ионизируемых липидов.

**Выводы.** Наиболее перспективными липидами для разработки мРНК-вакцин являются ионизируемые. Они не обладают постоянным положительным зарядом, что снижает их цитотоксичность и нежелательное связывание с компонентами иммунной системы. В целом, мРНК-вакцины могут стать универсальным и эффективным средством лечения различных типов заболеваний, но требуют тщательной оптимизации их состава.

## Ключевые слова

генная терапия, мРНК-вакцины, катионные липосомы, липидные наночастицы, катионные липиды, ионизируемые липиды

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## INTRODUCTION

The first clinical applications of gene therapy approaches show that this field has enormous potential for treating serious diseases [1, 2], including hereditary and tumor diseases.<sup>1</sup> However, it also carries potential risks. Various types of nucleic acids are used as therapeutic agents in gene therapy. Plasmid DNA (pDNA) and messenger RNA (mRNA) ensure the expression of proteins which are absent in the body, while small interfering RNA (siRNA) and antisense oligonucleotides block the expression of unwanted proteins [3]. CRISPR-Cas technologies occupy a special place as the most promising tool for direct genome editing available today [4].

Regardless of type, therapeutic nucleic acids are unable independently to overcome the biological barriers of the body, such as blood plasma proteins, nucleases, cell membranes and others [5]. Special delivery systems must be used to compact and protect nucleic acids on their way to the site of therapeutic effect. These can be divided into two types. The first type, viral, is highly effective in delivering nucleic acids. However, despite the progress made in the design of viral particles, they are highly immunogenic, toxic, and potentially mutagenic [6]. Less effective but safer are non-viral nucleic acid delivery systems based on lipids [7], polymers [8, 9] or inorganic materials [10].

The development of gene therapy and improvements in its effectiveness and safety have made it possible for a number of gene therapy drugs to be approved for use. However, gene therapy only became widely used during the COVID-19 pandemic as a new generation of vaccines. The most well-known are the Russian DNA vaccine *Sputnik V* [11] and the Western mRNA vaccines *Pfizer/BioNTech* (USA/Germany) [12] and *Moderna* (USA) [13]. This was followed by a significant increase in the research and development of mRNA vaccines not only against viral infections but also against cancer. Unlike pDNA, mRNA is easier to deliver to cells because it does not need to penetrate the nucleus, in order to exert its therapeutic effect. It is sufficient for it to penetrate the cytosol of the cell.

This review will analyze the pros and cons of using different lipids as components of mRNA vaccines, including the structure and properties of these compounds. It will also mention the specifics of creating a finished vaccine, current clinical trials, and the prospects for further development of mRNA technology.

## EVOLUTION OF LIPID STRUCTURES

In order to replace vaccines based on inactivated viral particles, mRNA vaccines are increasingly being developed and used. Their mechanism of action is to teach the body to produce antibodies to viruses or damaged cells. Unlike conventional vaccines, mRNA vaccines have a number of advantages:

- They do not cause a severe immune response;
- They are easily modified for mutating strains or other diseases;
- Production can be easily scaled up;
- They are purer (do not contain impurities from microorganisms);
- They are simpler and safer to produce.

Since the administration of “naked” mRNA into the body is ineffective and has no therapeutic effect, special delivery systems are required for the development of mRNA vaccines. The most biocompatible and safe systems are nanoparticles based on polymers or lipids. For example, lipid nanoparticles (LNPs) show a low level of toxicity and a high level of efficiency in delivering mRNA to the body’s cells, including helping to release mRNA into the cell cytosol. Despite a huge amount of development and research in the field of lipid-based delivery systems, there is no single universal compound or nanoparticle composition which always allows for the effective delivery of different types of mRNA. The effectiveness of delivery is influenced not only by the nature of the compounds, but also by their quantity and ratio in the composition, as well as the method of nanoparticle preparation. Thus, cationic liposomes are usually obtained from cationic lipids by hydrating the lipid film followed by ultrasonic treatment and/or extrusion. Complexes of cationic liposomes and nucleic acids are then obtained by simple mixing. In the case of ionizable lipids, ready-made LNPs are usually obtained immediately by mixing the lipid with nucleic acids using microfluidic technologies [3].

There are three types of lipids most commonly used in liposome formulation: cationic or ionizable lipids responsible for packaging and delivering nucleic acids; helper lipids which assist in releasing nucleic acids into cells; and PEG lipids (polyethylene glycol derivatives) which protect the particle from interacting with blood proteins on its way into the cell.

Cationic and ionizable lipids consist of four parts: a hydrophilic part, usually represented by amines; a hydrophobic part, including a spacer which may include both alkyl groups and various steroid derivatives;

<sup>1</sup> The Biotech Death of Jesse Gelsinger. The New York Times. <https://www.nytimes.com/1999/11/28/magazine/the-biotech-death-of-jesse-gelsinger.html>. Accessed November 23, 2025.

and a linker connecting the two domains and affecting biocompatibility [14].

Cationic lipids (Fig. 1), such as classic DOTMA (*N*-[1-(2,3-dioleoyloxy)propyl]-*N,N,N*-trimethylammonium chloride), DOTAP (*N*-[1-(2,3-dioleoyloxy)propyl]-*N,N,N*-trimethylammonium chloride), DOSPA (*N*-(2-(2,5-bis((3-aminopropyl)amino)pentanamido)-ethyl)-*N,N*-dimethyl-2,3-dioleoyloxypropane-1-aminium pentahydrochloride), and EDOPC (2-(2,3-bis(oleoyloxy)propoxyethoxyphosphoryl)oxyethyl trimethylazanium) retain a positive charge independent of pH because they contain a quaternary ammonium group in the polar part of the molecule. The first cationic lipids capable of effectively delivering mRNA were DOTMA and its analogue DOTAP. Several mRNA vaccines were developed based thereon. Thus, mRNA and liposome complexes based on DOTMA and the helper lipid DOPE (1,2-dioleoyl-*sn*-glycero-3-phosphatidylethanolamine, Fig. 2) ensured delivery to dendritic cells, thereby inducing an antigen-specific adaptive immune response and an associated innate immune response

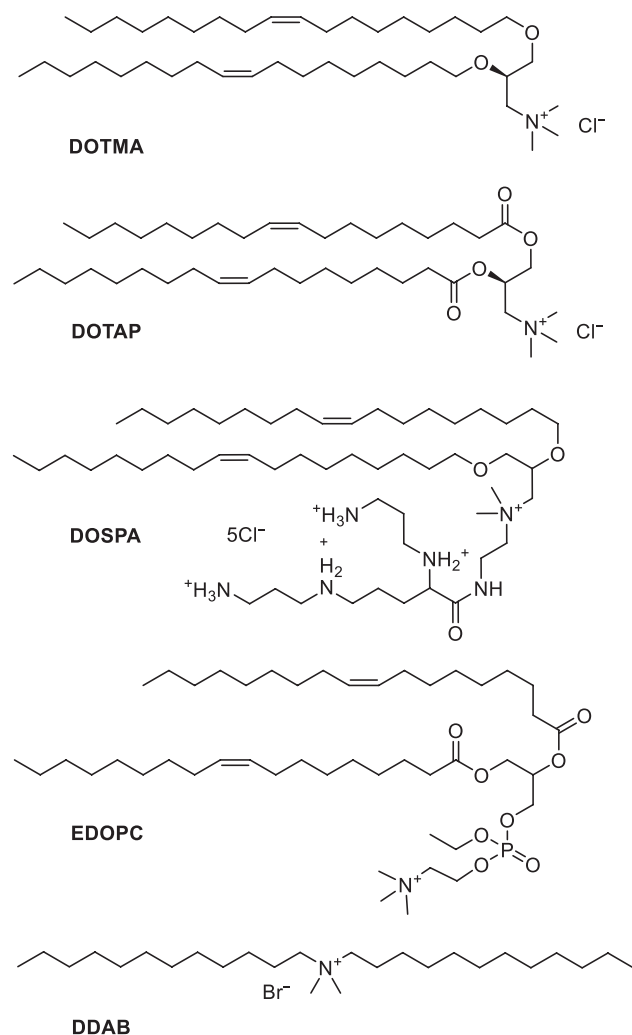


**Fig. 1.** Cationic lipids with quaternary ammonium groups

in immunogenic cancer therapy [15]. At a later stage, Phase I clinical trials of a drug based on DOTAP and mRNA against glioblastoma were initiated in the United States [16]. In 2019, an mRNA vaccine against HIV was developed using DOTAP and passed preclinical trials. It also included DSPC (1,2-distearoyl-*sn*-glycero-3-phosphatidylcholine), DSPE-PEG<sub>2000</sub> (PEGylated 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine),

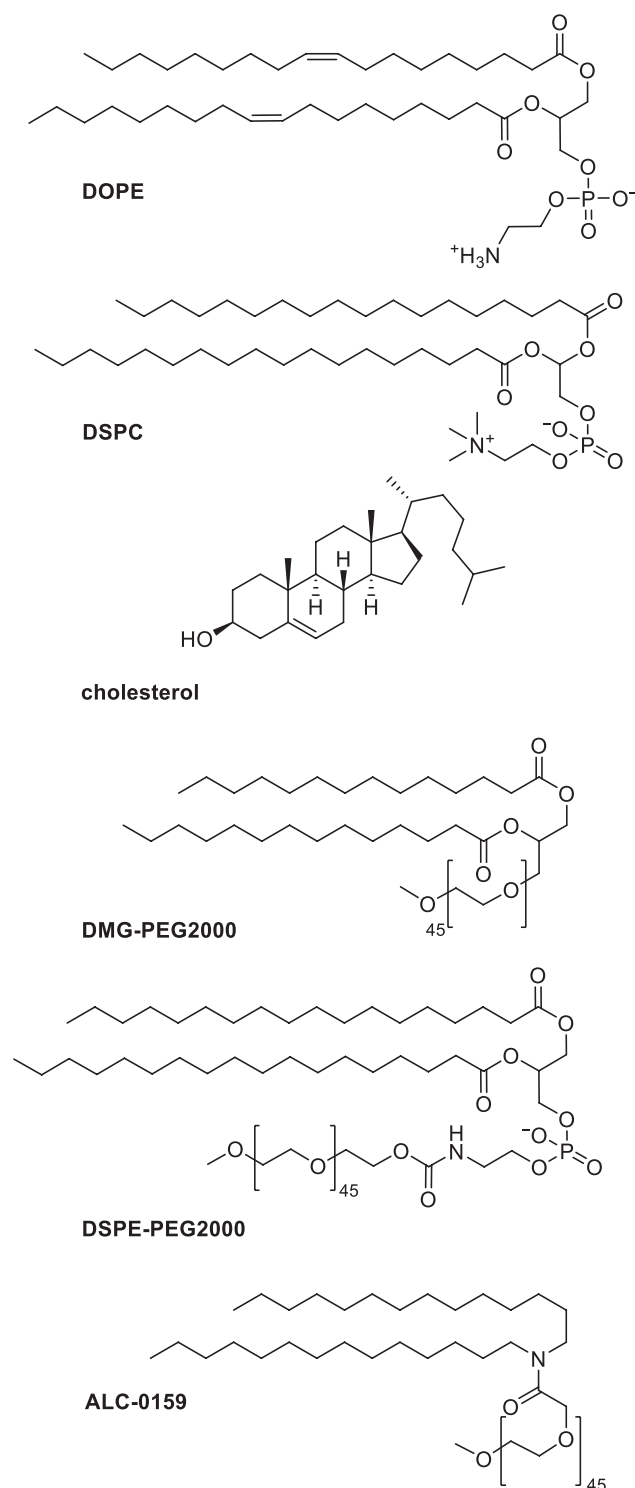


**Fig. 2.** Additional components of liposomal compositions

and cholesterol (Fig. 2) [17]. In 2021, complexes based on DOTAP and DOPE showed a good level of efficacy of mRNA vaccines for the treatment of autoimmune encephalomyelitis [18]. Cationic lipid-based nanoparticles have shown great promise for mRNA vaccines. This is not only because of their ability to package mRNA molecules, but also because of their ability to elicit an innate immune response, thus acting as immune adjuvants to enhance immunogenicity [19]. For example, DDAB (didodecyldimethylammonium bromide), being a cationic lipid, is capable of stimulating an immune response by activating macrophages and binding to antigens [20].

A number of cationic amphiphiles based on polyamines were developed under the guidance of M.A. Maslov. Spermine or triethylenetetramine was used as the cationic domain. By changing the design of the structures, a study was conducted on the influence of structural parts on transfection efficiency. Thus, the leading compounds were selected: cationic amphiphiles 2X3 (1,26-bis(cholest-5-en-3 $\beta$ -yloxy-carbonylamino)-7,11,16,20-tetraazahexacosane tetrahydrochloride); and 2X7 (1,30-bis(cholest-5-en-3 $\beta$ -yloxy-carbonylamino)-

9,13,18,22-tetraaza-3,6,25,28-tetraoxatriacontane tetrahydrochloride) (Fig. 3). When delivering mRNA *in vitro* and *in vivo*, they outperformed commercially available analogues in terms of efficacy [21].

However, there still remains the problem of cytotoxicity of cationic lipids due to the presence of a permanent positive charge. In order to expand the application of non-viral vectors based on LNPs as mRNA delivery systems, second-generation cationic lipids—ionizable lipids—have been developed. They contain tertiary nitrogen atoms or other functional groups which can acquire a positive charge due to changes in pH. Since the pH in the endosome is about 4–5, protonation of the ionizable lipid occurs in it. This contributes to the disruption of membrane stability and facilitates the release of mRNA before the onset of lysosomal degradation. In this case, the acid dissociation constant ( $pK_a$ ) of the lipid should be in the range of 4.5–7.0. Biocompatible drugs have been developed by changing the structural domains of cationic lipids. Lipids with a  $pK_a$  in the range of 6.2 to 6.4 showed the best results [22, 23]. Therefore, ionizable lipids do not carry a permanent positive charge and have a lower level of cytotoxicity compared to cationic lipids.

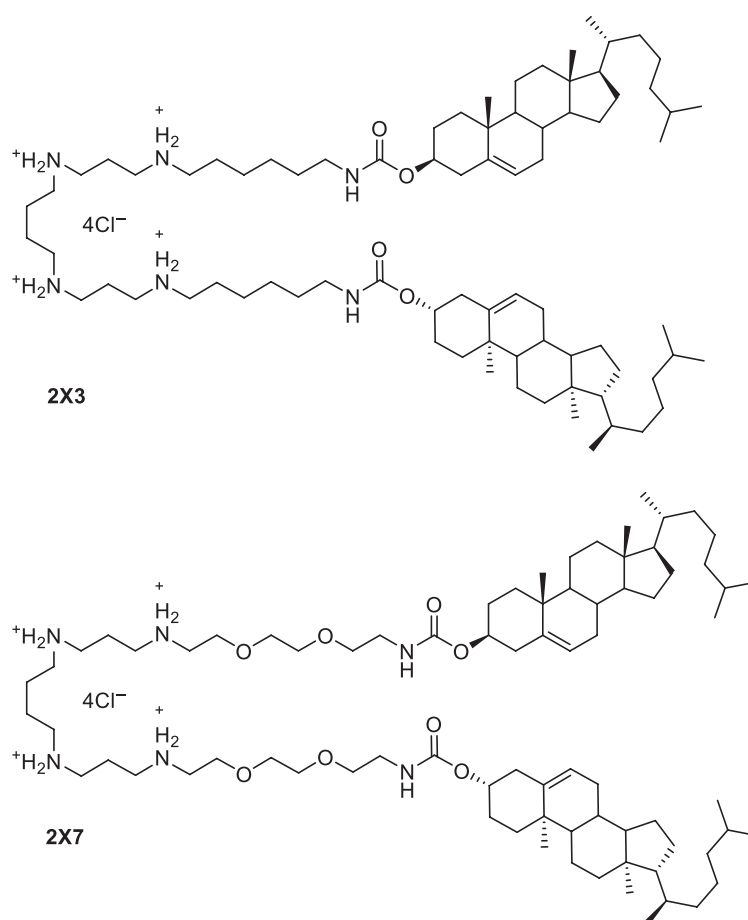


**Fig. 3.** Dimeric polycationic lipids

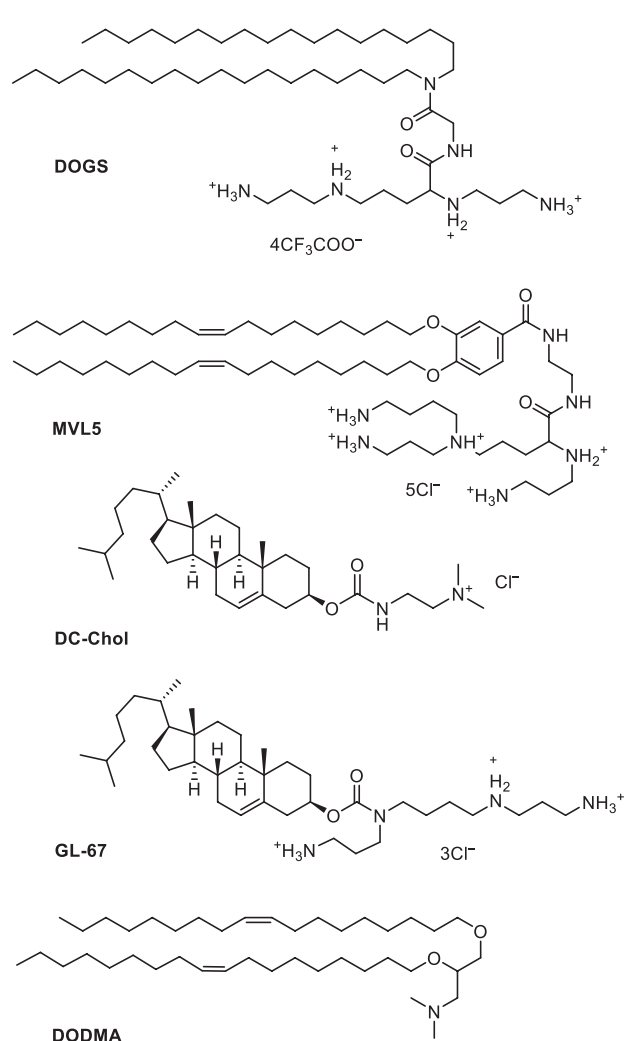


**Fig. 4.** Polycationic lipids

On the other hand, the absence of a permanent charge reduces the effectiveness of LNP interaction with target cells.

The transition stage from cationic lipids to ionizable lipids was marked by the emergence of DOGS (dioctadecylamidoglycylspermine) lipids, MVL5 (*N*<sup>1</sup>-[2-((1*S*)-1-[(3-aminopropyl)amino]-4-[di(3-aminopropyl)amino]butylcarboxamido)ethoxy]-3,4-di[oleoyloxy]-benzamide), DC-Chol (cholesteryl *N*-(2-dimethylaminoethyl)-carbamate), and GL67 (*N*<sup>4</sup>-cholesteryl-spermine hydrochloride) (Fig. 4). They were originally developed for DNA delivery, but later some of them were also investigated for mRNA therapy and showed promising results. Heyes and his colleagues synthesized DODMA (1,2-dioleoyloxy-3-dimethylaminopropane) by modifying DOTMA (1,2-di-*O*-octadecenyl-3-trimethylammonium propane) and further replacing the oleoyl tails with linoleyl chains to form DLinDMA (1,2-linoleoyloxy-*N,N*-dimethyl-3-aminopropane) (Fig. 5). They then compared the effect of different degrees of saturation on gene suppression

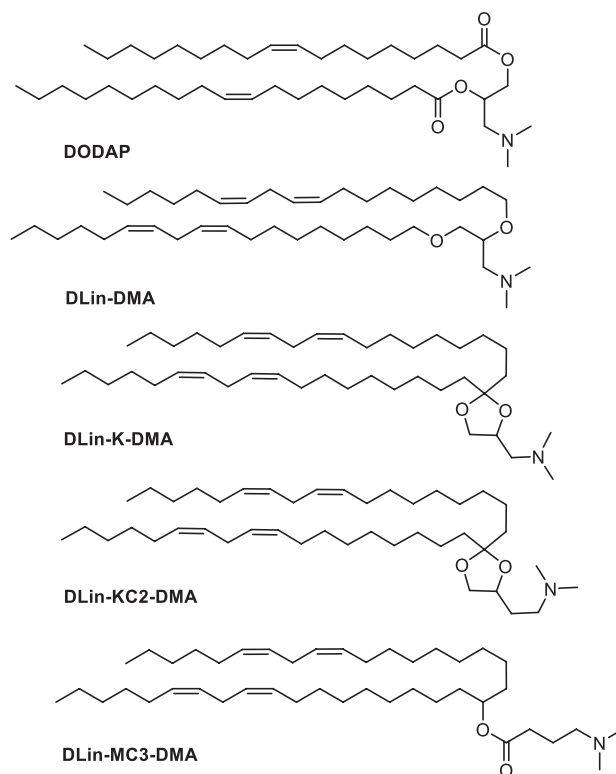


**Fig. 5.** Ionizable lipids-analogues of DODAP

ability [24]. DLinDMA-based LNPs delivered miRNA and mRNA better than their analogues. For example, after delivery of mRNA aimed at enhancing expression in the retinal pigment epithelium, an improvement in the condition was noted in monogenic degenerative retinal disease against the background of retinal pigment epithelium. It also showed promising results in mRNA-based drugs against cystic fibrosis, Crohn's disease and Friedreich's ataxia [25, 26]. In another study, DLinDMA demonstrated a higher capacity than DODMA for protective immunity against respiratory syncytial virus *in vivo* [27].

The results of the above studies showed that DLin-DMA-based LNPs and their analogues (Fig. 5) are a promising platform for the creation of mRNA vaccines. Thus, by replacing ether bonds in DLin-DMA with an orthoester linker, the lipid DLin-KC2-DMA (2,2-dilinolenyl-4-dimethylaminoethyl-[1,3]-dioxolane) with pK<sub>a</sub> values ranging from 6.2 to 6.7 can be obtained, surpassing its predecessor DLin-DMA in terms of mRNA delivery efficiency *in vivo* [28]. This lipid was the main component of the British COVAC1 mRNA vaccine against COVID-19. It also included DSPC, cholesterol, and ALC-0159 (Fig. 2). However, Phase I of clinical trials showed disappointing results: there was virtually no immune response [29].

With further modification of the linker group to an ester, the lipid DLin-MC3-DMA (dilinoleyl methyl 4-dimethylaminobutyrate) was developed (Fig. 5).

It formed the basis of the ONPATRO<sup>®</sup> drug (*Patisiran*, USA), approved for use in the European Union and the United States for the treatment of hereditary amyloid polyneuropathy (ATTR) by delivering siRNA [30]. The drug is not without side effects. These are prevented by the additional administration of immunosuppressants, antihistamines, and other agents [30]. Later, it was shown that this ionizable lipid is effective for the combined delivery of mRNA together with siRNA [27]. It also showed a high level of efficacy in an mRNA vaccine against dengue fever [31]. In 2017 clinical trials were conducted of an mRNA vaccine against ATTR. Studies proved its efficacy and safety for use with minimal side effects, and two years later it was subsequently approved by the U.S. Food and Drug Administration (FDA). DLin-MC3-DMA served as an important precursor and starting point for the development of biodegradable

ester-linked ionizable lipids which reduce cytotoxicity and increase mRNA delivery efficiency [32].

By changing the position of the ester bond, the leader compound—lipid L319—was discovered [33]. Similarly, the biodegradable lipids ATX-100, Lipid 5 [34], Lipid H (SM-102), ALC-0315, Acuitas A9 [35], and LP-01 (Fig. 6) showed improved pharmacokinetics for *in vivo* delivery when compared to cationic lipids [36]. It was found that branched alkyl tails can improve the release of mRNA molecules in the endosome. Furthermore, studies of SM-102-based liposomes helped to identify a relationship between particle size and immunogenicity in mice when using different drugs [37]. The SM-102 lipid was included in Moderna's COVID-19 mRNA vaccine. During 2020, three phases of clinical trials were conducted, proving the high efficacy of the drug (94.1%). At the same time, no serious inflammatory reactions were identified in response to vaccination. Therefore, the FDA approved this composition for use. In 2024, based on clinical trials of Moderna's COVID-19 vaccine, the FDA approved the use of the same composition for an mRNA vaccine against respiratory syncytial virus for people over 60 years of age, which was given the commercial name mRESVIA<sup>®</sup>.

Biodegradable ionizable lipids based on esters demonstrated higher efficiency in mRNA delivery compared to the ionizable lipid DLin-MC3-DMA (Fig. 5). Lipid 5 was found to be three times more active, while the Acuitas ALC-0315 lipid used in the Pfizer/BioNTech mRNA vaccine against COVID-19 [38], has a six times higher level of activity compared to the DLin-MC3-DMA lipid in the delivery of luciferase mRNA *in vivo*. The ALC-0315 lipid became the platform for mRNA delivery in the COVID-19 vaccine. In 2019, the Comirnaty<sup>®</sup> vaccine, developed by Pfizer/BioNTech, underwent clinical trials and was approved by the FDA for use in 2021, as it had no serious side effects and provided immunity in 90% of cases. However, its effectiveness lasted only six months. In 2023, using a similar composition, D.Yu. Logunov and his research group delivered antibodies against botulinum toxin A [39]. *In vivo* studies have yielded results showing the promise of this treatment method in emergency cases of botulism. In 2024, based on ALC-0315, in combination with ALC-0159, DSPC, and cholesterol, a Russian mRNA vaccine was created. It is a combined vaccine against influenza and COVID-19 [40], as well as a trivalent vaccine against influenza [41] which elicits a cross-specific humoral immune response. Furthermore, Lipid A6, synthesized under the guidance of Lei Miao, the hydrophobic tails of which contain a triple bond (Fig. 6), enhances the release of mRNA from endosomes due to its structure [42, 43].

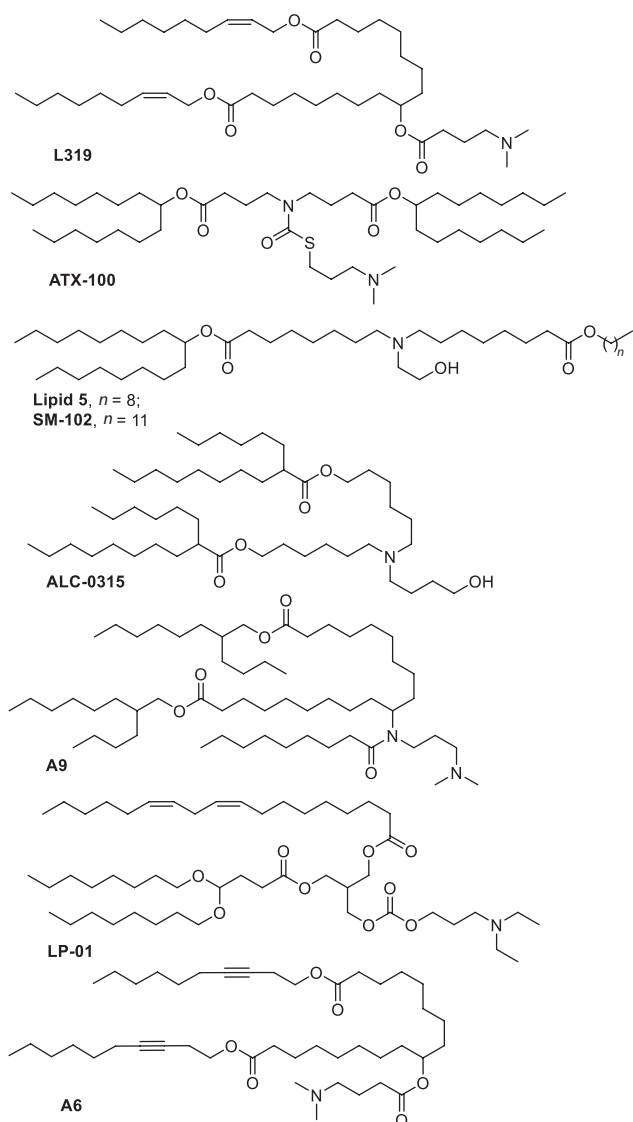


Fig. 6. Ionizable lipids with branched tails

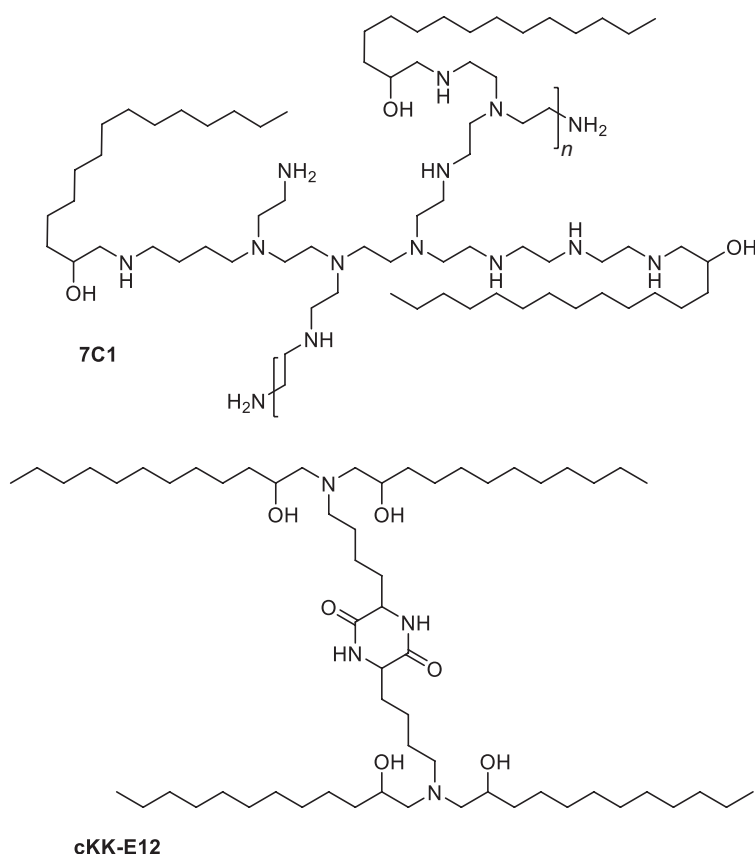


**Fig. 7.** Ionizable lipids 7C1 and cKK-E12

In 2019, Melissa Lokugamage and her colleagues from the US synthesized a library of various ionizable lipids. The leading compound was 7C1 which has a polymer structure based on ethylenediamine and branched hydrophobic tails. Based on this, LNPs of various compositions were studied *in vivo*. The most effective delivery of mRNA encoding an antibody targeting hemagglutinin was demonstrated by LNPs consisting of 7C1, cKK-E12, C<sub>14</sub>PEG<sub>2000</sub>, and cholesterol which protected mice from fatal infection with the H1N1 influenza virus [44].

It is known that cells contain reducing enzymes such as glutaredoxin and glutathione [45–47], enzymes of the thioredoxin family [48, 49], as well as gamma interferon-induced lysosomal thiol reductase (GILT) [50, 51]. When an additional disulfide bond linker is included in the composition of ionizable lipids, the effect of reducing enzymes can reduce cytotoxicity and increase transfection efficiency due to a better release of mRNA in the cell [52]. Thus, the disulfide lipid ssPalmE (Fig. 8) based on alpha-tocopherol contributed to the effective suppression of tumor growth [53, 54]. Its analogue ssPalmO-Phe (Fig. 8) showed excellent mRNA delivery efficiency due to the inclusion of an aromatic ring that facilitates the release of nucleic acid from endosomes [35, 53].

Miyabe and her team used the pH-sensitive lipid YSK05 (Fig. 9) to deliver adjuvants to vaccines. They found that it has a high level of adhesion to the cell membrane, increasing its effectiveness [55]. Its analogue YSK12-C4, based on aliphatic tertiary amine (Fig. 9), is more effective in knocking out genes in mouse dendritic cells [56, 57]. It was also found that the combination of YSK12-C4 and YSK05 with the addition of PEG<sub>2000</sub>-DMG and cholesterol to form liposomes increases the efficiency of mRNA delivery [25].

Using the CL4H6 lipid (Fig. 9), which has a lower degree of unsaturation compared to the above compounds, siRNA was delivered to hepatocytes, as well as to mice cells carrying the OS-RC-2 gene [25, 58]. CL4H6-based LNPs demonstrated a high level of stability in the bloodstream, tumor specificity, and strong gene suppression in the test groups. When delivering mRNA, LNPs based on this lipid showed the best biocompatibility. They also showed a high level of delivery efficiency, slightly surpassing the ALC-0315 lipid. Also, compared to ALC-0315 and SM-102, the stability of LNPs with CL4H6 was significantly higher [59].

Another representative of ionizable lipids is 98N12-5 based on triethylenetetramine and laurylamine

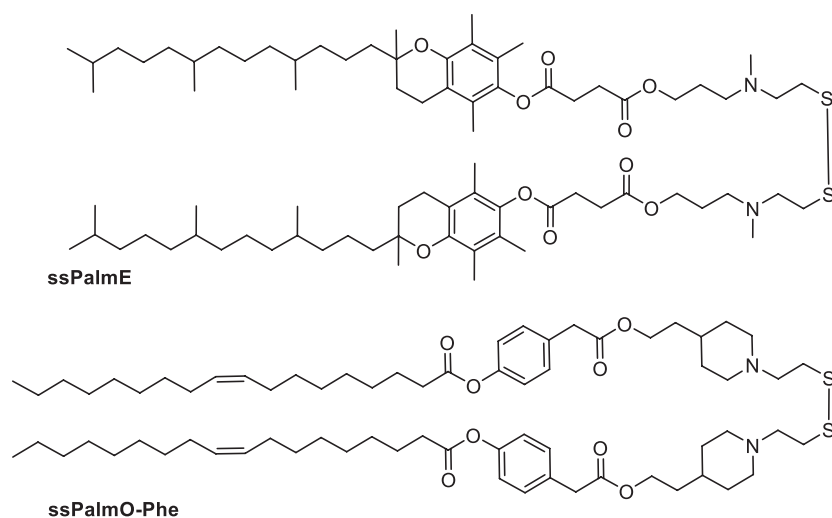


**Fig. 8.** Disulfide ionizable lipids

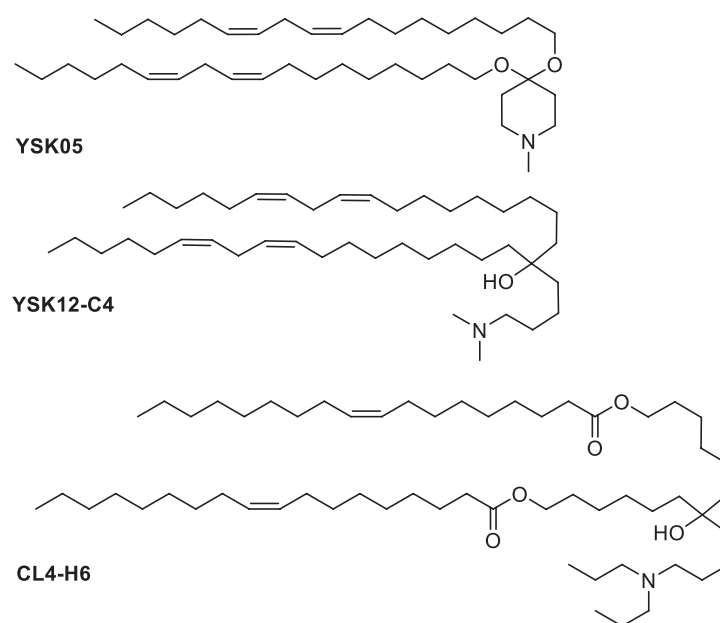


**Fig. 9.** Ionizable lipids with unsaturated hydrophobic tails

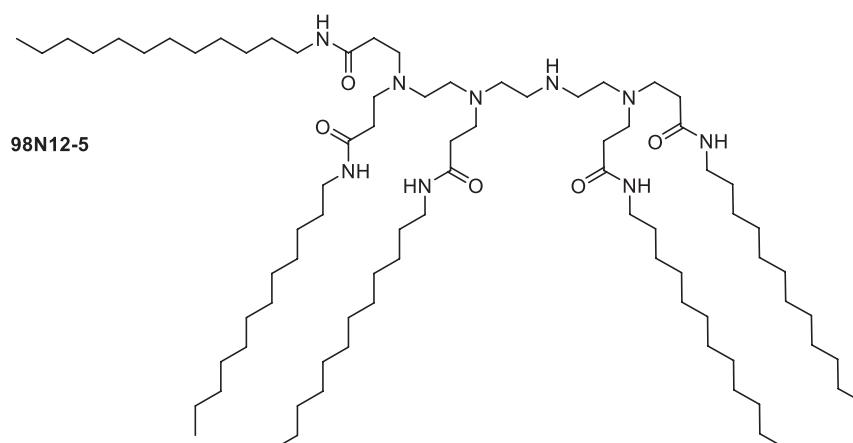


**Fig. 10.** Ionizable lipid 98N12-5

residues (Fig. 10) [50, 51]. This lipid showed the same transfection efficiency *in vitro* as Lipofectamine 2000. Unlike commercial transfection agents, its efficiency remained the same even when the lipid concentration was reduced. LNPs consisting of 98N12-5, cholesterol, and PEG lipid effectively delivered various siRNAs and mRNAs *in vivo* [60, 61].

Hydroxylated analogues of lipid 98N12-5, including C12-200 and C14-113 (Fig. 11), showed a greater level of efficiency in mRNA delivery and also ensured targeting of hepatocytes [62, 63]. Liu and colleagues reported that an analogue of the aforementioned lipids, TT3, enables effective delivery of mRNA molecules encoding CRISPR/Cas9 [64, 65], factor IX [66], and SARS-CoV-2 [67].

Based on studies conducted in 2014 [68], Suzuki and his research team synthesized a library of ionizable lipids with two asymmetric hydrocarbon tails, such as L021 (Fig. 12) [69]. Further replacement

of the cyclopropane fragment in the hydrophobic part with an ester bond led to the production of L101, a biodegradable lipid (Fig. 12) with high gene suppression efficiency in mouse hepatocytes and rapid clearance [70].

Further development of ionizable lipids is moving towards targeted delivery. The targeted delivery of vaccines and immunotherapeutic drugs to immune cells, as well as to primary and secondary lymphoid organs, avoids side effects in other cells and tissues. For example, lipids containing polycyclic tails and/or cyclic imidazole head groups, such as 93-O17S (Fig. 13) [71, 72], target T cells. It has been demonstrated that the presence of a cyclic amine in the polar part of the lipid A18-Iso5-2DC18 (Fig. 13) ensures binding to the stimulator of interferon genes (STING) protein, leading to the maturation of dendritic cells and exerts an antitumor effect through immune stimulation [73].

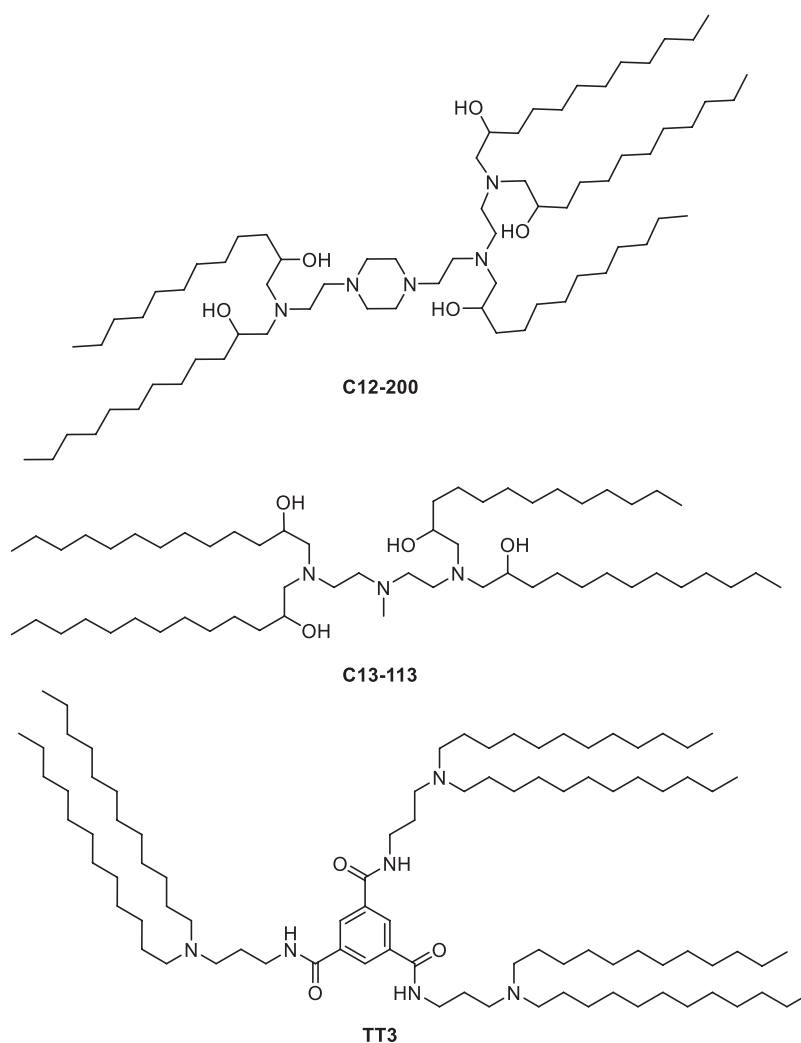


**Fig. 11.** Symmetric ionizable lipids with branched tails

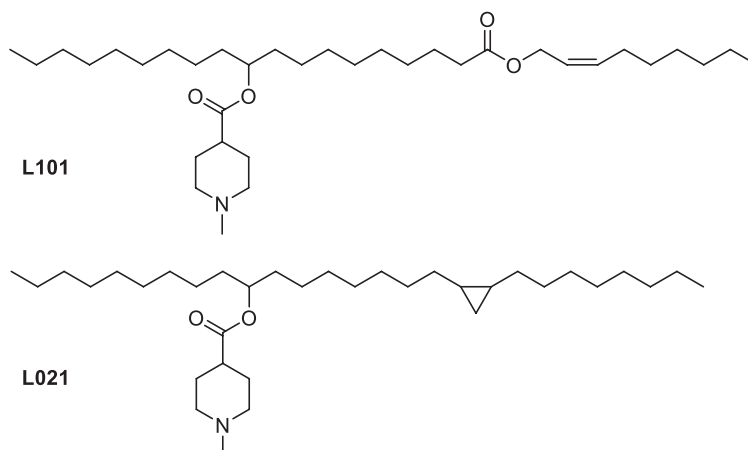


**Fig. 12.** Methylpiperidine-based ionizable lipids

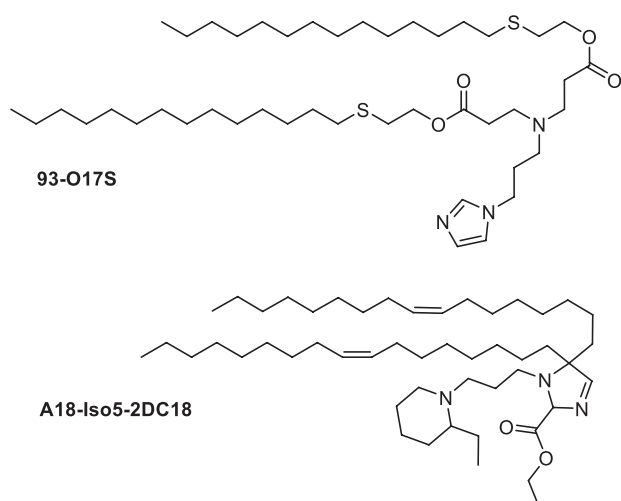


**Fig. 13.** Imidazole-containing lipids

Gene therapy using ionizable lipids also shows promise for use in fighting drug-resistant bacteria. For example, vitamin-based ionizable lipids (Fig. 14) deliver mRNA encoding antimicrobial peptides and cathepsin B, the accumulation of which in macrophages suppresses the growth and development of bacterial infections resistant to multiple antibiotics. The most effective of these were LNPs obtained from a lipophilic derivative of vitamin C, in combination with DOPE and cholesterol which protected mice from bacterial-induced sepsis [74].

When comparing cationic and ionizable lipids (Table 1), the main difference is the nature of their positive charge which determines the advantages and disadvantages of the two types of lipids. The constant positive charge of cationic lipids ensures the colloidal stability of nanoparticles and effective fusion with

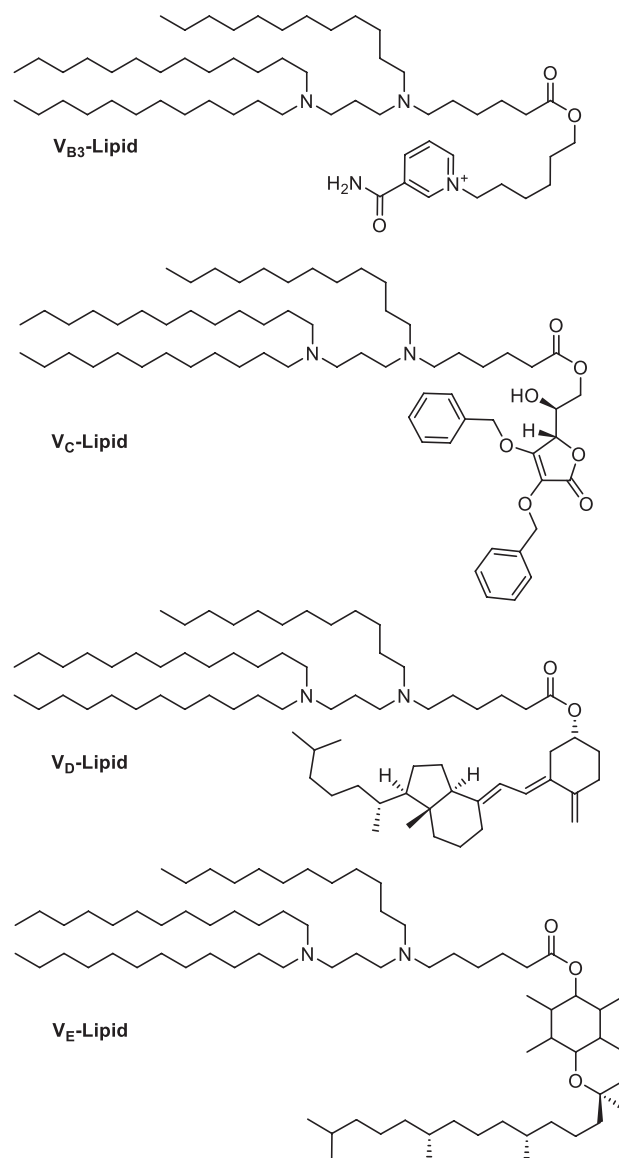


**Fig. 14.** Vitamin-based ionizable lipids

**Table 1.** Comparison of cationic and ionizable lipids

| Parameter                                                | Cationic lipids             | Ionizable lipids                                         |
|----------------------------------------------------------|-----------------------------|----------------------------------------------------------|
| Lipid charge                                             | Constant positive           | Neutral, positive at slightly acidic pH                  |
| Colloidal stability                                      | High                        | Average                                                  |
| Cytotoxicity                                             | High                        | Low                                                      |
| Efficiency of formation of complexes with therapeutic NA | High                        | High, but complexation requires a slightly acidic buffer |
| Efficiency cell membrane fusion                          | High                        | Average                                                  |
| The most commonly used method of preparation             | Lipid film hydration method | Microfluidic technologies                                |
| Capital and operating costs for nanoparticle formation   | Low                         | High                                                     |

the cell membrane. However, cytotoxicity increases proportionally to the charge [44]. In this regard, the application of ionizable lipids, without permanent charge, appears to be safer. An important aspect is the technology used to produce the finished product. As mentioned above, the main method for obtaining LNPs based on ionizable lipids is microfluidic technology which ensures greater reproducibility of nanoparticle characteristics and easy automation. However, it imposes strict requirements on the solubility of lipids in ethanol and increases capital and operating costs [20].

Thus, ionizable lipid-based LNPs are increasingly being used as mRNA delivery systems. Over the past five years, there has been an increase in positive clinical trial results. This in turn has expanded the range of clinically approved drugs for gene and immunotherapy for various diseases, from drug-resistant infections to severe orphan diseases [75].

## CLINICAL TRIALS OF MRNA VACCINES

Clinical trials are a mandatory part of drug efficacy and safety studies, necessary for registering a drug and obtaining permission for its use in medical practice. There are four phases of clinical trials [76].

Phase I studies are usually conducted on a small number of healthy volunteers. In the case of highly toxic drugs used to treat seriously or terminally ill patients, studies have been conducted with such patients, for example, those with cancer or acquired immunodeficiency syndrome (AIDS). During Phase I, parameters such as absorption, distribution, metabolism, excretion, as well as the preferred form of administration and safe dosage levels were evaluated.

The duration of such studies varies from several weeks to several years.

Several hundred people participate in Phase II clinical trials. An important goal of these studies is to determine the dosage and administration regimen for the next phase of testing. Sometimes Phases I and II are combined, allowing not only the effectiveness of the drug to be determined immediately, but also its safe doses.

Phase III trials are randomized controlled trials involving a large group of patients, up to several thousand people. The purpose of these trials is to confirm the safety and efficacy of the drug as previously assessed in the two previous phases. Phase III trials may also examine the relationship between the effect and the dose of the drug, or the effect of the drug when used in patients with varying degrees of severity or in combination with other drugs.

The final phase of clinical trials is Phase IV, also known as the post-registration phase. Its main purpose is to gather additional information on the safety of the drug in a sufficiently large group over a long period of time.

The percentage of drugs approved for use after clinical trials depends on the requirements of the country's regulatory authority and the field of medicine. The lowest percentage is in oncology. The strictest rules are in the US, where the FDA allows no more than 25–30% of drugs to be sold. In recent years the proportion of approved drugs has been declining, since the requirements for evidence of their efficacy and safety have become more stringent.

To sum up, clinical trials are a very complex and demanding part of the process. They are nevertheless necessary for the clinical application of drugs. In this regard, drugs which have successfully passed them, or

individual phases of research, deserve special attention. Unlike standard drugs, mRNA- and LNP-based drugs undergo more complex clinical trials, since they are two independent compositions brought together. If one of these compositions is unable to confirm its efficacy and safety in any phase, then the trials have to be started all over again. Therefore, the most convenient approach is to test the drug delivery system (LNP, cationic liposomes) and, after confirming its efficacy and safety, proceed to study the therapeutic activity of the nucleic acids loaded into this system.

Despite the existence of a huge number of lipids which have shown excellent efficacy *in vitro* and even *in vivo*, only a few of them have reached clinical trials. Only exceptional compounds have achieved success after Phase I clinical trials. Some have shown such impressive results that they are participating in several trials for mRNA vaccines against various diseases.

In Table 2, we have compiled a list of clinical trials of mRNA vaccines, mainly targeting various viral infections and tumors of different types. Furthermore, research is being conducted on a number of bacterial and parasitic infections, such as malaria.

Some of the mRNA vaccines listed in the table are in the final stages of testing. For example, mRNA-1283 (NCT05815498), an updated vaccine against COVID-19, is currently completing a randomized, double-blind Phase III study to evaluate safety, immunogenicity, and relative efficacy. Preliminary results show that vaccinated individuals of all age groups (12 years and older) have higher antibody titers against both the BA.4/5 strain and earlier strains of the coronavirus, when compared to the mRNA-1273 mRNA vaccine already in use.

Phase III of a randomized, double-blind, placebo-controlled clinical trial of an mRNA vaccine against norovirus infection (mRNA-1403, NCT06592794) has begun. Norovirus causes acute intestinal infection and is highly heterogeneous. Therefore, a multivalent vaccine against the two main genetic groups of the virus, including several strains, is used. Previous phases of the study demonstrated an increase in HBGA-blocking antibody titers on the 29th day after a single vaccination, especially for the genetic group II of norovirus. As a result of truncating the interim analysis data, no risk was identified in the use of this vaccine.

mRNA vaccines have great potential for cancer immunotherapy. Delivery of mRNA encoding a tumor antigen activates the patient's immune system to fight the tumor. For example, mRNA-4157 in combination with pembrolizumab has shown a high level of immunogenicity

against various types of solid tumors [77]. Phase III clinical trials (NCT05933577) have begun for melanoma and squamous cell carcinoma.

For the most part, the composition of mRNA vaccines undergoing clinical trials is confidential. The most well-known exceptions, where the components of the drug have been disclosed, are the *Pfizer/BioNTech* and *Moderna* vaccines against COVID-19. They used ionizable lipids ALC-0315 and SM-102, respectively (Fig. 6). The lipid ALC-0315 was also used in the mRNA vaccine from *CureVac* (Germany) which was expected to provide longer-lasting immunity compared to Comirnaty® from *Pfizer/BioNTech*. However, Phase III clinical trials showed an extremely low level of vaccine efficacy (47%)<sup>2</sup>. Later, Phase III trials began for another COVID-19 vaccine using the same liposomal composition but with a different mRNA design (NCT04860258). As for the SM-102 lipid, it is known to be used in vaccines under development against cytomegalovirus (NCT05085366), Zika virus (NCT04917861), and seasonal influenza virus (A/H1N1, A/H3N2, B/Victoria, and B/Yamagata) for people over 50 [78] (NCT05566639, Table 2).

In 2020, Phase I clinical trials were completed of an mRNA vaccine against Chikungunya virus (CHIKV) based on the DLin-MC3-DMA (MC3) lipid (Fig. 5) developed by *Moderna* (NCT03325075). Furthermore, its mRNA vaccines against Zika virus and H10N8 influenza successfully completed Phase I clinical trials in 2021 [79, 80]. *Patisiran's* (USA) ALN-TTR02 vaccine against ATTR successfully completed Phase II trials in 2024 (NCT01617967).

*Arcturus Therapeutics* (USA) chose the lipid ATX-100 (Fig. 6) to deliver mRNA in its vaccines. In 2021, Phase II clinical trials of the COVID-19 vaccine (NCT04480957) were completed. In 2023, Phase I trials for ornithine transcarbamylase deficiency (NCT04442347) and Phase Ib trials for cystic fibrosis (NCT05712538) were successfully completed. In 2024, clinical trials of mRNA vaccines against influenza (NCT06602531, Phase I) and cystic fibrosis (NCT06747858, Phase II) began.

In 2023, Phase I clinical trials of an mRNA vaccine against ATTR were completed. The preliminary results obtained indicate its safety and efficacy. For example, mRNA and CRISPR-Cas9 delivery systems (NCT04601051) targeting transthyretin (TTR) achieved 87% efficacy in reducing serum TTR levels in patients with ATTR [81]. This process was not accompanied by serious side effects, so Phase II trials are planned to start soon [82].

<sup>2</sup> CureVac Provides Update on Phase 2b/3 Trial of First-Generation COVID-19 Vaccine Candidate, CVnCoV – CureVac n.d. <https://www.curevac.com/en/curevac-provides-update-on-phase-2b-3-trial-of-first-generation-covid-19-vaccine-candidate-cvncov/>. Accessed April 13, 2025.

**Table 2.** Lipid-based mRNA vaccines on clinical trials

| mRNA vaccines                                                 | Application                                       | Sponsor                                                      | Phase of trials | Status     | NCT number  |
|---------------------------------------------------------------|---------------------------------------------------|--------------------------------------------------------------|-----------------|------------|-------------|
| ARCT-021                                                      | COVID-19                                          | <i>Arcturus Therapeutics</i> (USA)                           | 2               | Completed  | NCT04480957 |
| ChulaCov19                                                    | COVID-19                                          | Chulalongkorn University (Thailand)                          | 2               | Completed  | NCT04566276 |
| CVnCoV                                                        | COVID-19                                          | <i>CureVac</i> (Germany)                                     | 3               | Active     | NCT04860258 |
| mRNA-1283                                                     | COVID-19                                          | <i>Moderna</i> (USA)                                         | 3               | Completed  | NCT05815498 |
| Awcora                                                        | COVID-19                                          | <i>Walvax Biotechnology</i> (China)                          | 3               | Active     | NCT04847102 |
| mRNA-4157                                                     | Adjuvant treatment for melanoma                   | <i>Moderna</i> (USA)                                         | 3               | Active     | NCT05933577 |
| mRNA-4157                                                     | Adjuvant treatment for non-small cell lung cancer | <i>Moderna</i> (USA)                                         | 3               | Recruiting | NCT06077760 |
| mRNA-1975/1982                                                | Lyme disease                                      | <i>Moderna</i> (USA)                                         | 1/2             | Completed  | NCT05975099 |
| mRNA-1893                                                     | Zika virus                                        | <i>Moderna</i> (USA)                                         | 2               | Completed  | NCT04917861 |
| mRNA-1215                                                     | Nipah virus                                       | <i>Moderna</i> (USA)                                         | 1               | Completed  | NCT05398796 |
| BNT163                                                        | Herpes simplex virus                              | <i>BioNTech</i> (Germany) / University of Pennsylvania (USA) | 1               | Active     | NCT05432583 |
| mRNA-1608                                                     | Herpes simplex virus                              | <i>Moderna</i> (USA)                                         | 1/2             | Completed  | NCT06033261 |
| mRNA-1189                                                     | Epstein–Barr virus infection                      | <i>Moderna</i> (USA)                                         | 1/2             | Active     | NCT05164094 |
| mRNA-1195                                                     | Epstein–Barr virus infection                      | <i>Moderna</i> (USA)                                         | 2               | Recruiting | NCT06735248 |
| eOD-GT8 60mer mRNA Vaccine and Core-g28v2 60mer mRNA Vaccine  | HIV                                               | International AIDS Vaccine Initiative (USA)                  | 1               | Active     | NCT05001373 |
| G505 MD39.3, BG505 MD39.3 gp151, and BG505 MD39.3 gp151 CD4KO | HIV                                               | National Institute of Allergy and Infectious Diseases (USA)  | 1               | Active     | NCT05217641 |
| ARCT-2304                                                     | Influenza                                         | <i>Arcturus Therapeutics</i> (USA)                           | 1               | Active     | NCT06602531 |
| mRNA-1010                                                     | Influenza                                         | <i>Moderna</i> (USA)                                         | 3               | Completed  | NCT05827978 |
| mRNA-1010                                                     | Influenza                                         | <i>Moderna</i> (USA)                                         | 3               | Completed  | NCT05566639 |

**Table 2.** Continued

| mRNA vaccines    | Application                               | Sponsor                                  | Phase of trials | Status     | NCT number                 |
|------------------|-------------------------------------------|------------------------------------------|-----------------|------------|----------------------------|
| BNT161           | Influenza                                 | <i>Pfizer (USA) / BioNTech (Germany)</i> | 3               | Completed  | NCT05540522                |
| ARCT-810         | Ornithine transcarbamylase deficiency     | <i>Arcturus Therapeutics (USA)</i>       | 2               | Active     | NCT06488313                |
| BNT165           | Malaria                                   | <i>BioNTech (Germany)</i>                | 1/2             | Active     | NCT06069544                |
| BNT113           | Metastatic/Recurrent head and neck cancer | <i>BioNTech (Germany)</i>                | 2               | Recruiting | NCT04534205                |
| mRNA-3705        | Methylmalonic acidemia                    | <i>Moderna (USA)</i>                     | 1/2             | Recruiting | NCT04899310                |
| BNT142           | Multiple solid tumors                     | <i>BioNTech (Germany)</i>                | 1/2             | Active     | NCT05262530                |
| ARCT-032         | Cystic fibrosis                           | <i>Arcturus Therapeutics (USA)</i>       | 2               | Active     | NCT06747858                |
| ARCT-032         | Cystic fibrosis                           | <i>Arcturus Therapeutics (USA)</i>       | 2               | Recruiting | NCT06747858                |
| mRNA-3692/VX-522 | Cystic fibrosis                           | <i>Moderna (USA)</i>                     | 1/2             | Recruiting | NCT05668741                |
| mRNA-3745        | G6Pase Glycogen storage disorder, type 1a | <i>Moderna (USA)</i>                     | 1/2             | Recruiting | NCT05095727                |
| mRNA-1403/1405   | Norovirus                                 | <i>Moderna (USA)</i>                     | 3               | Active     | NCT06592794                |
| BNT167           | Shingles                                  | <i>Pfizer (USA)</i>                      | 2               | Recruiting | NCT05703607                |
| mRNA-4157        | Cutaneous squamous cell carcinoma         | <i>Moderna (USA)</i>                     | 2/3             | Active     | NCT06295809                |
| mRNA-4157        | Renal cell carcinoma                      | <i>Moderna (USA)</i>                     | 2               | Active     | NCT06307431                |
| BNT111           | Advanced melanoma                         | <i>BioNTech (Germany)</i>                | 2               | Active     | NCT04526899                |
| mRNA-3927        | Propionic acidemia                        | <i>Moderna (USA)</i>                     | 1/2             | Recruiting | NCT04159103<br>NCT05130437 |
| mRNA-4157        | Bladder cancer                            | <i>Moderna (USA)</i>                     | 1/2             | Recruiting | NCT06305767                |
| ALN-TTR02        | Transthyretin amyloidosis                 | <i>Alnylam Pharmaceuticals (USA)</i>     | 2               | Completed  | NCT01617967                |
| NTLA-2001        | Transthyretin amyloidosis                 | <i>Intellia Therapeutics (USA)</i>       | 1               | Active     | NCT04601051                |
| BNT164           | Tuberculosis                              | <i>Gates Foundation (USA)</i>            | 1/2             | Active     | NCT05547464                |
| mRNA-1647        | Cytomegalovirus infection                 | <i>Moderna (USA)</i>                     | 3               | Active     | NCT05085366                |
| VAL-181388       | Chikungunya                               | <i>Moderna (USA)</i>                     | 1               | Completed  | NCT03325075                |

In 2023, Phase I clinical trials of an mRNA vaccine against COVID-19 using lipid A9 as a delivery vehicle were completed [29], and in 2024, Phase II clinical trials of an mRNA vaccine against COVID-19 based on lipid CL1 — ChulaCov19 (NCT04566276) [83].

## CONCLUSIONS AND PROSPECTS

Gene therapy has enormous potential for treating a wide range of diseases. In recent years, mRNA vaccines, the main component of which are ionizable lipids, have attracted the most interest. Unlike cationic lipids, ionizable lipids do not have a permanent positive charge, which reduces the risks of cytotoxicity and binding to blood serum proteins. Lipids are used to form cationic liposomes or LNPs which ensure effective delivery of therapeutic nucleic acids.

Both types of lipids consist of the following components: (1) a hydrophobic domain necessary for fusion with the cell membrane; (2) a polar domain for binding and protecting the drug; (3) a spacer for separating the hydrophobic and polar domains in space; as well as (4) linkers which bind these components together. Furthermore, the combination of hydrophobic and polar domains provides the amphiphilic properties necessary for the formation of nanoparticles in an aqueous environment. All these components also influence other properties of nanoparticles: size, stability, cytotoxicity, and mRNA delivery efficiency.

The hydrophobic domain consists of alkyl tails (1 to 5), but less commonly sterol residues (cholesterol, sitosterol, tocopherol) (Fig. 3). The optimal length of alkyl tails, providing a reasonable balance between cytotoxicity and nucleic acid delivery efficiency, is 14–18 carbon atoms (Fig. 4). Branched alkyl substituents (Fig. 5), including asymmetric ones (Fig. 6), have proven themselves well in mRNA delivery. In this case, the branching point can be either a carbon atom (Fig. 12) or a nitrogen atom (Fig. 14).

The polar domain can be cationic or ionizable. In the case of cationic lipids, the best results are demonstrated by structures with a distributed charge system based on polyamines, especially spermine (Fig. 3). With an optimal positive charge/cytotoxicity ratio, such lipids with a constant positive charge show the highest mRNA delivery efficiency. However, ionizable lipids are becoming more promising for clinical application. Heterocycles (e.g., imidazole or piperidine) (Figs. 12, 13) and nitrogen atoms with a closely located electron-accepting group which lowers  $pK_a$  (Figs. 5, 7, 9) act as ionizable groups. Hydroxyalkyl groups with 2 to 4 carbon atoms perform well as electron acceptors (Fig. 6).

Furthermore, amide or ester linkers are electron acceptors.

Since the close proximity of hydrophobic and polar domains can interfere with nanoparticle formation, it is recommended that a hydrocarbon spacer 3–8 carbon atoms long be included in the lipid structure, especially in the presence of bulky functional groups. Individual structural elements of lipids are connected by linkers. They facilitate the synthesis of the compound and subsequently play an important role in the metabolism of lipids in the body. Therefore, it is important to maintain a balance between the stability of the compound in the bloodstream and tissues and its biocompatibility. After delivery, lipids must be broken down into simple fragments which can be easily utilized by the excretory system. The most “balanced” linkers are disulfide and carbamate linkers. Linkers based on ether bonds are more stable but can increase cytotoxicity. Ester linkers, on the other hand, do not cause side effects, but do not always provide sufficient stability.

Thus, lipids, primarily ionizable ones, form one of the main components of mRNA vaccines. Their modular structure determines the further behavior and properties of nanoparticles. Platforms for delivering mRNA in vaccines against COVID-19, influenza, and various tumors and genetic diseases have been developed based on ionizable lipids (Table 2). mRNA vaccines against COVID-19 and respiratory syncytial virus have already been approved for use. Many others are undergoing clinical trials.

Most mRNA vaccines under development use the principles of replacement gene therapy, where normally functioning mRNA is delivered, ensuring the synthesis of the desired protein for only a limited time. The administered mRNA gradually degrades. In the treatment of viral or tumor diseases, one or more injections are usually sufficient to prevent infection or achieve recovery (remission). Treatment of a hereditary disease using this approach will require lifelong administration of the drug. The solution to this problem may be a transition to corrective gene therapy, in which a malfunctioning copy of the gene is corrected at a specific point. The most promising tool for such genome editing is CRISPR-Cas technology. An important milestone are Phase I clinical trials of a drug for the treatment of transthyretin amyloidosis without the need for repeated therapy (NCT04601051). In this study, LNPs deliver mRNA encoding the Cas9 protein and single-stranded guide RNA targeting the transthyretin gene. Preliminary results show that this composition reduces the amount of amyloid in patients after a single application. It can be assumed that with the

increase in the selectivity of genome editing and the efficiency of delivery of the CRISPR-Cas nucleic acid complex, this approach will be widely introduced into the clinical practice of treating hereditary diseases.

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RESEARCH ARTICLE

## The use of nitrile butadiene rubber in the composition of intumescent fire-retardant materials based on plasticized polyvinyl chloride

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### Abstract

**Objectives.** To investigate the properties of intumescent fire-retardant materials based on plasticized polyvinyl chloride and oxidized graphite as functions of their content of nitrile butadiene rubber.

**Methods.** Intumescent fire-retardant materials with different contents of nitrile butadiene rubber (from 0 to 20 wt %) were obtained. The materials were prepared in the form of a sheet 38–52 mm wide and 1.5–1.9 mm thick by means of flat-die extrusion using a twin-screw compounding extruder. The raw materials used were plasticized polyvinyl chloride with a K-value of 71, nitrile butadiene rubber with a bound acrylonitrile content of 31–35%, oxidized graphite, and ultrafine aluminium hydroxide. The properties of the raw materials and the resulting fire-retardant materials were investigated using infrared spectroscopy, thermal analysis, scanning electron microscopy, as well as mechanical tests, flammability tests, and thermal shock foaming tests.

**Results.** The mechanical, thermal, and fire-retardant properties of the obtained materials were studied as functions of their contents of nitrile butadiene rubber. The dynamics of foaming in the temperature range from 300 to 800°C were also explored. The flammability rating was determined. The dependence of fire-retardant properties on the melt viscosity of fire-retardant materials was described. The thermal properties were found to be in the temperature range of 40 to 900°C.

**Conclusions.** The study found that the introduction of nitrile butadiene rubber into fire-retardant materials leads to a change in a number of properties: a decrease in density and hardness; a decrease in tensile strength; an increase in relative elongation; an increase in melt viscosity by 16 times; and, accordingly, a decrease in foaming rate by a factor of 1.43–1.65. It was established that the foaming rate has a linear dependence on the viscosity of the melt of fire-retardant materials. The introduction of rubber leads to an increase in the strength of foamed char by a factor of 4.8. Thermal analysis showed that increasing the rubber content leads to an increase in heat resistance from 222 to 236°C, and resistance to oxidation of foamed graphite in the composition of foamed char from 601 to 659°C. The presence of rubber does not have a noticeable effect on flammability. The established flammability rating for all compositions is V-0.

### Keywords

fire-retardant material, oxidized graphite, intumescent material, polyvinyl chloride, plasticizer, foaming rate, tensile strength, flammability, melt flow index

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НАУЧНАЯ СТАТЬЯ

# Использование бутадиен-нитрильного каучука в составе интумесцентных огнезащитных материалов на основе пластифицированного поливинилхлорида

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## Аннотация

**Цели.** Исследование свойств интумесцентных огнезащитных материалов на основе пластифицированного поливинилхлорида и окисленного графита в зависимости от содержания в них бутадиен-нитрильного каучука.

**Методы.** В настоящей работе были получены интумесцентные огнезащитные материалы с различным содержанием бутадиен-нитрильного каучука (от 0 до 20 мас. %). Материалы были изготовлены в виде полотна шириной 38–52 мм и толщиной 1.5–1.9 мм методом плоскощелевой экструзии с использованием двухшнекового экструдера-компаундера. В качестве сырья были использованы пластифицированный поливинилхлорид с константой Фикентчера, равной 71, бутадиен-нитрильный каучук с содержанием связанного акрилонитрила 31–35%, окисленный графит и ультрадисперсный гидроксид алюминия. Свойства сырья и полученных огнезащитных материалов были исследованы методами инфракрасной спектроскопии, термического анализа, сканирующей электронной микроскопии, а также при помощи механических испытаний, испытаний на воспламеняемость и вспенивание при термоударе.

**Результаты.** Представлены результаты исследований механических, термических и огнезащитных свойств полученных материалов в зависимости от содержания в них бутадиен-нитрильного каучука. Определена динамика вспенивания в температурном интервале от 300 до 800°C. Определена группа воспламеняемости. Приведена зависимость огнезащитных свойств от вязкости расплава огнезащитных материалов. Определены термические свойства в температурном интервале от 40 до 900°C.

**Выводы.** В исследовании установлено, что введение бутадиен-нитрильного каучука в огнезащитные материалы приводит к изменению ряда свойств: снижению плотности и твердости, снижению прочности на растяжение, увеличению относительного удлинения, росту вязкости расплава в 16 раз и, соответственно, снижению степени вспенивания в 1.43–1.65 раз. Установлено, что степень вспенивания имеет линейную зависимость от вязкости расплава огнезащитных материалов. Введение каучука приводит к повышению прочности пенококса в 4.8 раз. Термический анализ показал, что увеличение содержания каучука приводит к росту термостойкости с 222 до 236°C и стойкости к окислению вспененного графита в составе пенококса с 601 до 659°C. Наличие каучука не оказывает заметного влияния на воспламеняемость. Установлена группа воспламеняемости для всех составов — V-0.

## Ключевые слова

огнезащитный материал, окисленный графит, интумесцентный материал, поливинилхлорид, пластификатор, степень вспенивания, прочность при растяжении, воспламеняемость, показатель текучести расплава

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## INTRODUCTION

Fire protection is currently a pressing issue for most of the infrastructure of public utilities and various industries. During a fire, structures and facilities are subject to significant loads which can lead to severe damage and cause colossal losses to the national economy. This issue is addressed by using passive fire protection materials based on various polymers and fire retardants, such as paints, enamels, impregnations, pastes, tapes, profiles, *inter alia* [1]. In recent years, fire protection tapes and profiles based on polyvinyl chloride (PVC) and expandable graphite have found widespread use [2–6]. Their applications include fire sleeves and fire-retardant materials (FRMs) for fire doors, windows, ventilation boxes and ducts, and elevators in civil and industrial facilities. Under thermal shock conditions, such materials foam repeatedly to form a non-combustible foamed char, filling process openings and gaps. The foam acts as a thermal barrier, and prevents flame spread. The effectiveness of intumescent FRMs depends on a combination of factors: the thickness of the foamed char; the foaming rate; and the properties of the foamed char (structure, chemical composition, cross-linking density, mechanical strength, viscoelastic properties, density, porosity, thermal conductivity, etc.). Under fire conditions, the resulting foamed char is subject to mechanical stress (stretching, compression, shear, impact loads) due to various factors: expansion of metal structural parts under the influence of heat flow, vibration, physical contact with various objects (due to falling objects during a fire), and the action of turbulent flows [7]. In this regard, one of the most important characteristics is the mechanical strength of the foamed char, both under maximum operating temperatures and during fire dynamics.

The use of PVC as a polymer base in intumescent FRMs is an important trend in the development of passive fire protection products. However, PVC itself is a rigid polymer. The use of plasticizers allows the final material to acquire the desired properties such as: elasticity, flexibility, and frost resistance. Plasticized materials have a lower viscosity, allowing for lower processing temperatures, a higher degree of filling, and higher homogeneity of mixture [8]. However, the disadvantages of such polymer materials (PMs) include a low oxygen index (LOI) (up to 19–22%) and high smoke generation [9], as well as low durability due to the presence of a low-molecular-weight plasticizer, which can migrate to the product surface [10]. The use of high-molecular-weight plasticizers can mitigate or, in some cases, completely eliminate these disadvantages [11].

Several studies [12–15] have demonstrated the compatibility of PVC with nitrile butadiene rubber (NBR). PMs based on these components have been available as commercial products for the past 80 years [16]. PVC and NBR have been shown [17] to be compatible in any ratio at an acrylonitrile content in the rubber of 23–45%. The introduction of NBR into PVC allows for PMs to be obtained with properties characteristic of elastomers: increased resistance to oils and solvents; high tensile strength; abrasion resistance; bending resistance; increased residual deformation under compression and resistance to plasticizer migration; and loss of volatiles. For example, replacing half of the low-molecular-weight plasticizer dioctyl phthalate (DOP) with NBR in PVC plasticate leads to an increase in tensile strength by 25%, an increase in relative elongation by 6%, and a decrease in plasticizer migration from 3 to 0.5%. Complete replacement of the low-molecular-weight plasticizer with NBR is impossible, since a plasticizing effect is observed only at an NBR content of 30%. Such mixtures are not always convenient for processing and filling due to the high melt viscosity [15].

PMs based on NBR and plasticized PVC are characterized by high thermal stability. For complex material, this parameter is higher than that for NBR due to the lower fraction of double bonds in the mixture and the presence of chlorine.

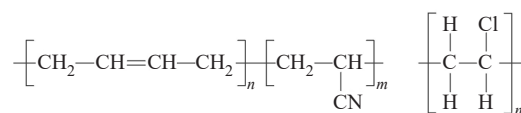


Fig. 1. Structural formulas of NBR (left) and PVC (right)

Thermal oxidation of NBR is a single-stage process. It begins to degrade at 360°C [18]. In the range of 360–500°C, the polymer chain ruptures to release degradation products. These are polymer chain constituents: polybutadiene and polyacrylonitrile, as well as products of the interaction of diene fragments with the nitrile group [19, 20]. This is the range with the highest weight loss: 87.7% [20]. Pyrolysis takes place in the temperature range above 600°C with formation of butadiene, acrylonitrile, benzene, 1,4-cycloheptadiene, 4-vinylcyclohexene, benzonitrile, and other saturated cyclic products [21]. At temperatures up to 900°C, NBR completely degrades, leaving almost no carbon residue.

Thermal and thermo-oxidative degradation of PVC is a more complex process. Pure PVC begins to

degrade at a temperature of 250°C. This stage occurs in the temperature range of 250–350°C, accompanied by a dehydrochlorination reaction with a weight loss of up to 65%. In addition to hydrochloric acid, the degradation products are benzene, toluene, and other unsaturated cyclic hydrocarbons. In the second stage (350–525°C), the dehydrochlorinated residues undergo cracking and degradation to release polyene chains [22]. In the case of plasticized PVC, the low-molecular-weight plasticizer evaporates in the first and second stages. For individual substances, the boiling points are as follows: for DOP, 380°C; for diisononyl phthalate, 252°C, for dioctyl terephthalate, 400°C; and for the plasticizer in the PM, the weight loss temperatures shift to higher temperatures [23]. At temperatures above 525°C, polyene chains degrade to toluene and other low-molecular-weight alkylbenzenes. At temperatures up to 900°C, the yield of carbon residue ranges from 5 to 10% [24, 25].

Thermal degradation of PVC–NBR blends is a two-stage process. In the first and second stages of degradation, the weight loss is lower than for the individual components. The yield of carbon residue at 600°C is 3–4 times higher than that for PVC and NBR. The weight loss curves are not additive with respect to the components of the blend. The degradation products are dominated by low-molecular-weight substances: toluene, acrylonitrile, butenenitrile, and hydrogen cyanide [20]. The increase in the yield of carbon residue probably results from the formation of free radicals of components of the binary mixture and the interaction of macromolecules to form polycyclic structures.

When inorganic fillers (kaolin,  $\text{Mg}(\text{OH})_2$ ) are introduced into the binary mixture, the degradation rate decreases and the degradation maximum shifts to higher temperatures. This is due to the formation of a thermal barrier. The amount of HCl formed by the reaction with the filler also decreases. During degradation, the yield of carbon residue increases non-additively [20]. This phenomenon is also characteristic of both polyolefins and their copolymers [26].

The yield of carbon residue and its mechanical strength are important characteristics for intumescent FRMs. They are critical, especially in the case of a jet fire or the occurrence of turbulent gas flow during the use of intumescent materials under real-life conditions. A high level of hardness and a developed crack structure lead to rapid destruction and ablation of the foamed char. Foamed char with low mechanical strength does not ensure long-term performance under turbulent combustion conditions [7].

The effect of NBR content in intumescent materials based on plasticized PVC and oxidized graphite has not been studied widely. The aim of this study was to investigate the effect of NBR content on the mechanical, thermal, and fire-retardant properties of intumescent FRMs based on plasticized PVC and oxidized graphite.

## EXPERIMENTAL

### Materials

Intumescent FRMs of various compositions were studied, obtained from the following components:

**Component 1:** suspension PVC (*SIBUR Holding*, Russia), 271PC grade, the Fikentscher constant  $K = 71.0 \pm 1.0$ , bulk density 0.46–0.57 g/cm<sup>3</sup>, TU 20.16.30-001-83385954-2018;

**Component 2:** DOP (*VitaKhim*, Russia), premium grade, GOST 8728-88<sup>1</sup>;

**Component 3:** RITMIKS-2040/2 complex lead-based stabilizer (*SKhK*, Russia), TU 20.59.56-020-21996423-2020;

**Component 4:** NBR powder (*SIBUR Holding*), PBNK-3365 grade, bound acrylonitrile content 31–35%, Mooney viscosity (ML 1+4 at 100°C) 65 MU, TU 38.30328-2008;

**Component 5:** ultrafine aluminum hydroxide  $\text{Al}(\text{OH})_3$ , TS 303 grade, D50 3–6 μm, moisture content 0.3%, loss on ignition 33.0–34.5%, aqueous suspension pH 9.2, pycnometric density 2.401 g/cm<sup>3</sup>, TU 2322-001-23374430-2015;

**Component 6:** stearic acid (China), SA1860 grade;

**Component 7:** oxidized bisulfate graphite (*Ningbo Borhe*, China), EG-250 grade, expansion volume 250 cm<sup>3</sup>/g, foam graphite yield 65%, moisture content 0.5%, aqueous extract pH 2.9, pycnometric density 1.587 g/cm<sup>3</sup>, particle size composition—see Table 1.

### Methods

The materials were produced by a three-stage process.

**Stage 1.** In the first stage, PVC plasticate powder was obtained by mixing components 1–3 in a weight ratio of 100 : 70 : 6 (final mixing temperature 110°C). The plasticate was then conditioned at 18–25°C for 24 h.

**Stage 2.** In the second stage, five samples with varying NBR contents were produced by mixing the PVC plasticate powders and components 4–7. In all cases, the total polymer content (PVC plasticate + NBR) was the same, 60 wt %. Within this total content, the NBR content was varied so that the NBR content

<sup>1</sup> GOST 8728-88. Interstate Standard. Plasticizers. Specifications. Moscow: IPK Izdatelstvo standartov; 1990 (in Russ.).

**Table 1.** Particle size composition (wt %) of oxidized bisulphate graphite, EG-250 grade (mm)

| Particle size, mm | +1.0 | −1.0 + 0.63 | −0.63 + 0.4 | −0.4 + 0.315 | −0.315 + 0.2 | −0.2 + 0.16 | −0.16 + 0.1 | −0.1 + 0.05 | −0.05 |
|-------------------|------|-------------|-------------|--------------|--------------|-------------|-------------|-------------|-------|
| Content, %        | 0    | 0           | 0.5         | 1.7          | 54.8         | 27.4        | 0.1         | 13.9        | 1.5   |

**Table 2.** Composition (wt %) of PMs and FRMs with various NBR contents

| Material code | Component |       |            |              |       |                     |                   |
|---------------|-----------|-------|------------|--------------|-------|---------------------|-------------------|
|               | PVC       | DOP   | Stabilizer | Stearic acid | NBR   | Al(OH) <sub>3</sub> | Oxidized graphite |
| PM-0          | 56.72     | 39.59 | 3.40       | 0.29         | 0     | 0                   | 0                 |
| PM-5          | 51.88     | 36.32 | 3.11       | 0.29         | 8.40  | 0                   | 0                 |
| PM-10         | 47.21     | 33.05 | 2.83       | 0.29         | 16.62 | 0                   | 0                 |
| PM-15         | 42.47     | 29.72 | 2.55       | 0.29         | 24.97 | 0                   | 0                 |
| PM-20         | 37.76     | 26.44 | 2.27       | 0.29         | 33.24 | 0                   | 0                 |
| FRM-0         | 34.06     | 23.84 | 2.04       | 0.18         | 0     | 9.88                | 30                |
| FRM-5         | 31.22     | 21.85 | 1.87       | 0.18         | 5.00  | 9.88                | 30                |
| FRM-10        | 28.37     | 19.87 | 1.70       | 0.18         | 10.00 | 9.88                | 30                |
| FRM-15        | 25.54     | 17.87 | 1.53       | 0.18         | 15.00 | 9.88                | 30                |
| FRM-20        | 22.70     | 15.88 | 1.36       | 0.18         | 20.00 | 9.88                | 30                |

in the final composition was 0, 5, 10, 15, and 20 wt %. The total aluminum hydroxide and oxidized graphite contents were the same in all compositions (10 and 30%, respectively). In order to evaluate the dynamics of the properties of PMs upon the introduction of fire retardants, five polymer samples were also obtained. They contained no fire retardants and the weight ratio between PVC and NBR remained the same. Table 2 presents the compositions of the resulting mixtures.

**Stage 3.** In the third stage, each of the mixtures obtained (FRM and PM) was extruded by a twin-screw extruder with corotating screws ( $D_S = 20$  mm and  $L_S/D_S = 44$ .  $D_S$  and  $L_S$  are the extruder screw diameter and length, respectively) at a temperature of 165–170°C and a screw speed of 170 rpm using a T-shaped flat die.

During extrusion, the screw motor load was recorded as a percentage of the maximum value. A two-roll calender with water-cooled rolls was used to form a sheet. Thus, for each composition, a sheet 38–52 mm wide and 1.5–1.9 mm thick was obtained. The characteristics of the resulting materials were determined using a number of methods.

## RESEARCH METHODS

### Composition of fire retardants

The study ascertained the pHs of the aqueous suspension (for aluminum hydroxide, according to GOST 21119.3-91<sup>2</sup>) and aqueous extract (for oxidized graphite, according to GOST 17818.6-90<sup>3</sup>) of the fire retardants.

<sup>2</sup> GOST 21119.3-91. Interstate Standard. General methods of test for pigments and extenders. Determination of pH value of an aqueous suspension. Moscow: IPK Izdatelstvo standartov; 1999 (in Russ.).

<sup>3</sup> GOST 17818.6-90. State Standard of the USSR. Graphite. Method for determination of hydrogen ions concentration of water suspension and water extract. Moscow; 1990 (in Russ.).

The composition of the fire retardants was analyzed using a TENSOR 27 FTIR spectrometer (*Bruker*, Germany) with a DLaTGS detector in the 4000–400  $\text{cm}^{-1}$  range with a resolution of 4  $\text{cm}^{-1}$  using pellets of alkali metal halides (KBr) with  $\text{Al}(\text{OH})_3$  or oxidized graphite in ratios of 1 : 500 and 1 : 850, respectively.

### Density and hardness

The density  $D$  and Shore A hardness  $H_A$  of the materials obtained (PMs and FRMs) were determined according to GOST 15139-69<sup>4</sup> and GOST 24621-2015<sup>5</sup>, respectively.

### Melt flow index (MFI)

In the case of FRMs, MFI was measured according to GOST 11645-2021<sup>6</sup> using an XNR-400 analytical plastometer at a temperature of 190°C and a load of 5.0 kg.

### Tensile strength

In the case of the PM and FRM samples, the tensile strength  $\sigma_t$  and relative elongation  $\epsilon_t$  were determined according to GOST 270-75<sup>7</sup>. The test was conducted at room temperature on Type II specimens (detailed notations and dimensions are specified in the regulatory documentation GOST 270-75) using an HxK-S/U series universal testing machine, modification H5K-S (*Tinius Olsen*, United Kingdom) at a travel speed of (500 ± 50) mm/min.

### Thermal properties

The thermal properties of the raw materials, PMs, and FRMs were determined using dynamic thermogravimetric analysis in an air atmosphere (60  $\text{cm}^3/\text{min}$ ) using an STA 449 simultaneous thermal analyzer (*Netzsch*, Germany) in the temperature range of 40–900°C at a temperature increase rate of 20 K/min. Based on the results of thermal analysis, thermal stability was

found from the onset degradation temperature  $T_i$ , and the temperature  $T_{\text{max}}$  of the maximum decomposition rate [5].

### Foaming rate

The foaming rate  $FR$  of the FRM samples was determined as a function of the specified isothermal holding temperature. The test was conducted in air using the method described in GOST R 59637-2021<sup>8</sup>. FRM samples with a diameter of  $40 \pm 0.5$  mm, and an actual initial thickness  $T_0$  measured with a caliper, were placed in a hollow steel cylinder with a diameter of 41 mm and a height of 60 mm. Next, the steel cylinder containing the sample was mounted on a steel support and then placed in a muffle furnace preheated to the specified temperature. After 5 min, the steel cylinder was removed from the furnace and cooled to room temperature. The test was performed in triplicate for each sample. The heights  $T_0$  and  $T_1$  of the initial and foamed samples, respectively, were measured with a caliper.

The foaming rate was determined at temperatures ranging from 300 to 800°C in 100°C increments. The foaming rate  $FR$  was calculated using the following equation

$$FR = [(T_1 - T_0)/T_0] \times 100\%.$$

The foaming dynamics was determined for each FRM as a function of the specified holding temperature.

The sample heating rate was determined for each preset furnace temperature from 300 to 800°C. A thermocouple was installed at the sample location to record the temperature over a period of up to 5 min (Fig. 2).

As can be seen in Fig. 2, the higher the preset furnace temperature, the higher the sample heating rate  $v_0$  at the initial time. Temperature is known to be a key factor in the foaming process of expandable graphite: with increasing temperature, the foaming rate increases and the bulk density of the expanded graphite decreases [27].

<sup>4</sup> GOST 15139-69. State Standard of the USSR. Plastics. Methods for the determination of density (volume mass). Reprint, February, 1988, with correction 1. Moscow: IPK Izdatelstvo standartov; 1999 (in Russ.).

<sup>5</sup> GOST 24621-2015. Interstate Standard. Plastics and ebonite. Determination of indentation hardness by means of a durometer (Shore hardness). Moscow: Standartinform; 2015 (in Russ.).

<sup>6</sup> GOST 11645-2021. Interstate Standard. Plastics. Methods for determination of flow index of thermoplastics melt. Moscow: Russian Standardization Institute; 2025 (in Russ.).

<sup>7</sup> GOST 270-75. Interstate Standard. Rubber. Method of the determination elastic and tensile stress-strain properties. Moscow: Standartinform; 2008 (in Russ.).

<sup>8</sup> GOST R 59637-2021. National Standard of the Russian Federation. Fire protection means for buildings and structures. Means of fire protection. Methods of quality control of fire-retardant works during installation (application), maintenance and repair. Moscow: Russian Standardization Institute; 2021 (in Russ.).

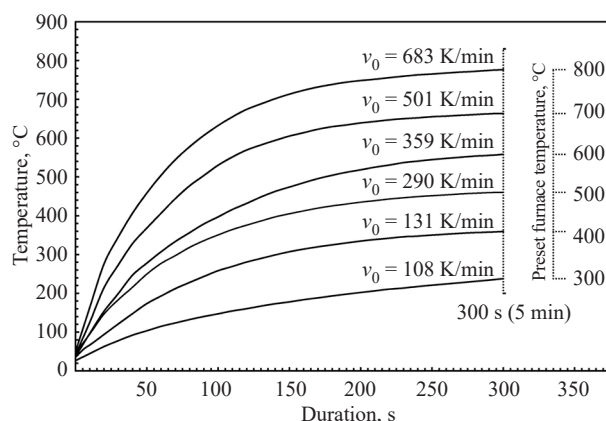


**Fig. 2.** Dependence of the temperature of a FRM sample on the duration of holding at a preset furnace temperature

### Mechanical strength of foamed char

In the case of the FRM samples foamed at 600°C, the mechanical strength  $\sigma_f$  of the foamed char was determined according to a published procedure [28]. The foamed char sample was placed between two horizontal plates secured to the crosshead of a testing machine. The test was conducted at room temperature using an HxK-S/U universal testing machine, modification H5K-S, at a travel speed of 2.5 mm/min with a force meter accuracy of  $\pm 2.5$  N. Each sample was tested in such a way that the final distance between the plates was 2 mm. Since foamed char produced from such FRMs has a gradient structure and its upper and middle parts have the highest porosity [6], the calculations were made at 75% deformation (for the lower part of the foamed char sample).

### Flammability

The flammability of the FRM samples was determined according to UL-94 “Test for Flammability of Plastic Materials for Parts in Devices and Appliances”<sup>9</sup>. For the purposes of testing, specimens with a length of  $125 \pm 5$  mm, a width of  $13.0 \pm 0.5$  mm, and a thickness of 1.5–1.9 mm were cut from fragments of the extruded FRM sheet. The specimens were then conditioned at a temperature of  $23 \pm 2^\circ\text{C}$  and a relative humidity of  $50 \pm 5\%$  for 48 h. All specimens were tested for compliance with the V-0 flammability rating: vertical specimen position, gas burner flame height 20 mm, flame self-extinguishing within 10 s after flame removal, burning droplets not allowed, and afterglow for 30 s. Three replicate specimens were tested in one single test.

### Scanning electron microscopy (SEM)

The structure and morphology of the fire-retardant powders and fracture surfaces of the PM and FRM samples were examined using a TESCAN VEGA3 LMU scanning electron microscope (*Tescan Orsay Holding*, Czech Republic) at an accelerating voltage of 20 V.

## RESULTS AND DISCUSSION

The FRMs being studied here are often used as elastic profiles and tapes in structures for various purposes. Therefore, their performance attributes are not limited to fire protection characteristics, but also include their physical and mechanical properties. Table 3 presents the results of characterizing the obtained PMs and FRMs.

In this study, we investigated the effect of NBR on density, Shore A hardness, and tensile strength.

In order to assess the effect of fire-retardant properties on the mechanical properties of FRMs, oxidized graphite and aluminum hydroxide were studied by IR spectroscopy. The pH was determined, and fire-retardant particles were examined by SEM. According to the IR spectrum (Fig. 3), oxidized graphite bisulfate, EG-250 grade, has a number of functional groups: O–H ( $3438\text{ cm}^{-1}$ ); carboxyl COOH ( $1388\text{ cm}^{-1}$ ); carbonyl  $\text{C}=\text{O}$  ( $1700\text{ cm}^{-1}$ ); and aromatic C=C group ( $1633\text{ cm}^{-1}$ ). The presence of several bands in the range from  $1050\text{--}950\text{ cm}^{-1}$  may be due to the vibrations of the S=O group. Their low intensity is associated with the low concentration of these groups in the oxidized graphite. The band at  $1114\text{ cm}^{-1}$  may be attributed to both the vibrations of the oxygen-containing C–O group and the asymmetric vibrations of  $\text{SO}_4^{2-}$  [29–31]. Hydroxyl groups are located on the surface of the basal layers. The high intensity of the peak at  $3438\text{ cm}^{-1}$  suggests that their content is high.

<sup>9</sup> UL 94 BULLETIN-2018 UL Standard for Safety Tests for Flammability of Plastic Materials for Parts in Devices and Appliances. Underwriters Laboratories Inc. (UL). Northbrook, IL. Fifth Edition, Dated October 29, 1996.

**Table 3.** Properties of the obtained PMs and FRMs

| Material code | NBR content | MFL,<br>g/10 min | D, g/cm <sup>3</sup> | H <sub>A</sub> , c.u. | σ <sub>t</sub> MPa | ε <sub>t</sub> % | σ <sub>f</sub> MPa | Thermal analysis data   |                        |                        |     | UL-94 |
|---------------|-------------|------------------|----------------------|-----------------------|--------------------|------------------|--------------------|-------------------------|------------------------|------------------------|-----|-------|
|               |             |                  |                      |                       |                    |                  |                    | T <sub>onset</sub> , °C | T <sub>peak</sub> , °C | Residue at 900°C,<br>% |     |       |
| PM-0          | 0           | 35.0             | 1.236                | 61                    | 10.9               | 249.7            | —                  | —                       | —                      | —                      | —   | —     |
| PM-5          | 8.40        | 27.7             | 1.236                | 59                    | 10.9               | 355.6            | —                  | —                       | —                      | —                      | —   | —     |
| PM-10         | 16.62       | 17.0             | 1.219                | 55                    | 10.8               | 386.1            | —                  | —                       | —                      | —                      | —   | —     |
| PM-15         | 24.97       | 8.8              | 1.175                | 49                    | 10.6               | 421.9            | —                  | —                       | —                      | —                      | —   | —     |
| PM-20         | 33.24       | 2.9              | 1.085                | 41                    | 9.5                | 465.6            | —                  | —                       | —                      | —                      | —   | —     |
| FRM-0         | 0           | 14.6             | 1.382                | 77                    | 6.2                | 152.4            | 129.2              | 222                     | 253                    | 9.47                   | V-0 | V-0   |
| FRM-5         | 5.00        | 9.4              | 1.423                | 77                    | 6.0                | 211.6            | 315.6              | 226                     | 254                    | 8.74                   | V-0 | V-0   |
| FRM-10        | 10.00       | 5.0              | 1.405                | 75                    | 5.8                | 254.8            | 321.4              | 228                     | 260                    | 8.80                   | V-0 | V-0   |
| FRM-15        | 15.00       | 2.9              | 1.367                | 73                    | 5.1                | 314.2            | 448.4              | 233                     | 264                    | 8.49                   | V-0 | V-0   |
| FRM-20        | 20.00       | 0.9              | 1.350                | 69                    | 4.6                | 384.6            | 615.4              | 236                     | 264                    | 9.43                   | V-0 | V-0   |

Note:  $D$ , density;  $H_A$ , Shore A hardness;  $\sigma_t$ , tensile strength;  $\epsilon_t$ , relative tensile elongation;  $\sigma_f$ , mechanical strength of foamed char;  $T_{onset}$ , onset degradation temperature;  $T_{peak}$ , temperature of the maximum degradation rate; and UL-94, flammability rating according to UL-94.

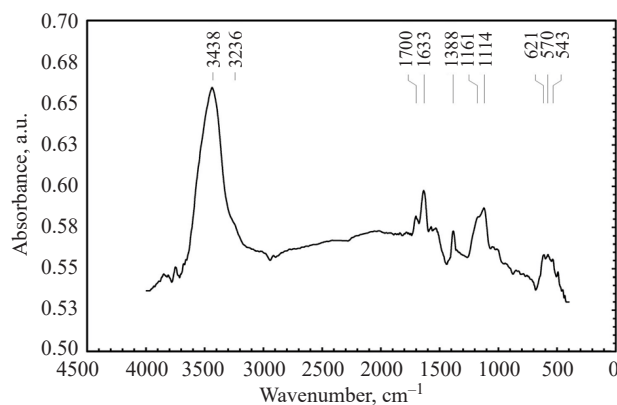


**Fig. 3.** IR absorption spectra of oxidized bisulphate graphite, EG-250 grade

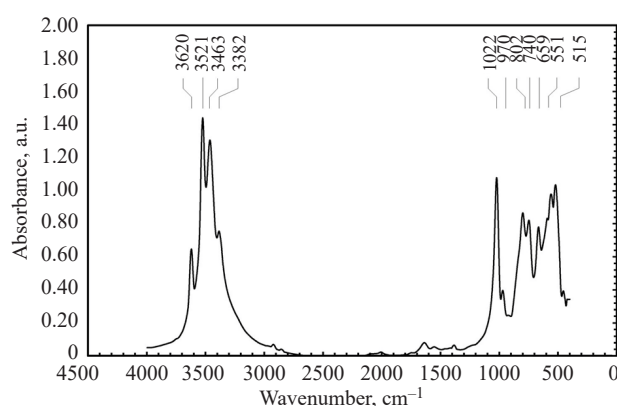


**Fig. 4.** IR absorption spectra of ultrafine aluminium hydroxide, TS 303 grade

The IR absorption spectrum of ultrafine aluminum hydroxide, TS 303 grade (Fig. 4), shows mainly bands of stretching (in the range from 3620 to 3382  $\text{cm}^{-1}$ ) and bending (1022 and 970  $\text{cm}^{-1}$ ) vibrations of the HO group. The bands in the range from 650 to 515  $\text{cm}^{-1}$  are assigned to the bending vibrations of the HO group and the vibrations of the AlO group [32].

The fire retardants have different pH values. The pHs of the aqueous extract/suspension are 2.9 and 9.2 for oxidized graphite and aluminum hydroxide, respectively.

Figures 5 and 6 present SEM images of fire-retardant particles.

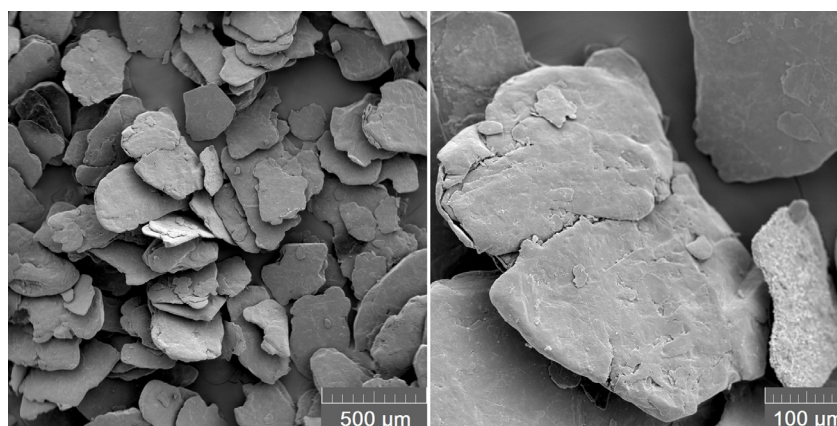


**Fig. 5.** SEM images of oxidized bisulphate graphite, EG-250 grade

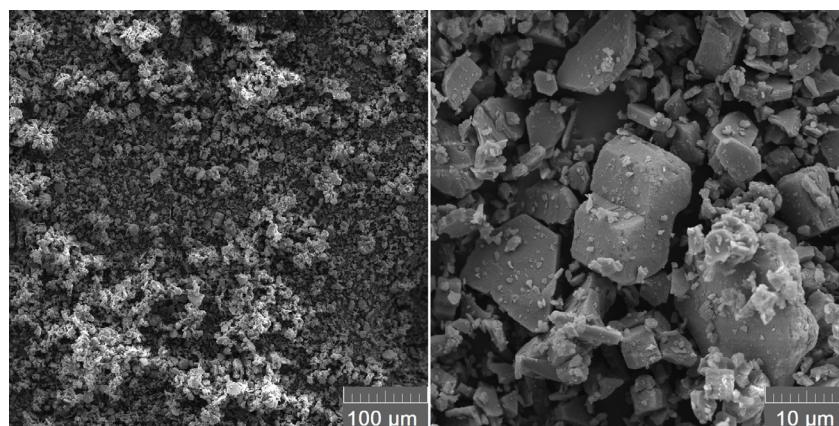


Fig. 6. SEM images of ultrafine aluminium hydroxide, TS 303 grade

As can be seen from Table 3 and Fig. 7, an increase in the NBR content leads to a decrease in density by 12% for PMs. For FRMs, the density remains virtually unchanged (decreases by 2.3%).

The introduction of fire retardants in a given quantity leads to an average increase in density of 12–25%. This is as a result of the addition of denser fillers, the densities of which are 1.587 and 2.401 g/cm<sup>3</sup> for oxidized graphite and aluminum hydroxide, respectively.

An increase in the NBR content leads to a decrease in the Shore A hardness of PMs and FRMs by 33 and 10%, respectively (Fig. 7). These changes are due to the hardness of NBR (49 c.u.) which acts as a high-molecular-weight plasticizer, increasing the mobility of PVC macromolecules, thereby reducing indentation resistance [33]. The introduction of the fire retardants leads to an increase in hardness by a factor of 1.3–1.7. This change is typical of PVC-based PMs with a wide range of fillers at a high degree of filling [34]. In FRMs, the filler strengthens the bonds between macromolecules, hindering their sliding relative to each other. As Fig. 7 shows, the hardness of PMs and FRMs in the range considered changes differently: decreasing

by 33 and 10%, respectively. This may be due to the fact that increasing NBR content in FRMs strengthens the bonds between the fillers and the polymer chain units.

Determining the strength characteristics showed that with an increase in the NBR content in PMs and FRMs, the tensile strength  $\sigma_t$  decreases by 13 and 25%, respectively. The relative tensile elongation  $\varepsilon_t$  increases by a factor of 1.9 and 2.5, respectively. The introduction of the fire retardants leads to a decrease in  $\sigma_t$  and  $\varepsilon_t$  by a factor of 1.8–2.1 and 1.2–1.7, respectively (Fig. 8).

In the case of PMs, the decrease in  $\sigma_t$  is uneven. In the range up to 15 wt % (based on the FRM composition), this characteristic remains virtually unchanged which is consistent with literature data [13]. However, at a content of 20 wt %, it decreases by 13%.

The effect of fillers on the strength properties of PVC-based PMs has been studied using a wide range of materials. It was noted that the filler is selected based on its compatibility with the PM which depends on the adhesion at the polymer–filler interface [35] and on at least two other factors: the chemical interaction at the interface; and the shape and size of the filler particles.

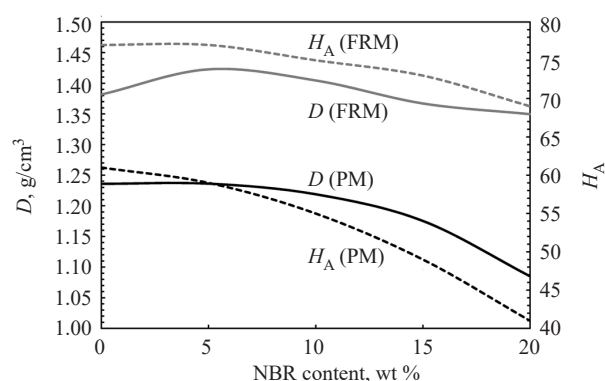


Fig. 7. Dependencies of the density  $D$  and Shore A hardness  $H_A$  of PMs and FRMs on NBR content

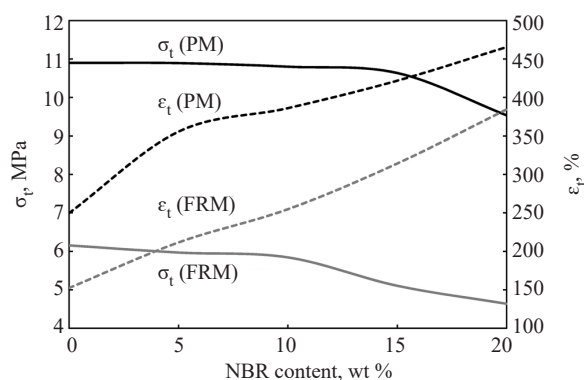


**Fig. 8.** Dependencies of the density  $\sigma_t$  and relative tensile elongation  $\epsilon_t$  of PMs and FRMs on NBR

PVC has weak acidic properties. Its  $\alpha$ -hydrogen atoms can form bonds with proton-acceptor substances [36]. A method for increasing interfacial strength is based on increasing the number of hydroxyl groups on the filler surface [37, 38]. At the interface, PVC interacts with basic fillers containing reactive HO groups. Conversely, fillers with pronounced acidic properties exhibit poor compatibility with PVC [37]. According to IR spectroscopy (Fig. 3), a characteristic of oxidized graphite is its high content of surface HO groups. An aqueous extract of this fire retardant is also acidic (pH 2.9). However, it should be noted that the acidity of the aqueous extract is determined by the presence of residual sulfuric acid. Sulfuric acid and hydrosulfate anions are readily washed out of the interlayer space of oxidized graphite by water, passing to solution upon pH determination. However, HO groups are strongly bonded to carbon atoms in the graphite crystal lattice. Overall, based on the peak intensity in the IR spectrum of oxidized graphite, it can be concluded that this fire retardant has basic properties.

Aluminum hydroxide also exhibits basic properties due to the presence of HO groups (Fig. 4). However, despite the apparent chemical compatibility of the materials, the introduction of fire retardants into PMs causes a decrease in their strength properties. The size and shape of the particles are known to affect the properties of PMs under deformation, especially under stretching. Dynamic testing is accompanied by cavitation, i.e., delamination to form cavities near the filler surface [39]. The size of the filler particles determines the formation of defects at the matrix–filler interface in the form of either oval or diamond-shaped pores [40, 41]. The oval pores are created when the filler particle size is up to 100  $\mu\text{m}$ . Such pores do not reduce the mechanical properties. The diamond-shaped pores are formed when the filler particle size is greater than

100  $\mu\text{m}$ ; in this case, defects arise that initially grow as oval pores and then transform into diamond-shaped pores. These defects are microcracks growing transversely to the stretching direction. This leads to early failure of the PM. When stretched, the matrix is delaminated along diamond-shaped defects, resulting in a characteristic decrease in strength. It can thus be concluded that, despite the chemical compatibility of fire retardants with the PM, the particle size of oxidized graphite determines the decrease in strength of FRMs.

In this study, we compared the foaming rates of FRMs with different NBR contents, including the dependence on the specified isothermal holding temperature (the sample heating rate, see Fig. 2). The results showed that with an increase in NBR content from 0 to 20%, the foaming rate decreases by a factor of 1.43–1.65. Increasing the holding temperature leads to an increase in the foaming rate of FRMs, which is typical of oxidized graphite [27]. Figure 9 shows that the FRM foaming process can be divided into two stages: 1) before 400°C, when samples of all FRM compositions rapidly foam; and 2) after 400°C, when the foaming is smooth with the sample height changing slightly. In the temperature range of 700–800°C, the sample height decreases because of oxidation of the foamed char. This is especially characteristic of the sample with a large foamed char height, when its upper portion is exposed to an oxidizing environment (sample FRM-0).

Foaming rate is an important parameter of fire protection materials which determines their performance properties. As noted above, rolled FRMs are applied in fire doors, and fire sleeves, inter alia, where one of the fire protection performance characteristics is complete response time which determines the fire resistance limit (GOST R 53306-2009<sup>10</sup>). Figure 9 also shows that NBR

<sup>10</sup> GOST R 53306-2009. National Standard of the Russian Federation. Enclosing building structures crossing junction points by using pipe, which is made of polymeric materials. Fire resistance test. Moscow: Standartinform; 2019 (in Russ.).

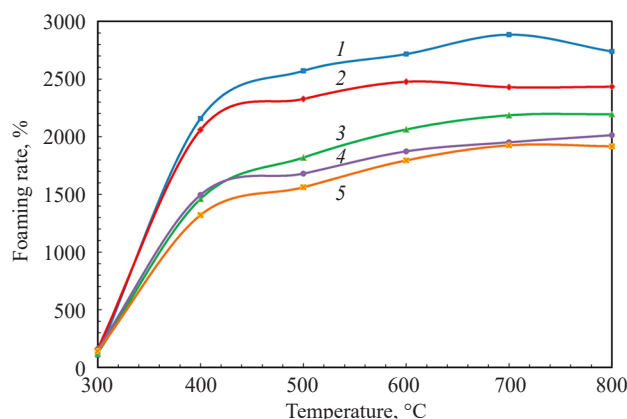


**Fig. 9.** Dependencies of the foaming rate of FRM on specified isothermal holding temperature at various NBR contents: (1) FRM-0, (2) FRM-5, (3) FRM-10, (4) FRM-15, and (5) FRM-20

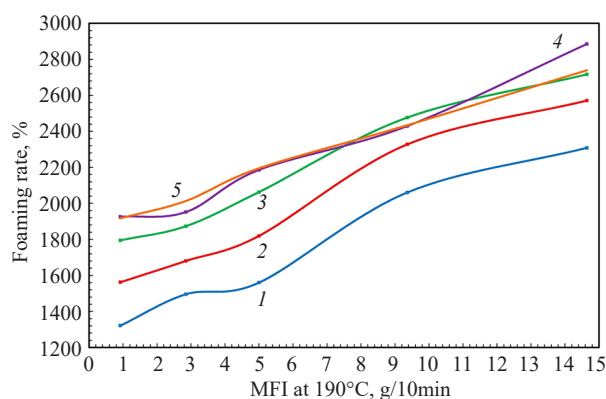


**Fig. 10.** Dependence of the foaming rate of FRMs on their MFI at different NBR contents and various specified isothermal holding temperatures: (1) 400 °C, (2) 500 °C, (3) 600 °C, (4) 700 °C, and (5) 800 °C

content in FRMs affects the maximum foaming rate and foaming speed. Over the entire temperature range, an increase in the NBR content leads to a decrease in the foaming rate which may be due to an increase in the melt viscosity of FRMs in the FRM-0, ..., FRM-20 series (Table 3). The rate-limiting stage of the foaming process is nucleation in the bulk of the liquid phase [6, 42]: gas bubble nuclei are formed in the bulk of the PM during its transition to a viscoelastic flow state with a certain viscosity value. Figure 10 presents the dependence of the foaming rate on the MFI of FRMs at various temperatures.

The results obtained show that the dependence of the foaming rate of FRMs on their MFI is generally linear over the entire temperature range.

The effect of the NBR content in FRMs on the strength of foamed char is of practical interest. As Fig. 11 and Table 3 show, increasing the NBR content in FRMs from 0 to 20% leads to a 4.7-fold increase in the compressive strength of foamed char.

This may be due to the fact that, during the combined pyrolysis of PVC and NBR, the decomposition products of PVC and NBR interact to form condensed compounds. Furthermore, with increasing NBR content, the fraction of low-boiling, low-molecular-weight plasticizer in the PM decreases. This can lead to an increase in thermal stability and a shift in pyrolysis processes toward higher temperatures [43].

As can be seen in Fig. 12 and Table 3, the introduction of NBR alters the pyrolysis process of FRMs in an oxidizing atmosphere.

With an increase in NBR content, the onset degradation temperature of FRMs increases from 222 to 236 °C. This is due to the high thermal stability of NBR (280 °C). The temperature of the maximum degradation rate at this stage also increases: from 253 to 264 °C. Figure 12 shows that at the first stage of degradation, the temperature behavior of all the FRMs considered (dehydrochlorination) is similar. Predominantly NBR pyrolysis occurs in the temperature range of 300–500 °C. With an increase in the NBR content

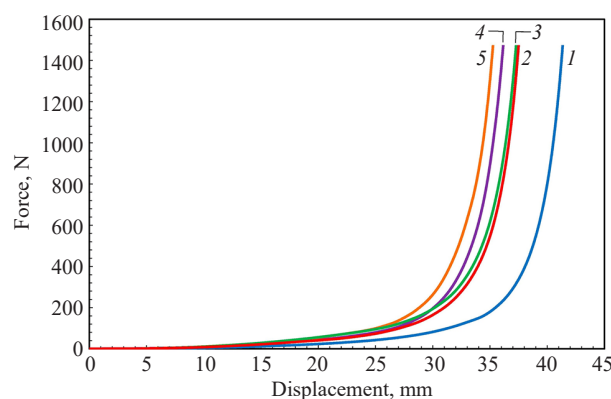


**Fig. 11.** Compressive load *versus* displacement curves for FRMs with various NBR contents: (1) FRM-0, (2) FRM-5, (3) FRM-10, (4) FRM-15, and (5) FRM-20

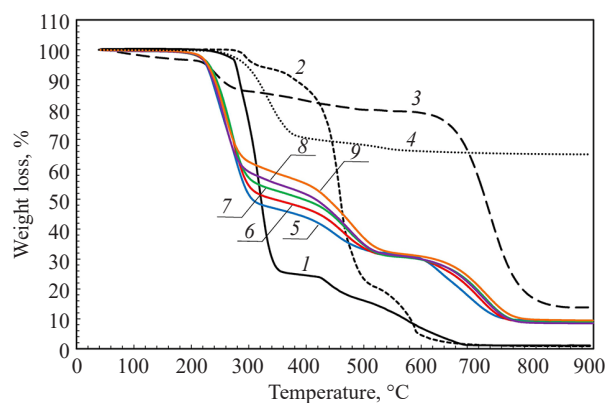


**Fig. 12.** Weight loss curve of the initial materials and FRM samples in the temperature range of 40–900°C: (1) PVC plasticate, (2) NBR, (3) oxidized graphite, (4) aluminium hydroxide, (5) FRM-0, (6) FRM-5, (7) FRM-10, (8) FRM-15, and (9) FRM-20

in FRMs, the weight loss at this stage increases (from 14.7 to 26.3%). In the temperature range of 600–750°C, foamed graphite in FRMs is oxidized. The presence of NBR leads to a shift of the oxidation process to higher temperatures. The onset oxidation temperature increases from 601°C (for FRM-0) to 659°C (for FRM-20). The NBR content does not significantly affect the residue after oxidation in the temperature range up to 900°C. The content of this residue is in the range of 8.74–9.47%. Also the content of  $\text{Al}(\text{OH})_3$  in FRMs is 9.88%. Its decomposition occurs according to the equation



The decomposition gives  $\text{Al}_2\text{O}_3$  to a content in FRMs of 6.4%. The difference is determined by the non-zero residue left after the oxidation of the expanded graphite in FRMs.

The flammability of the FRMs studied here is not markedly affected by the presence of NBR in them. When tested according to UL-94, all the materials

self-extinguish within no more than 1–2 s. This is determined by the high content of fire retardants, primarily oxidized graphite. The established flammability rating for all compositions is V-0.

## CONCLUSIONS

The study found that an increase in the fraction of NBR in FRMs results in a decrease in density and hardness (by 2.3 and 10%, respectively), a decrease in tensile strength by 25%, and an increase in elongation by a factor of 2.5. The introduction of fire retardants increases density by an average of 12–25%. It also increases hardness by a factor of 1.3–1.7, and decreases strength and tensile elongation by a factor of 1.8–2.1 and 1.2–1.7, respectively. The investigation of fire-retardant properties showed that an increase in the rubber content causes a decrease in the foaming rate by a factor of 1.43–1.65 in the temperature range from 400 to 800°C. Increasing the rubber content from 0 to 20%

brings about a 16-fold increase in the viscosity of the fire-retardant melt. This affects the foaming rate. It was determined that the foaming rate in the temperature range from 400 to 800°C has a linear dependence on the viscosity of the FRM melt. The addition of rubber increases the strength of foamed char by a factor of 4.8. Thermal analysis demonstrated that increasing the rubber content increases the heat resistance from 222 to 236°C, and the oxidation resistance of expanded graphite in foamed char from 601 to 659°C. The NBR content has no significant effect on the residue after oxidation in the temperature range up to 900°C, with the content of this residue ranging from 8.74 to 9.47%. The presence of NBR in FRMs has no marked effect on flammability. The established flammability rating for

all materials is V-0. The results obtained are of great practical interest, since they can be used to predict the optimal composition for producing intumescent FRMs.

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### Authors' contributions

**A.A. Galiguzov**—conducting experiments, preparing graphic materials, analyzing results, writing individual sections.

**N.V. Yashin**—writing the introduction, planning the experiments.

**V.V. Avdeev**—scientific editing, formulating the conclusions.

*The authors declare no conflicts of interest.*

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Synthesis and processing of polymers  
and polymeric composites

Синтез и переработка полимеров  
и композитов на их основе

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RESEARCH ARTICLE

## Composite material obtained based on track-etched membranes and silver nanoparticles of different shapes

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### Abstract

**Objectives.** To study the effect of shape on the intensity of surface-enhanced Raman light scattering when depositing nanoparticles on track membranes. The resulting composite material can be further used as a substrate for sensors. The efficiency of such sensors is determined by the effect of surface-enhanced Raman scattering of light.

**Methods.** Silver nanoparticles were obtained by reduction of silver ions in solution under various conditions. Nanoparticles from the obtained colloidal solutions were deposited on polyethylenimine-modified polyethylene terephthalate track-etched membranes. The samples were examined using absorption spectroscopy in the ultraviolet and visible region, scanning and transmission electron microscopy, dynamic light scattering, and Raman spectroscopy.

**Results.** Silver nanoparticles of spherical, triangular, and nanowire shape were synthesized. The sizes and zeta potential of the nanoparticles were determined. The obtained nanoparticles were deposited on the surface of track-etched membranes. For the composite membrane samples, the relative enhancement factors of the Raman light scattering signal of the 4-aminothiophenol test substance were calculated based on the substrate with a known enhancement factor.

**Conclusions.** The effect of surface-enhanced Raman light scattering was found to be greater when transitioning from spherical to various nonspherical-shaped nanoparticles. The highest value of the relative enhancement factor was  $4 \cdot 10^7$  on the composite membrane with silver nanowires.

### Keywords

surface-enhanced Raman scattering, silver nanoparticles, track-etched membranes, nanoplasmonics, SERS sensors

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НАУЧНАЯ СТАТЬЯ

# Получение композитного материала на основе трековых мембран и наночастиц серебра различной формы

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## Аннотация

**Цели.** Изучение влияния формы наночастиц на эффект гигантского комбинационного рассеяния света при осаждении их на трековые мембраны. В дальнейшем полученный композитный материал может использоваться в качестве подложки для сенсоров, работа которых основана на эффекте гигантского комбинационного рассеяния света.

**Методы.** Наночастицы серебра получали методом восстановления ионов серебра в растворе при различных условиях. Наночастицы из полученных коллоидных растворов осаждали на модифицированные полиэтиленгликолем полиэтилентерефталатные трековые мембраны. Для исследования образцов использовали спектроскопию поглощения в ультрафиолетовой и видимой области, растровую и просвечивающую электронные микроскопии, лазерный доплеровский микроэлектрофорез, спектроскопию комбинационного рассеяния.

**Результаты.** Синтезированы наночастицы серебра сферической, треугольной формы и в форме нанопроволок, определены размеры и дзета-потенциал наночастиц. Полученные наночастицы осажжены на поверхность трековых мембран. Для образцов композитных мембран рассчитаны относительные коэффициенты усиления сигнала комбинационного рассеяния света тестового вещества 4-аминотиофенола по отношению к подложке с известным коэффициентом усиления.

**Выводы.** Показано, что при переходе от сферической формы наночастиц к различным несферическим усиливается эффект гигантского комбинационного рассеяния света. Наибольшее значение относительного коэффициента усиления составило  $4 \cdot 10^7$  на композитной мембране с серебряными нанопроволоками.

## Ключевые слова

гигантское комбинационное рассеяние света, наночастицы серебра, трековые мембраны, композитные мембраны

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## INTRODUCTION

Surface-enhanced Raman light scattering (SERS) spectroscopy is increasingly being applied for the qualitative and quantitative analysis of chemical compounds and biological objects at the level of low concentrations. This method is used to identify antibiotics [1], dyes [2, 3], fungicides [4], and drugs [5] at concentrations from  $10^{-9}$  to  $10^{-12}$  M.

Silver and gold nanoparticles are widely used to create SERS-active structures [2]. A number of studies report the use of copper [6], nickel [7], and mixed composites [8] as nanoparticle materials. However, silver nanoparticles (SNPs) enable the greatest enhancement of the Raman scattering signal [9].

The key characteristics of metal nanoparticles that influence signal enhancement include the material, size, and stabilizer. In addition, the shape of nanoparticles also makes a significant contribution [10, 11]. When transitioning from spherical nanoparticles to various nonspherical forms, the charge of surface atoms is localized at the angles and roughness. This leads to an increase in the electric field density between nanoparticles by more than an order of magnitude [12, 13], thus significantly enhancing the Raman signal. Hence, the synthesis and deposition of nanoparticles of various nonspherical shapes is a pressing research topic.

Nonspherical nanoparticles can be produced using spatially confined systems, such as membrane pores, or by adding reagents that are selectively adsorbed on individual faces of nanoparticle nuclei. Polyvinylpyrrolidone [14], cetyltrimethylammonium bromide [15], as well as salts of citric [14] and ascorbic acids [16], are capable of exhibiting this ability. In this case, nanoparticle growth is confined to individual directions, which enables the production of nanocubes, nanorods, triangular nanoprisms, and other shapes.

SERS spectroscopy can be conducted both in colloidal solutions and on planar substrates. The use of track-etched membranes (TMs) as a substrate permits the separation and concentration of the analyzed sample, thus improving the analysis selectivity. TMs are produced by irradiating polymer films with high-energy ions, which form latent tracks. These tracks are then converted into pores through further selective etching. The advantage of TMs consists in their ability to control pore concentration and size. To immobilize nanoparticles to the TM, its surface should be modified. In the case of SNPs, compounds containing carboxyl, thiol, or amino groups are typically used. Polyethyleneimine (PEI) is the most suitable modifier due to the presence of  $\text{NH}_x^+$  terminal groups. PEI binds SNPs to the TM surface electrostatically as well as chemically due to the lone

electron pair on the nitrogen atom [17]. PEI outperforms other modifiers in terms of its high solubility in water.

Thus, changing the SNP shape will significantly increase the Raman signal. Additionally, the use of TM as a substrate will improve the selectivity of SERS analysis. In this study, we aim to synthesize SNPs of various shapes and immobilize them on the TM surface in order to study the effect of nanoparticle shape on SERS intensity.

## EXPERIMENTAL

### Reagents and materials

The following reagents and materials were used in the work:  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5.5\text{H}_2\text{O}$  (98%, *PanReac*, Spain); branched polyethyleneimine ( $M_n = 60000$ , 50% aqueous solution, *Acros Organics*, Belgium); 4-aminothiophenol (4-ATP) (97%, *Sigma-Aldrich*, USA); ethanol (99.9%, *Merck*, Germany);  $\text{AgNO}_3$  (chemically pure, *LenReaktiv*, Russia);  $\text{NaBH}_4$  (99%, *Acros Organics*, Belgium);  $\text{H}_2\text{O}_2$  (special purity grade, *Khimreaktivsnab*, Russia);  $\text{NH}_3$  (25% aqueous solution, *PanReac*, Spain);  $\text{NaOH}$  (chemically pure, *LenReaktiv*, Russia); cetyltrimethylammonium bromide (99%, *Sigma-Aldrich*, USA);  $\text{C}_6\text{H}_{12}\text{O}_6$  (chemically pure grade, *Vekton*, Russia); polyvinylpyrrolidone ( $M_w = 55000$ , *Sigma-Aldrich*, USA); deionized water (*Milli-Q*, *Millipore*, Germany) with a specific resistance of  $18 \mu\text{Ohm} \cdot \text{cm}$  at  $22^\circ\text{C}$ ; TM from polyethylene terephthalate (thickness  $19 \mu\text{m}$ , pore concentration  $2.7 \cdot 10^8 \text{ cm}^{-2}$ , pore diameter  $0.4 \mu\text{m}$ ) obtained at the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research (Dubna, Russia) according to the method presented in [18].

### SNP synthesis

Spherical SNPs were prepared using the citrate method based on the procedure described in [19]. To that end, 12.5 mL of a  $10^{-3}$  M silver nitrate solution were added dropwise to 50 mL of a  $10^{-3}$  M sodium citrate solution heated to  $95^\circ\text{C}$ . Prior to the synthesis, 1 M sodium hydroxide solution was added to the sodium citrate solution until a pH value became 9.8. The resulting mixture was maintained under constant stirring at the same temperature for 1 h.

Triangular nanoplates were prepared using the procedure described in [20]. Thus,  $10^{-2}$  M silver nitrate (0.5 mL), 1% sodium citrate solution (2.3 mL), 2% polyvinylpyrrolidone solution (0.6 mL), 3% hydrogen peroxide solution (1.2 mL), and  $2 \cdot 10^{-2}$  M sodium borohydride solution (1 mL) were successively added into 4.1 mL of water. Prior to adding sodium borohydride, the reaction mixture was heated to  $55^\circ\text{C}$ . The synthesis duration was 2 min.

Silver nanowires were synthesized by the hydrothermal method based on the procedure detailed in [21]. To that end, 0.17 g of silver nitrate was dissolved in 20 mL of water, then a 1 M aqueous ammonia solution was added to obtain silver ammine with a concentration of  $10^{-3}$  M. 2.8 mL of the resulting silver ammine solution, 1.7 mL of a  $5 \cdot 10^{-3}$  M solution of cetyltrimethylammonium bromide, and 5.6 mL of a  $10^{-3}$  M glucose solution were added to the autoclave. The reaction mixture was maintained to 120°C for 8 h.

## TM modification

The surface modification of the TMs was conducted based on the method described in [22]. The TMs were pre-washed in ethyl alcohol and water followed by immersion in a 0.1% aqueous solution of PEI and maintained on a laboratory shaker for 30 min. Following modification, the TMs were rinsed with water for 5 min.

The immobilization of spherical and triangular SNPs was conducted on PEI-modified TMs; native TMs were used for nanowires. For this purpose, 20 mL of the nanoparticle solution was filtered through the TMs in an Amicon Stirred Cells filtration cell (Millipore, Germany).

## Methods

In order to evaluate the stability of colloidal SNP solutions, the zeta potential was measured using dynamic light scattering with a Zetasizer Nano ZSP particle size analyzer (Malvern, United Kingdom).

The shape of silver nanoparticles was determined by transmission electron microscopy (TEM) using a Talos F200iS/TEM microscope (Thermo Scientific, USA). Copper TEM grids with an amorphous carbon film (SPI, USA) were used as substrates. In order to deposit the SNP, the substrate was immersed in the colloidal silver nanoparticle solution followed by drying.

The presence of SNPs on the TM surface was determined from micrographs obtained by scanning electron microscopy (SEM) using an SU 8020 scanning electron microscope (Hitachi, Japan). A 5-nm thick layer

of a platinum-palladium alloy was sputter-deposited on the samples.

The SNP size was determined using the JMicroVision 1.3.4 software<sup>1</sup> from the obtained micrographs.

The optical properties of the resulting SNPs were studied using ultraviolet (UV) and visible absorption spectroscopy on an Evolution 600 dual-beam spectrophotometer (Thermo Scientific, USA) at an optical path length of 1 cm.

The SERS effect on the resulting composites was determined using Enspectr R532 (*Spectr-M*, Russia) and Enspectr R638 (*Spectr-M*, Russia) Raman spectrometers with excitation wavelengths of 532 nm and 638 nm, respectively. Excitation was performed for 1 s in 10 repetitions. A solution of 4-ATP in ethanol was used as the test substance. 2  $\mu$ L of 4-ATP solution at a concentration of  $10^{-5}$  M were applied to the TM with immobilized SNPs, and Raman spectra were obtained after evaporation of the solvent.

## RESULTS AND DISCUSSION

The conducted synthesizes resulted in stable colloidal solutions with spherical, triangular, and nanowire-shaped nanoparticles.

The following zeta potentials were obtained for the colloidal solutions of nanoparticles:  $-51 \pm 5$  mV for spherical nanoparticles,  $-29 \pm 6$  mV for triangular nanoplates, and  $+8 \pm 1$  mV for nanowires. The citrate and borohydride methods for synthesizing nanoparticles result in a negative charge of the obtained spherical and triangular nanoparticles. Therefore, these nanoparticles were immobilized on a PEI-modified membrane with a positive surface charge. Silver nanowires had a positive zeta potential; therefore, native TM, whose surface is negatively charged due to the presence of carboxyl groups, was used for nanoparticles deposition.

The surface plasmon resonance (SPR) maxima characteristic of the SNPs (Fig. 1) were determined by absorption spectroscopy in the UV and visible regions.

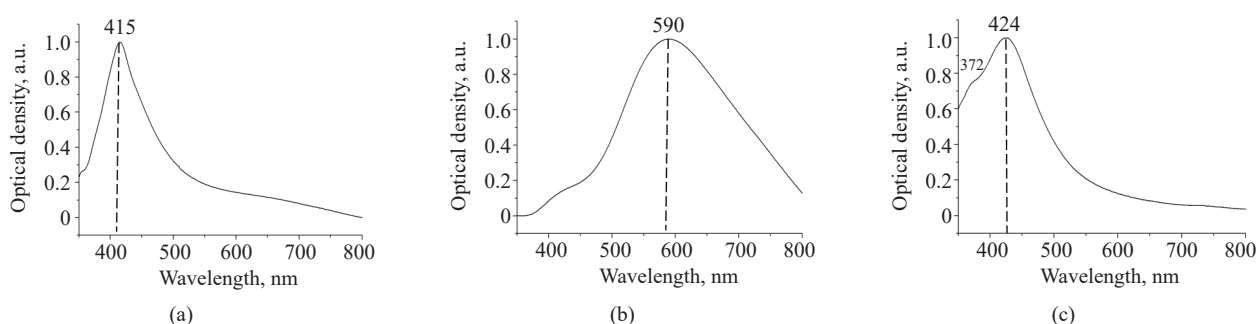


**Fig. 1.** Absorption spectra in the UV and visible regions of colloidal solutions of SNPs: (a) spherical; (b) triangular; (c) nanowires

<sup>1</sup> <https://jmicrovision.github.io/download.htm>. Accessed November 19, 2025.

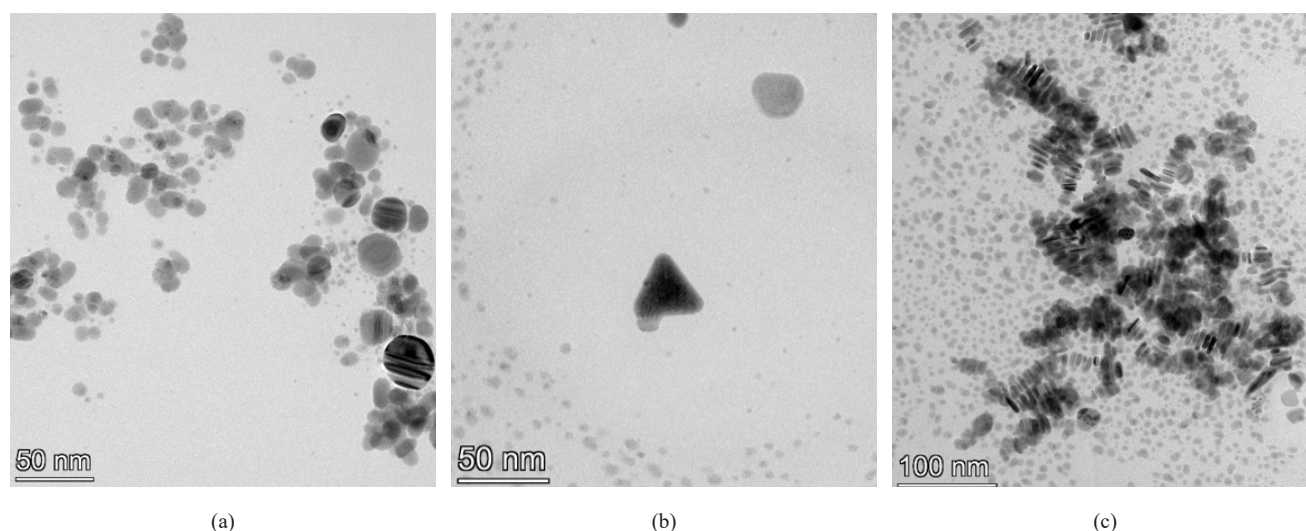


**Fig. 2.** TEM images: (a) spherical nanoparticles; (b) triangular nanoparticles; (c) stacks of triangular nanoparticles

The absorption maximum of the SPR of the nanoparticles obtained by the citrate method is located at 415 nm, which corresponds to spherical nanoparticles (Fig. 1a) [23]. The absorption spectrum of the nanoparticles obtained by the borohydride method (Fig. 1b) has an absorption maximum at 590 nm, which confirms the presence of triangular nanoparticles [24]. The absorption spectrum of the colloidal solution of silver nanowires (Fig. 1c) has a maximum at 424 nm, which corresponds to the SPR of nanowire-shaped nanoparticles [25].

The TEM micrographs (Fig. 2) clearly show the shape of spherical nanoparticles (Fig. 2a), as well as triangular nanoplates (Fig. 2b), which form characteristic stacks when dried on the TEM grids (Fig. 2c).

At the next stage, the sizes of the nanoparticles were determined. The diameter of the spherical nanoparticles ranged  $25 \pm 5$  nm, while the edge length of the triangular nanoparticles was  $38 \pm 8$  nm, and their thickness was  $4 \pm 1$  nm. The determination of silver nanowire length is a challenging task due to their multiple entanglement; their thickness was  $26 \pm 4$  nm.

SEM micrographs (Fig. 3) clearly show silver nanoparticles on the TM surface, all of which are uniformly distributed. Note that the triangular nanoparticles exhibit an admixture of spherical nanoparticles. The silver nanowires exhibit an admixture of cubic nanoparticles.

The Raman spectrum of the original TM is a spectrum of polyethylene terephthalate with the most intense peaks at  $1614\text{ cm}^{-1}$  and  $1727\text{ cm}^{-1}$  corresponding to  $\nu_{\text{CC}}$  and  $\nu_{\text{CO}}$  vibrations, respectively [26]. The Raman spectrum of 4-ATP has peaks at  $463$  ( $\delta_{\text{CC}}$ ),  $1085$  ( $\nu_{\text{CS}}$ ), and  $1592\text{ cm}^{-1}$  ( $\nu_{\text{CC}}$ ) [27]. It can be seen from Fig. 4 that when the signal is enhanced on spherical and triangular SNPs, the characteristic peaks of 4-ATP corresponding to  $\nu_{\text{CS}}$  and  $\nu_{\text{CC}}$  vibrations are preserved. At the same time, maxima also appear at  $1380$  and  $1427\text{ cm}^{-1}$ , which can be attributed to  $\nu_{\text{NN}}$  vibrations [27]. The discrepancy between the peak values of the Raman and SERS spectra of 4-ATP on spherical and triangular SNPs ranges within the instrumental error. The significant difference in 4-ATP spectrum on silver nanowires can be explained by 4-ATP sorption on silver nanowires not only by the SH group, but also by the  $\text{NH}_2$  group. Figure 3c shows that the

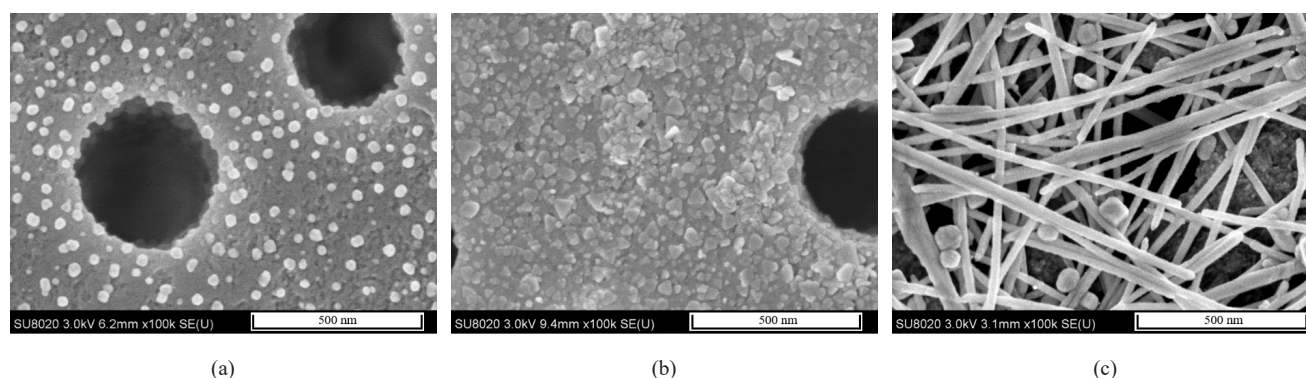


**Fig. 3.** SEM images of SNPs on the TM surface: (a) spherical nanoparticles; (b) triangular nanoparticles; (c) silver nanowires

silver nanowires are arranged to several layers and are repeatedly intertwined forming 3D sorption cavities. The peaks at 1283 and 1351  $\text{cm}^{-1}$  can be attributed to  $\nu_{\text{CN}}$  and  $\delta_{\text{CH}}$  vibrations, respectively [11, 27]. Similar differences in the spectra were observed in [11] upon 4-ATP sorption between a gold substrate and gold nanoparticles forming a sandwich structure.

Enhancement factors (EFs) of the obtained samples were calculated relative to EF of a commercial substrate manufactured by *Spektr-M* (Russia). The commercial substrate represents a silicon crystal with SNPs formed from thin silver films obtained by thermal spraying, having the known EF. For the obtained samples, EFs were calculated according to the formula:

$$K_2 = K_1 \frac{N_2}{N_1},$$

wherein  $K_1 = 7 \cdot 10^6$  is the EF on a commercial substrate;  $K_2$  is the EF on a TM with immobilized SNPs;  $N_1$  is the Raman peak intensity on a commercial substrate;  $N_2$  is the Raman peak intensity on a TM in the region of 1465  $\text{cm}^{-1}$ . The values were  $9 \cdot 10^6$  for spherical SNPs,  $1 \cdot 10^7$  for triangular SNPs, and  $4 \cdot 10^7$  for silver nanowires.

When shifting from the shape of spherical SNP to various anisotropic shapes, the EF increases. The highest EF is observed for silver nanowires. The nanowires are arranged in several layers on the TM surface. Interactions occur not only between nanowires within a single layer, but also between adjacent layers, which leads to a significant amplification of the analytical signal.

## CONCLUSIONS

In this study, we synthesized nanoparticles of various shapes, including spherical, triangular, and nanowire-shaped. The shape and zeta potential were determined for all nanoparticles. The diameter of the spherical nanoparticles was  $25 \pm 5$  nm; the edge length of the triangular nanoplates was  $38 \pm 8$  nm; and the thickness of the silver nanowires was  $26 \pm 4$  nm. The resulting nanoparticles were immobilized on TM surface followed by studying the SERS effect on the resulting composites. It was found that the EF increases upon the transition from a spherical nanoparticle shape to anisotropic

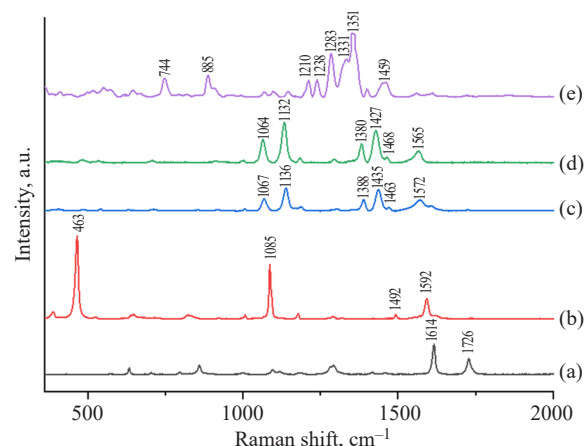


**Fig. 4.** Raman spectra of the native TM, 4-ATP, 532 nm laser (a); 4-ATP, 532 nm laser (b), and SERS spectra of 4-ATP on TM with SNPs of spherical, 532 nm laser (c), triangular, 638 nm laser (d) and nanowire, 638 nm laser (e) shapes

shapes. The highest EF value was  $4 \cdot 10^7$  for composite TM samples with silver nanowires. This renders these materials promising as substrates for sensors operating on the SERS effect.

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## Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

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Synthesis and processing of polymers  
and polymeric composites

Синтез и переработка полимеров  
и композитов на их основе

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EDN EUJEZL



RESEARCH ARTICLE

## Morphology features of biodegradable plastic–elastomer blends

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### Abstract

**Objectives.** To obtain data on the compatibility of a polymer blend based on poly-3-hydroxybutyrate and butadiene-nitrile rubber for the development of a biodegradable polymer with improved mechanical properties.

**Methods.** Film samples of biodegradable plastic–elastomer blends, using mixtures of poly-3-hydroxybutyrate and butadiene-nitrile rubber as a case study, were investigated by means of optical and scanning electron microscopy with computer-aided image analysis, differential scanning calorimetry, mathematical analysis, and Fourier transform infrared spectroscopy.

**Results.** The mixtures studied herein were found to have a heterogeneous heterophase structure. The interaction between the carbonyl group of poly-3-hydroxybutyrate and the nitrile group of acrylonitrile block of acrylonitrile butadiene-nitrile rubber is shown due to kinetic compatibility. A change in the crystalline regions of poly-3-hydroxybutyrate when it is mixed with rubber was also noted. The results of the Gibbs energy calculation of mixing confirmed the interaction of carbonyl and nitrile groups. Microscopy results show the localization of poly-3-hydroxybutyrate particles around rubber particles. The reasons for this phenomenon are discussed here.

**Conclusions.** Studies have shown a relationship between morphology and component content of the samples. The change in composition affects the structure and properties of the surface and volume. The formation of associates leads to the formation of an interface which attracts the second component. The Flory–Huggins theory, Avrami equations, and microscopic data established a complex interaction mechanism: convergence and formation of chemical bonds, rearrangement of crystalline regions, transition of spherulitic particles into lamellar particles, diffusion of rubber macromolecules, association of poly-3-hydroxybutyrate particles around the rubber, and completion of chemical bonds.

### Keywords

biopolymers, poly-3-hydroxybutyrate, butadiene-nitrile rubber, polymer compatibility, structure morphology, component compatibility

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НАУЧНАЯ СТАТЬЯ

## Особенности морфологии смесей биodeградируемый пластик–эластомер

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### Аннотация

**Цели.** Получение данных о совместимости полимерной смеси на основе поли-3-гидроксibuтирата и бутадиен-нитрильного каучука для создания биodeградируемого полимера с улучшенными механическими свойствами.

**Методы.** Методами оптической и сканирующей электронной микроскопии с применением компьютерной обработки, дифференциальной сканирующей калориметрии, математического анализа, инфракрасной Фурье-спектроскопии изучены пленочные образцы смесей биodeградируемого пластика и эластомера на примере смесей полигидроксibuтирата и бутадиен-нитрильного каучука.

**Результаты.** Установлено, что изучаемые смеси имеют гетерогенно-гетерофазную структуру. За счет кинетической совместимости проявляется взаимодействие между карбонильной группой полигидроксibuтирата и нитрильной группой блока акрилонитрила бутадиен-нитрильного каучука. Замечено изменение кристаллических областей полигидроксibuтирата при его смешении с каучуком. По результатам проведенного расчета энергии Гиббса смешения подтверждено взаимодействие карбонильных и нитрильных групп. Результатами микроскопии показана локализация частиц полигидроксibuтирата вокруг частиц каучука. Обсуждаются причины такого явления.

**Выводы.** Исследования показали связь между морфологией и содержанием компонентов в образцах. Изменение состава влияет на структуру и свойства поверхности и объема. Формирование ассоциатов приводит к образованию границы раздела, притягивающей второй компонент. По теории Флори–Хаггинса, уравнениям Аврами и микроскопическим данным выявлен сложный механизм взаимодействия: сближение и образование химических связей, перестройка кристаллических областей, переход сферолитных частиц в ламеллярные, диффузия макромолекул каучука, ассоциация частиц полигидроксibuтирата вокруг каучука и завершение химических связей.

### Ключевые слова

биополимеры, полигидроксibuтират, бутадиен-нитрильный каучук, совместимость полимеров, морфология структуры, совместимость компонентов

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## INTRODUCTION

The use of traditional materials in industry remains an important aspect of production. This is due to their proven reliability, availability, and well-studied properties, ensuring consistent product quality and optimizing costs [1]. As fossil resources naturally deplete, nonmetallic and composite structural materials have gained increasing importance [2]. At the present time, there has been rapid growth in the production of polymer composites, as well as their integration into various technical sectors, and successful displacement of traditional materials such as metals and ceramics, *inter alia* [3, 4]. The high growth rate of the polymer composite materials market is determined by their wide range of properties. They surpass those of traditional materials, as well as a versatile approach to product creation—from modeling its structure, properties, and form to selecting manufacturing technologies [5].

A disadvantage of these materials is the need for disposal and recycling, since unprocessed plastic waste harms the environment [6, 7]. The majority of plastic produced is single-use plastic. Approximately 40% of plastic produced is used in the packaging sector. The most commonly used thermoplastics for packaging are polyethylene, polyethylene terephthalate, polypropylene, and polystyrene. In 2016, they accounted for over 60% of the total plastic demand in Europe. In Russia, the main share of plastics is also used for packaging, constituting over 40% of the polymer market. This, combined with a culture of single-use, leads to two main consequences: environmental pollution and loss of a valuable resource. In the European Union, 70% of collected plastic waste is sent to landfills or incinerated. In the USA, 53% of all municipal solid wastes ends up in landfills, with plastic waste making up 13% of municipal solid waste. The situation in Russia also remains challenging. Over 3.5 mln tons of plastic waste is generated annually, of which only about 10–12% is recycled [8, 9].

The potential for recycling plastic waste remains largely untapped worldwide. The global plastic recycling rate remains extremely low—only 6% of the total plastic demand. In Russia, recycling also faces challenges such as a lack of infrastructure, low public awareness, and a high proportion of mixed waste which complicates sorting and further disposal [10, 11].

Polymer materials are known to decompose in soil over a period of 100 to 500 years, depending on their composition. When plastics enter the soil, they break down into small particles and begin releasing toxic substances into the environment, such as chlorine, styrene, formaldehyde, phenol, chloroprene, urethane, and others [12, 13]. The use of biodegradable materials could be a solution to this problem.

Biopolymers differ from conventional plastics in their ability to degrade under natural conditions through physical processes and the action of microorganisms such as bacteria and fungi. These polymers are based on biodestruction, i.e., the totality of chemical and physical processes which break down the material under the influence of microorganisms [14].

Biopolymers today account for approximately 1% of the 335 mln tons of polymers produced annually. However, as demand grows and more advanced biopolymers emerge, the market is steadily expanding [15].

When developing and creating new polymeric biodegradable materials, the issue of component compatibility arises. In order to achieve the required set of properties, the problem of stiffness in biodegradable plastics needs to be addressed. The addition of an elastomer is a solution, but then another problem arises. This consists of thermodynamic incompatibility between poly-3-hydroxybutyrate (P3HB) and butadiene-nitrile rubber, due to differences in their solubility parameters, polarity, and macromolecular structure. Thermodynamic incompatibility leads to the formation of a multiphase morphology which can have both negative and positive effects on the blend's properties. In this context, the morphology of such systems becomes of particular interest.

This work is devoted to the study of morphology in a biodegradable plastic–elastomer blend.

## MATERIALS AND METHODS

P3HB, produced by microbial synthesis, was selected from the wide variety of bioresorbable polyhydroxyalkanoates. Due to its biosynthetic origin, P3HB is considered to be one of the safest polyesters of fatty acids. It is a fully biodegradable plastic, resistant to ultraviolet radiation with a number of advantages over others: high biocompatibility, stable properties, and controlled biodegradation across a wide temperature range. Although this polymer is stable in an aqueous environment, it is biodegradable in seawater, soil, composting environments, and waste processing facilities. In compost with 85% humidity and temperatures of 20–60°C, it decomposes into water and carbon dioxide within 7–10 weeks [16–18].

However, films made from P3HB are extremely rigid and brittle which are disadvantages for their use [19]. In order to increase elasticity and, consequently, improve physic-mechanical characteristics, P3HB is blended with butadiene-nitrile synthetic rubber BNKS-28AMN. The main properties of these materials are presented in Tables 1 and 2.

**Table 1.** Main characteristics of P3HB

| Characteristics                                                    | Indicator |
|--------------------------------------------------------------------|-----------|
| Particle size, $\mu\text{m}$                                       | 40        |
| Melt flow rate, g/10 min ( $T = 185^\circ\text{C}$ , 2.16 kg load) | 3.2–3.6   |
| Molecular weight (viscosity average)                               | 250000    |
| Density, $\text{g}/\text{cm}^3$                                    | 1.25      |
| Tensile breaking stress, MPa, no less                              | 35–40     |
| Relative elongation at break, % at least                           | 5–7       |
| Glass transition temperature, $^\circ\text{C}$                     | 5–10      |
| Melting temperature, $^\circ\text{C}$                              | 173–180   |
| Temperature of thermal destruction onset, $^\circ\text{C}$         | 150       |
| Crystallinity level, %                                             | 65–80     |

**Table 2.** Main characteristics of BNKS-28AMN

| Indicator                                                                          | BNKS-28AMN 2nd group | Testing method                           |
|------------------------------------------------------------------------------------|----------------------|------------------------------------------|
| Mooney viscosity (1+4) $100^\circ\text{C}$ , a.u.                                  | 61–70                | Technical Specification TU 38.30313-2006 |
| Variation of Mooney toughness within the MB batch (1+4) $100^\circ\text{C}$ , a.u. | $\leq 8$             | Technical Specification TU 38.30313-2006 |
| Mass fraction of bound acrylic acid nitrile, %                                     | 27–30                | Technical Specification TU 38.30313-2006 |
| Weight loss during drying, %                                                       | $\leq 0.8$           | Technical Specification TU 38.30313-2006 |
| Mass fraction of ash, %                                                            | $\leq 1.0$           | Technical Specification TU 38.30313-2006 |
| Methyl ethyl ketone solubility, %                                                  | $\geq 95$            | Technical Specification TU 38.30313-2006 |
| Antioxidant type                                                                   | Nonstaining          | –                                        |
| Mass fraction of agidol-2 antioxidant, %                                           | 0.5–1.2              | Technical Specification TU 38.30313-2006 |

The polymer blends under study, consisting of P3HB (*Biopolymer*, Germany) and BNKS-28AMN (*Krasnoyarsk Synthetic Rubber Plant*, Russia), were prepared using a solution-based technology. The films were formed by mechanically mixing 2% solutions of the components at  $80^\circ\text{C}$ .

The interaction of the components was studied using Fourier transform infrared (FTIR) spectroscopy on a SIMEX FT-801 IR spectrometer (*SIMEX*, Russia) equipped with a diamond attenuated total reflectance accessory.

The feasibility of mixing and component compatibility was assessed based on the results of calculating the enthalpy, entropy, and Gibbs free energy of mixing according to the Flory–Huggins theory.

Morphology analysis was performed using microphotographs obtained with a Levenhuk MedPro 600 FLUO microscope (*Levenhuk*, Russia) equipped with an Altami UCMOC2000KPB digital eyepiece camera (*Altami*, Russia). Additional morphology visualization was carried out using scanning electron microscopy (SEM) by means of a

MIRA 3 LMH microscope (*TESCAN*, Czech Republic) with a Schottky cathode. The surface of the film samples for SEM was sputter-coated with a gold layer approximately 10 nm thick using an S150A Sputter Coater (*Edwards*, United Kingdom). The calculation and determination of crystalline region characteristics were performed using Avrami equations in OriginPro 8 software, based on data from differential scanning calorimetry (DSC) at a scanning rate of 8° per minute, obtained using a DSM-2M microcalorimeter (Russia).

## RESULTS AND DISCUSSION

In order to form a unified system from thermodynamically incompatible polymers, the physical, physicochemical, or purely chemical interaction need to be established. The results of the component compatibility calculation are presented in Tables 3 and 4.

**Table 3.** Gibbs energy  $\Delta G_{\text{mix}}$  of mixing P3HB with acrylonitrile

| Mixture composition, % |               | $\Delta G_{\text{mix}}$ , J/mol |
|------------------------|---------------|---------------------------------|
| P3HB                   | Acrylonitrile |                                 |
| 10                     | 90            | −0.006                          |
| 20                     | 80            | −0.011                          |
| 30                     | 70            | −0.014                          |
| 40                     | 60            | −0.017                          |
| 50                     | 50            | −0.018                          |
| 60                     | 40            | −0.019                          |
| 70                     | 30            | −0.018                          |
| 80                     | 20            | −0.015                          |
| 90                     | 10            | −0.011                          |

Using the Flory–Huggins theory, it was shown that  $\Delta G_{\text{mix}} < 0$ , when attempting to combine P3HB structures and blocks of acrylic acid nitrile.

However, when calculating for the complete molecules of the components, the calculation results ( $\Delta G_{\text{mix}} > 0$ ) confirm the thermodynamic incompatibility of these polymers.

Thus, for P3HB and BNKS, the interaction can be expressed as the formation of bonds between carbonyl and nitrile groups. According to FTIR spectroscopy data, blending these components leads to intermolecular interactions involving the nitrile groups of the rubber and the carbonyl groups of P3HB with the formation of crosslinks. This is evidenced by the intensity of the peak at 2250 cm<sup>−1</sup>, absent in the spectra of the individual components.

The results of FTIR spectroscopy (Fig. 1a) show that the surface spectra contain a band at ~967 cm<sup>−1</sup>,

**Table 4.** Gibbs energy  $\Delta G_{\text{mix}}$  of mixing P3HB with BNKS-28AMN

| Mixture composition, % |      | $\Delta G_{\text{mix}}$ , J/mol |
|------------------------|------|---------------------------------|
| P3HB                   | BNKS |                                 |
| 10                     | 90   | 8585.964                        |
| 20                     | 80   | 15263.937                       |
| 30                     | 70   | 20033.918                       |
| 40                     | 60   | 22895.907                       |
| 50                     | 50   | 23849.903                       |
| 60                     | 40   | 22895.907                       |
| 70                     | 30   | 20033.918                       |
| 80                     | 20   | 15263.937                       |
| 90                     | 10   | 8585.964                        |

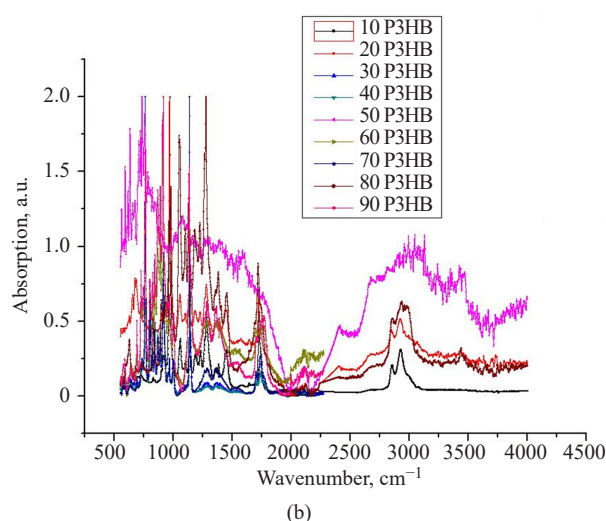
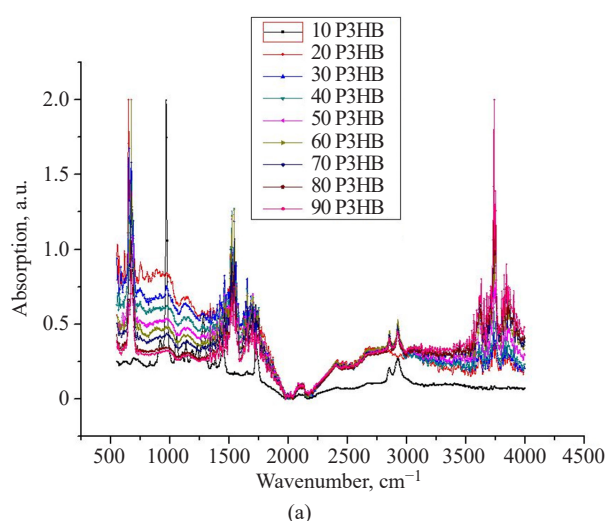


**Fig. 1.** Infrared spectra of the surfaces (a) and volumes (b) of the samples

corresponding to trans-structures in BNKS, as well as a band at  $\sim 2250\text{ cm}^{-1}$ , indicating interaction.

The presence of the  $2250\text{ cm}^{-1}$  band characterizes, on the one hand, the nitrile group of the BNKS-28 rubber, and on the other hand, the occurrence of the reaction shown in Fig. 2.

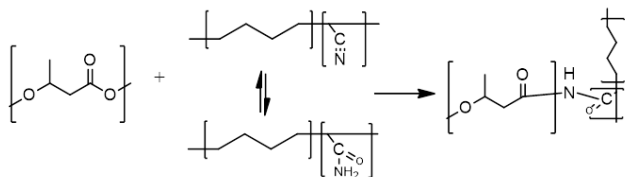


**Fig. 2.** Scheme of chemical interaction between P3HB and BNKS through amide bond formation

In addition to the chemical process, the formation of a compound based on physical interaction is possible (Fig. 3).

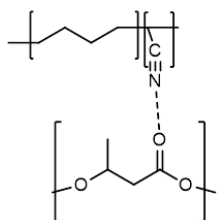


**Fig. 3.** Scheme of compound formation via physical bonds

In the bulk material (Fig. 1b), the  $2250\text{ cm}^{-1}$  band practically disappears, the intensity of the  $\sim 967\text{ cm}^{-1}$  band decreases, and a series of bands appear in the region of  $\sim 1500\text{--}1580\text{ cm}^{-1}$ , indicating double bonds.

It can thus be concluded that BNKS is the matrix across the entire range of component content, and the interaction between components is stronger on the surface of the samples.

Such interaction should influence the processes of crystallization and melting. Based on this, the parameters of the isothermal crystallization process were calculated using the Avrami equations (Table 5).

The data obtained shows that a transition from spherulitic to lamellar structures occurs, and such structures distribute themselves around the bound rubber chains.

The localization of P3HB particles around rubber chains on the surface can be visualized due to the charging of P3HB particles under an electron beam, and this is confirmed by the results of scanning electron microscopy (Fig. 4).

Microscopy results show that a portion of the P3HB disperses onto the surface. Depending on the composition and strength of component interaction, the presence of P3HB on the surface varies. Analysis of SEM micrographs reveals the localization and aggregation of P3HB particles around the particles of the rubber matrix. Based on the results obtained, and considering the concept of a possible component mechanism, the following conclusions can be drawn:

- When rubber is introduced into P3HB, two modifications of crystallites form during the mutual diffusion of the components which interact differently with the rubber.
- A portion of the crystallites clearly remains in the bulk of the material, while another portion diffuses to the surface. Upon interacting with the rubber, the latter undergoes a transformation from spherulitic to lamellar structures and localizes around the rubber macromolecules bound to them.

Similar processes occur both in the bulk and on the surface. As shown in micrographs taken in transmitted and reflected light (Figs. 5 and 6), the formation of associates takes place in the samples of the studied compositions, occurring primarily on the sample surfaces.

**Table 5.** Parameters of the crystallization process

| Sample    | Temperature, °C | Parameters of isothermal crystallization |                       |       |                      |                  |
|-----------|-----------------|------------------------------------------|-----------------------|-------|----------------------|------------------|
|           |                 | $n_1$                                    | $k_1$                 | $n_2$ | $k_2$                | $\tau_{0.5}$ , s |
| 100% P3HB | 105             | 3.66                                     | $1.10 \cdot 10^{-10}$ | 2.25  | $1.10 \cdot 10^{-6}$ | 400              |
| 90% P3HB  |                 | 2.33                                     | $3.16 \cdot 10^{-7}$  | 2.0   | $1.10 \cdot 10^{-5}$ | 285              |
| 80% P3HB  |                 | 2.56                                     | $5.10 \cdot 10^{-7}$  | 1.25  | $1.10 \cdot 10^{-3}$ | 190/380          |
| 70% P3HB  |                 | 3.3                                      | $4.10 \cdot 10^{-9}$  | 1.4   | $1.58 \cdot 10^{-4}$ | 165/240          |

*Note:*  $n_1$  is the Avrami exponent for the primary crystallization stage;  $k_1$  is the rate constant for isothermal crystallization for the primary stage;  $n_2$  is the Avrami exponent for the secondary crystallization stage;  $k_2$  is the rate constant for isothermal crystallization for the secondary stage;  $\tau_{0.5}$  is a half-crystallization period.

The computer processing of micrographs allowed particle sizes to be assessed in the bulk and on the surface of the samples (Figs. 7 and 8).

As can be seen from the dependencies presented here, there are more particles on the surface of the samples, and their size distribution is broader. A shift in the size maximum from 70% to 80% P3HB is also observed.

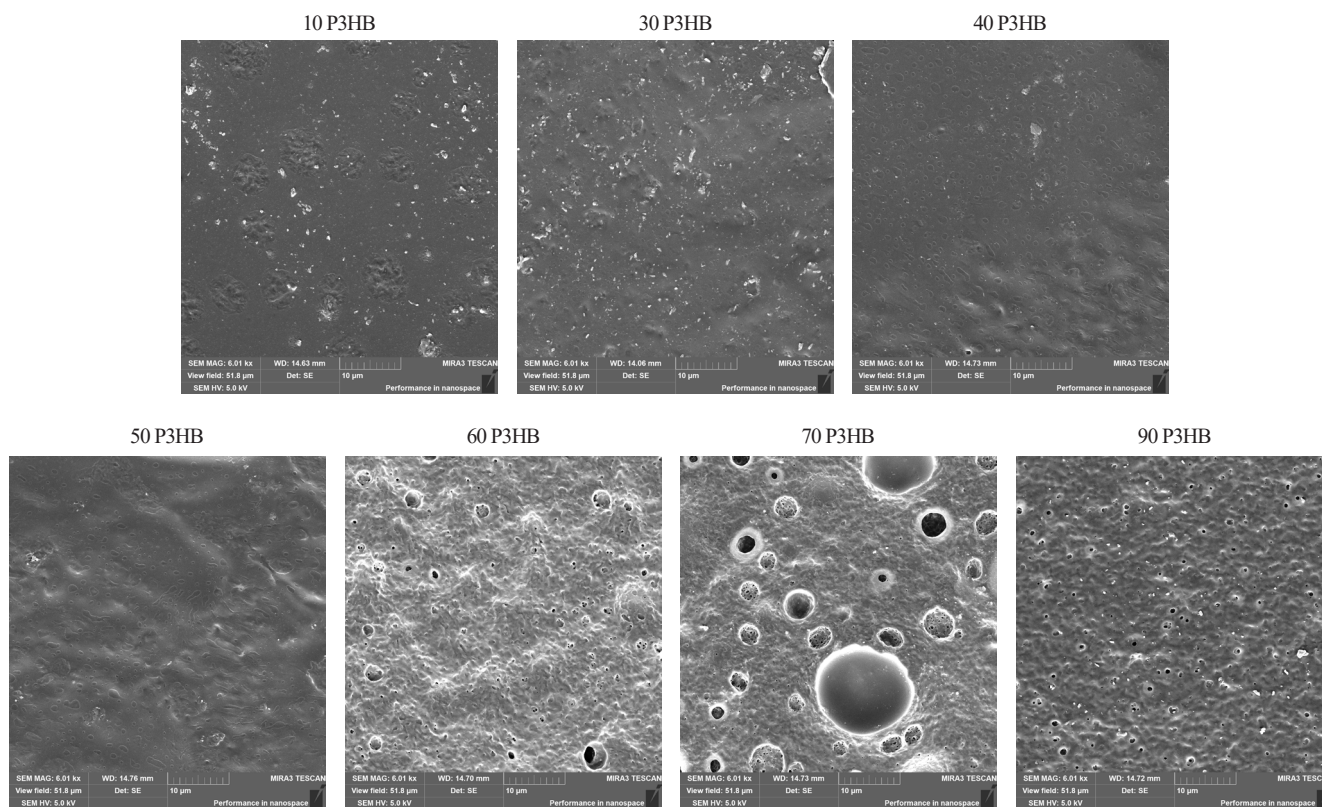


**Fig. 4.** SEM microphotographs

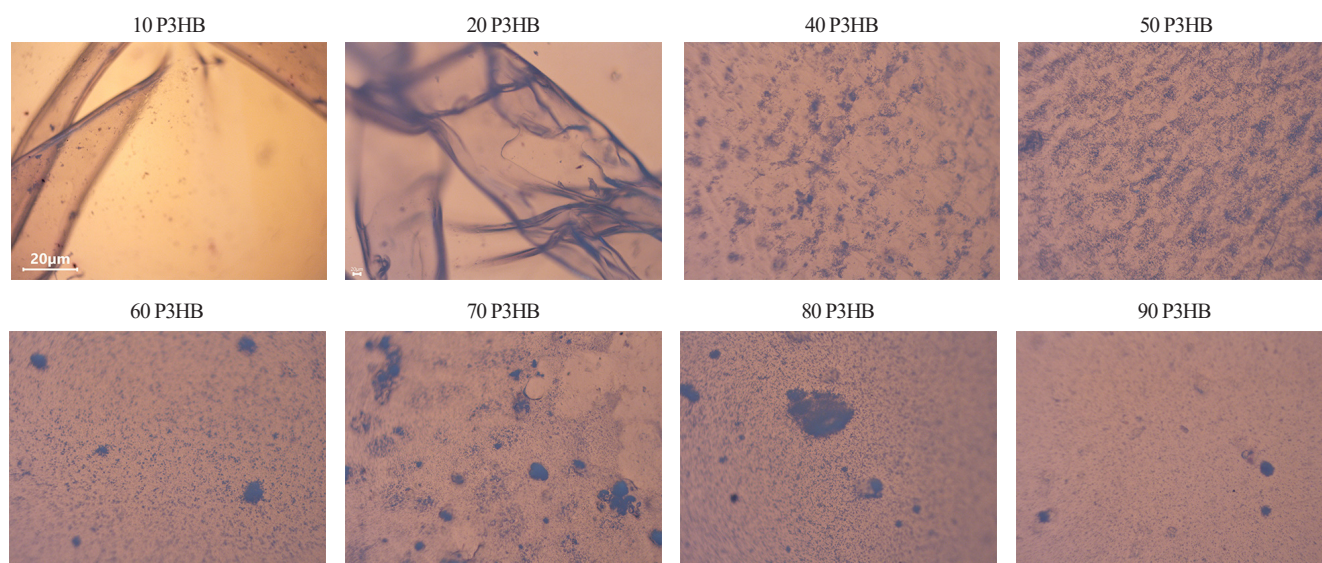


**Fig. 5.** Microphotographs of sample volume (transmitted light, magnification 10×)

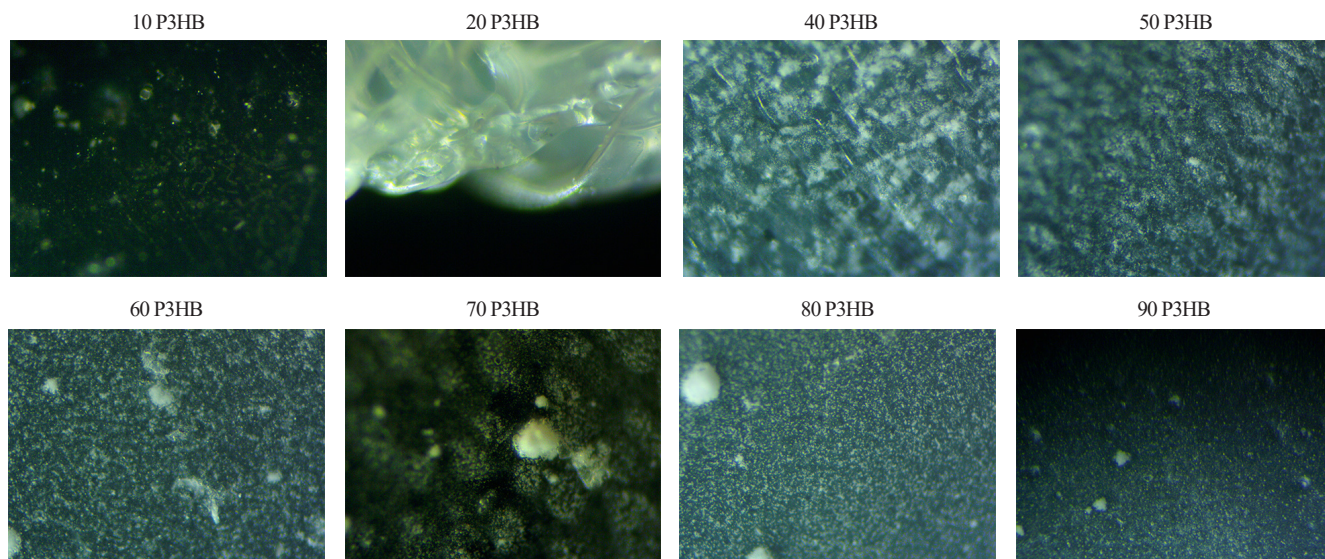


**Fig. 6.** Microphotographs of sample surface (reflected light, magnification 10×)

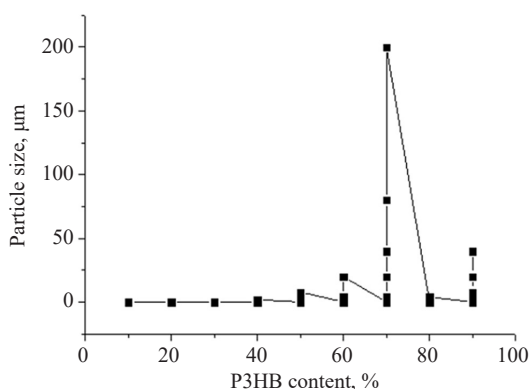


**Fig. 7.** Estimation of particle sizes in the sample volume

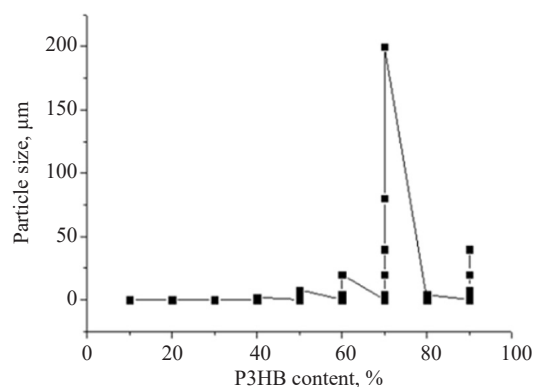


**Fig. 8.** Estimation of particle sizes on the surface of samples

## CONCLUSIONS

The studies conducted herein reveal a relationship between morphology and component content in the samples under investigation. The influence of composition changes on the structure and properties of both the surface and the bulk was also demonstrated. It was shown that the formation of associates leads to the creation of an interface that attracts the second component.

Based on calculations using the Flory–Huggins theory, the particle geometry criterion  $n_1$  of the Avrami equations, and the results of optical and scanning electron microscopy, the interaction identified here manifests as quite a complex mechanism. This mechanism sequentially consists of:

- approach of acrylic acid nitrile blocks to P3HB spherulites during heating, initiation of chemical bond formation;
- reorganization of crystalline regions in P3HB upon the introduction of rubber;

- transition of spherulitic particles into lamellar ones;
- diffusion of rubber macromolecules bound to the unfolded spherulites to the surface;
- association of P3HB particles and their localization around rubber particles;
- completion of chemical bond formation.

## Authors' contributions

**N.D. Blinov**—obtaining samples for the study, writing the text of the article.

**L.S. Shibryaeva**—research idea, methodological support, general management.

**M.O. Kulpina**—carrying out the study of the crystallization process.

**A.N. Neretina**—carrying out electron microscopy and its interpretation.

**V.E. Slavkina**—literature review, editing the article.

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## RESEARCH ARTICLE

# Surface and bulk thermodynamic factors of $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Me}_x\text{O}_{3-\delta}$ (Me = Ta, W) oxides

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## Abstract

**Objectives.** In this work, we consider the relationship between the tracer ( $k^*$ ) and chemical ( $k^\delta$ ) oxygen exchange coefficients for  $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Me}_x\text{O}_{3-\delta}$  (Me = Ta, W) oxides. The aim is to analyze the experimental dependencies of the chemical ( $k^\delta$ ) and tracer ( $k^*$ ) coefficients of oxygen exchange, evaluate the surface thermodynamic factor  $w_0|_{x=\pm L}$ , and compare its value with the bulk thermodynamic factor  $w_0|_{x=0}$  determined from the dependence of oxygen content in oxides on the temperature and partial pressure of oxygen. Possible reasons for the discrepancy between these two thermodynamic factors are discussed.

**Methods.** The oxygen exchange kinetics between the gas phase and the surface of oxide materials under nonequilibrium conditions was studied using the method of oxygen pressure relaxation. The surface thermodynamic factor was calculated based on data obtained under both equilibrium and nonequilibrium conditions.

**Results.** Comparison of the tracer ( $k^*$ ) and chemical ( $k^\delta$ ) oxygen exchange coefficients allowed the  $w_0|_{x=\pm L}$  surface thermodynamic factor to be estimated by the  $k^\delta = k^* w_0|_{x=\pm L}$  equation.

**Conclusions.** The surface thermodynamic factor was found to differ from the bulk thermodynamic factor of the oxide material,

$w_0 = \frac{1}{2} \frac{\partial \ln(p_{\text{O}_2})}{\partial \ln(3-\delta)}$ , which can be calculated from the dependence of oxygen content in oxides on the temperature and partial pressure of oxygen. This difference can be explained by the difference in the defect structure of the surface layers of oxide materials.

## Keywords

surface oxygen exchange, oxygen diffusion, BSCF, oxygen pressure relaxation, mixed ionic-electronic conduction membrane, thermodynamic factor

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НАУЧНАЯ СТАТЬЯ

# Объемный и поверхностный термодинамические факторы оксидов $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Me}_x\text{O}_{3-\delta}$ (Me = Ta, W)

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## Аннотация

**Цели.** Работа посвящена анализу взаимосвязи изотопного  $k^*$  и химического  $k^\delta$  коэффициентов обмена кислородом для оксидов  $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Me}_x\text{O}_{3-\delta}$  (Me = Ta, W). Целью работы является анализ экспериментальных зависимостей химического и изотопного коэффициентов обмена кислорода, оценка поверхностного термодинамического фактора  $w_0|_{x=\pm L}$  и сравнение его с объемным термодинамическим фактором  $w_0|_{x=0}$ , определенным из зависимости содержания кислорода в оксидах от температуры и парциального давления кислорода. В статье обсуждаются возможные причины несовпадения двух термодинамических факторов.

**Методы.** Изучение кинетики обмена кислородом газовой фазы с поверхностью оксидных материалов в неравновесных условиях проведено методом релаксации давления кислорода. Расчет поверхностного термодинамического фактора проведен на основе данных, полученных в равновесных и неравновесных условиях.

**Результаты.** Сравнение изотопного  $k^*$  и химического  $k^\delta$  коэффициентов обмена кислорода позволило оценить поверхностный термодинамический фактор  $w_0|_{x=\pm L}$  через уравнение  $k^\delta = k^* w_0|_{x=\pm L}$ .

**Выводы.** Было обнаружено, что поверхностный термодинамический фактор отличается от термодинамического фактора, относящегося к объему оксидного материала  $w_0 = \frac{1}{2} \frac{\partial \ln(p_{\text{O}_2})}{\partial \ln(3-\delta)}$ , который может быть рассчитан из зависимостей содержания кислорода в оксидах от температуры и парциального давления кислорода. Такое различие было объяснено различием в дефектной структуре поверхностных слоев оксидных материалов.

## Ключевые слова

поверхностный обмен кислорода, диффузия кислорода, BSCF, релаксация давления кислорода, мембрана со смешанной ионно-электронной проводимостью, термодинамический фактор

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## INTRODUCTION

Mixed oxygen-electronic conduction (MOEC) oxides have found wide application in high-temperature electrochemical devices, such as solid oxide fuel cells and electrolyzers, membranes for selective oxygen separation, and catalytic membrane reactors [1–3]. Oxygen transport membrane (OTM) technology, the most promising application of MOEC oxides, is considered an accessible and affordable method for producing high-purity (over 99%) oxygen [4, 5], as well as a basis for partial and selective catalytic oxidation of hydrocarbons [6, 7]. The main challenge in developing such membranes is to identify a suitable oxide material that could meet the requirements of mechanical strength, chemical resistance, and high oxygen flux through the membrane.

The oxygen flux is influenced by both the mobility of oxygen ions within the OTM and the rate of oxygen reduction/oxidation reactions on both sides of the membrane [8–13]. At a given temperature  $T$  and partial pressure of oxygen  $p_{\text{O}_2}$ , the oxygen flux through the membrane can be limited either by a surface reaction or by oxygen diffusion, which depends on the membrane thickness. In order to separate the contribution of each process to the total oxygen flux, Bouwmeester *et al.* [8] derived an expression for calculating the characteristic

thickness  $L_c$ , which is defined as  $L_c = \frac{D_0}{k_s}$ , wherein

$D_0$  is the oxygen self-diffusion coefficient, and  $k_s$  is the surface oxygen exchange coefficient. It should be noted that this formula for  $L_c$  is valid for oxides with predominantly electronic conduction. Under given experimental conditions ( $T$  and  $p_{\text{O}_2}$ ), the total oxygen

flux through a membrane with a thickness exceeding  $L_c$  is determined by the rate of oxygen diffusion in the bulk. In this case, the oxygen flux through the membrane is proportional to the ambipolar electrical conductivity  $\sigma_{\text{amb}}$  in accordance with Wagner's approach [14–16] and is expressed by the formula

$$J_{\text{O}_2} = -\frac{RT}{16F^2L} \int_{\ln(p'_{\text{O}_2})}^{\ln(p''_{\text{O}_2})} \sigma_{\text{amb}} d \ln(p_{\text{O}_2}), \quad (1)$$

$$\sigma_{\text{amb}} = \frac{\sigma_{\text{ion}} \sigma_{\text{el}}}{\sigma_{\text{ion}} + \sigma_{\text{el}}}, \quad (2)$$

wherein  $R$  is the universal gas constant;  $T$  is the absolute temperature;  $F$  is the Faraday constant;  $L$  is the membrane thickness;  $p_{\text{O}_2}$  is the partial pressure of oxygen;  $\sigma_{\text{ion}}$  is the oxygen-ionic conductivity;  $\sigma_{\text{el}}$  is the electronic conductivity; and  $p'_{\text{O}_2}$  and  $p''_{\text{O}_2}$  are the partial pressures of oxygen on the one and other sides of the membrane, respectively.

For oxides with predominantly electronic conductivity, oxygen ion diffusion is the limiting factor in membrane performance. Conversely, for membranes thinner than  $L_c$ , the oxygen flux is primarily determined by oxygen exchange reactions on the surface. At a sufficiently low gradient of the oxygen chemical potential on the surface, the reaction rate is proportional to the difference between the oxygen concentration on the surface at a given time and the equilibrium oxygen concentration, and the oxygen exchange rate constant is the proportionality constant. Consequently, both kinetic parameters—the oxygen diffusion coefficient  $D_0$  and the surface exchange coefficient  $k_s$ —can serve as criteria for selecting an oxide material for OTMs (Fig. 1).

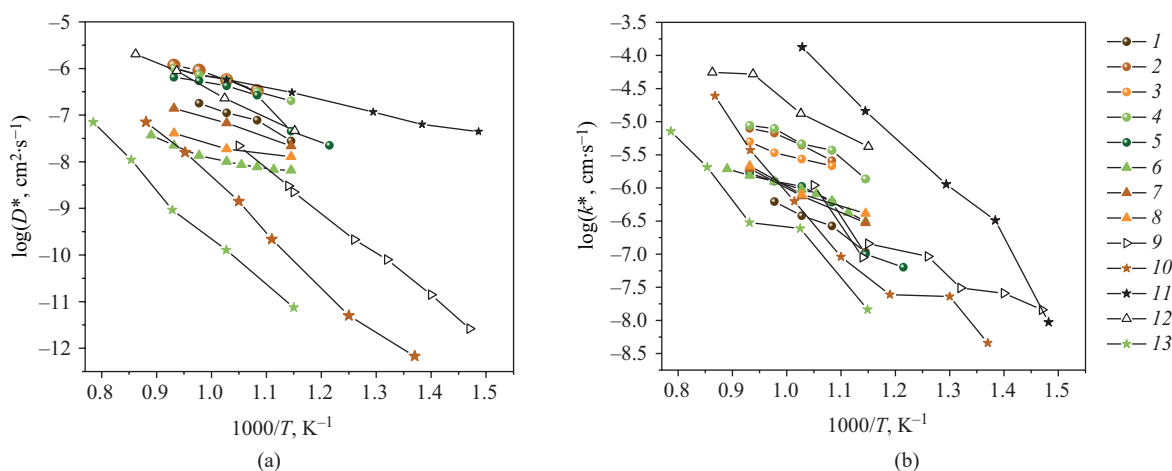


**Fig. 1.** Temperature dependencies of the (a) tracer oxygen diffusion coefficient  $D^*$  and (b) tracer oxygen exchange coefficient  $k^*$  of MOEC oxides. Lines are shown for perception convenience: (1)  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.725}\text{Fe}_{0.125}\text{Ta}_{0.15}\text{O}_{3-\delta}$  [17], (2)  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.78}\text{Fe}_{0.2}\text{W}_{0.02}\text{O}_{3-\delta}$  [17], (3)  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.775}\text{Fe}_{0.175}\text{Nb}_{0.05}\text{O}_{3-\delta}$  [17], (4)  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.775}\text{Fe}_{0.175}\text{Nb}_{0.05}\text{O}_{3-\delta}$  [17], (5)  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  [18], (6)  $\text{GdBaCo}_2\text{O}_{6-\delta}$  [19], (7)  $\text{PrBaCo}_2\text{O}_{6-\delta}$  [19], (8)  $\text{SmBaCo}_2\text{O}_{6-\delta}$  [19], (9)  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$  [20], (10)  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  [21], (11)  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  [22], (12)  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  [23], (13)  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  [24]

It can be seen from Fig. 1 that the  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  barium strontium cobaltite ferrite (BSCF) oxide exhibits the highest values of surface oxygen exchange and oxygen diffusion coefficients among oxides of various compositions. Indeed, BSCF oxides have attracted attention due to their exceptional oxygen ion transport rate at elevated temperatures. BSCF oxides possess a large number of mobile oxygen vacancies [18, 22, 25–32] in their highly symmetric perovskite lattice, which ensures a high oxygen flux over a wide temperature range.

Currently, the oxygen diffusion coefficient  $D_0$  and the surface exchange coefficient  $k_s$  can be estimated using two fundamentally different experimental techniques, including tracer oxygen exchange and relaxation methods. Tracer oxygen exchange methods can be carried out under adsorption–desorption equilibrium conditions. In this case, the  $^{18}\text{O}$  tracer concentration gradient between the gas phase and the solid phase acts as a driving force behind the gas-phase composition equilibration process, while the ambient oxygen pressure and, consequently, oxygen content in the oxide material remain constant.

The fundamental condition of adsorption–desorption equilibrium, which is inherent in tracer methods, is not met when using relaxation methods. This leads to a difference in oxygen content between the gas phase and the bulk of the oxide material. During sample equilibration with the environment, the oxygen content in the bulk of the oxide material, as well as parameters related to its content in the sample (mass, electrical conductivity, or oxygen pressure around the oxide), changes to a value corresponding to the equilibrium state. The chemical oxygen diffusion coefficient  $D_0^\delta$  and the chemical oxygen exchange coefficient  $k^\delta$ , which are found by relaxation methods, are related to the tracer oxygen diffusion coefficient  $D_0^*$  and the tracer oxygen exchange coefficient  $k^*$ , which are determined by tracer oxygen exchange methods, through the thermodynamic factor  $w_0$  [33] under the condition that the oxide be predominantly an electronic conductor and the correlation effect be negligible:

$$k^\delta = k^* w_0|_{x=\pm L}, \quad (3)$$

$$D_0^\delta = D_0^* w_0|_{x=0}, \quad (4)$$

wherein

$$w_0 = \frac{1}{2} \frac{\partial \ln(p_{\text{O}_2})}{\partial \ln(3-\delta)}. \quad (5)$$

The thermodynamic factor reflects the oxygen capacity of the oxide system and is related to the concentration of oxygen vacancies; therefore, it characterizes the

response of the oxide system to changes in the partial pressure of oxygen. From general considerations, the bulk thermodynamic factor  $w_0|_{x=0}$  and the surface thermodynamic factor  $w_0|_{x=\pm L}$  are expected to have different values. This is related to the different structure of defects in the bulk and on the surface, which has been observed for various oxide materials [17, 19, 23, 34–36]. While the bulk thermodynamic factor  $w_0|_{x=0}$  can be estimated directly from the dependence of oxygen content in the oxide on the partial pressure of oxygen, the same approach is difficult to apply to the surface thermodynamic factor  $w_0|_{x=\pm L}$ . Instead, the latter can be calculated directly using Eq. (3) provided that both kinetic constants are known.

In this work, we aim to analyze experimental dependencies of the chemical ( $k_s$ ) and tracer ( $k^*$ ) oxygen exchange coefficients, estimate the surface thermodynamic factor  $w_0|_{x=\pm L}$ , and compare its value with the bulk thermodynamic factor  $w_0|_{x=0}$  determined from the dependencies of oxygen content in oxides on temperature and partial pressure of oxygen. Further, we discuss possible reasons for the discrepancy between these two thermodynamic factors.

## EXPERIMENTAL

### Samples

The research objects in this work were  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF),  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.725}\text{Fe}_{0.125}\text{Ta}_{0.15}\text{O}_{3-\delta}$  (BSCFTa15), and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.78}\text{Fe}_{0.2}\text{W}_{0.02}\text{O}_{3-\delta}$  (BSCFW2) oxides. All oxides were synthesized by the solid-phase method [37].  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , W, and Ta with a purity of at least 99.9% (*RusKhim*, Russia) were used as initial reagents. The synthesized samples were then pressed into cylindrical tablets followed by annealing in air at 1300°C for 7 h.

All the studied oxides were characterized in detail in our previous work [17]. The crystal structure of the synthesized oxides was examined using a Rigaku D/MAX-2200VL/PC diffractometer (*Rigaku*, Japan). According to X-ray powder diffraction analysis, the samples were single-phase and exhibited a cubic structure (space group  $Pm\bar{3}m$ ). The surface morphology and elemental composition were investigated by scanning electron microscopy using a MIRA 3 LMU microscope (*TESCAN*, Czech Republic). Analysis of backscattered electron images revealed that all oxides were homogeneous in the bulk and had no additional phases different in terms of chemical composition.

### Oxygen pressure relaxation

The kinetics of oxygen exchange was studied using the method of oxygen pressure relaxation. This method

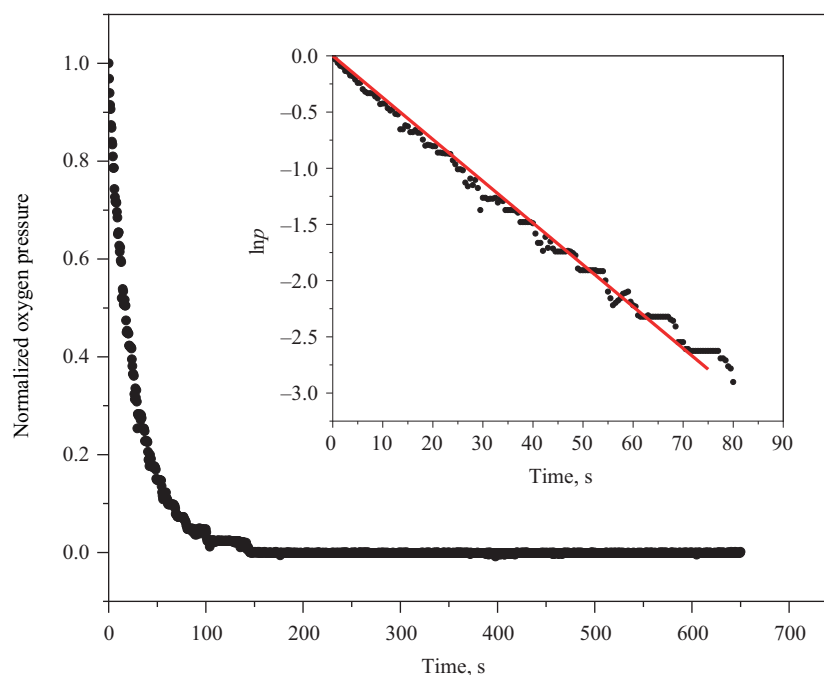


**Fig. 2.** Time dependence of normalized oxygen pressure  $p$  during equilibration from 1.33 to 3.06 mbar at 750°C. The inset shows the same dependence in semilogarithmic coordinates [38]

consists in a stepwise change in oxygen pressure above an oxide sample in a closed space of known volume, followed by recording the relaxation curve of oxygen pressure. Figure 2 presents a typical oxygen pressure relaxation curve corresponding to a step from 1.33 to 3.06 mbar at a temperature of 750°C. The experimental setup and experimental conditions were described in detail earlier [38].

Similar relaxation curves were obtained for other oxygen pressure jumps over the temperature range of 600–800°C and at oxygen pressures of 1–35 mbar. The equilibration process was carried out in both oxidation and reduction directions at a temperature of 700°C and a final pressure of 7 mbar. No statistically significant differences were found in the recorded oxidation and reduction relaxation curves.

In the corresponding coordinates, the time dependence of the natural logarithm of the normalized oxygen pressure  $p$  is linear (Fig. 2, inset), and any deviation from linearity is due to slow oxygen diffusion in the bulk of the oxide. Using the data obtained from the tracer oxygen exchange experiment in previous studies [17, 18], the characteristic thicknesses of the BSCF, BSCFTa15, and BSCFW2 oxides can be calculated to be 0.4, 0.3, and 0.16 cm, respectively (at 700°C and 6.5 mbar). Since the thicknesses of the oxide samples in this study did not exceed the corresponding characteristic thicknesses (less than 0.08 cm), it can be assumed that oxygen exchange during equilibration is governed primarily by the surface oxygen exchange

reaction. This assumption is confirmed by the linearity of the time dependence of the normalized oxygen pressure in semilogarithmic coordinates (Fig. 2). From the obtained linear time dependencies, the chemical oxygen exchange coefficient  $k^\delta$  can be calculated.

## RESULTS AND DISCUSSION

The calculated values of the chemical oxygen exchange coefficients  $k^\delta$ , as well as their temperature and pressure dependencies, are available in the literature [38] (Fig. 3). It was shown that the absolute values of chemical oxygen exchange coefficients  $k^\delta$ , as well as exponents  $n$  in the pressure dependencies  $k^\delta \sim p_{\text{O}_2}^n$  for the BSCF and BSCFTa15 oxides ( $n \approx 0.5$ ), differ from those for BSCFW2 ( $n \approx 0.25$ ).

The observed differences between the values of exponents  $n$  of pressure dependencies for the BSCF and BSCFTa15 oxides ( $n \approx 0.5$ ) and the BSCFW2 oxide ( $n \approx 0.25$ ) were explained within the framework of Fleig's *et al.* theory [39]. During pressure relaxation at the onset of oxygen exchange, the degree of surface coverage by the dominant type of ionized oxygen species changes; therefore, it is assumed that the rate of oxygen exchange during oxygen pressure equalization is directly proportional to the degree of surface coverage by ionized oxygen species. In this case, the dependence of oxygen exchange rate  $r^\delta$  during oxygen pressure equalization on  $p_{\text{O}_2}$  will be directly proportional to the dependence  $[\theta_j] = f(p_{\text{O}_2})$  of the degree  $[\theta_j]$  of surface coverage

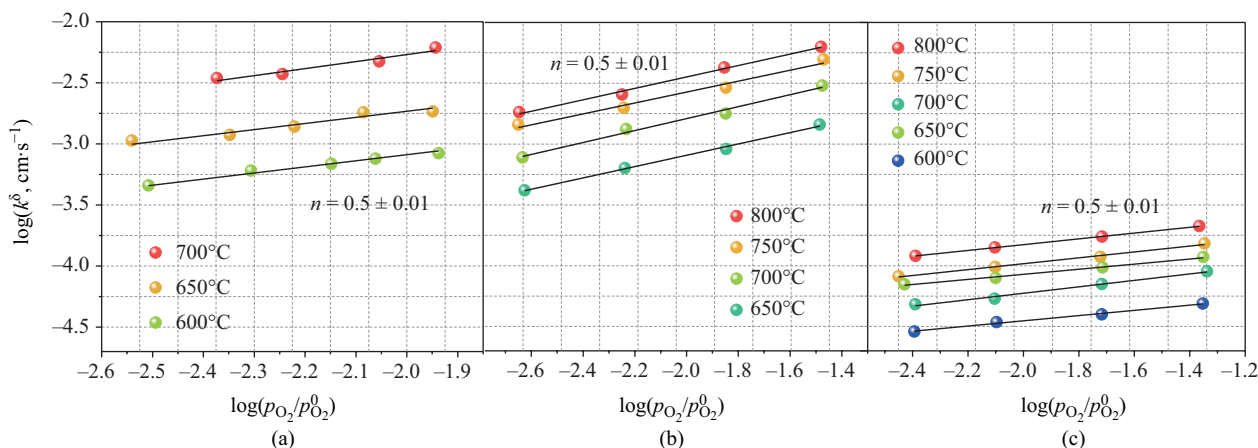


**Fig. 3.** Dependencies of chemical oxygen surface exchange coefficient  $k^\delta$  on oxygen pressure: (a) BSCF, (b) BSCFTa15, and (c) BSCFW2 [38]

by ionized oxygen species  $\text{O}_{\text{ad}}^-$ ,  $\text{O}_{2,\text{ad}}^-$ , or  $\text{O}_{2,\text{ad}}^{2-}$  on  $p_{\text{O}_2}$ ;  $j$  is the type of particles that cover the surface. Then,

$$r^\delta \propto [\theta_j]. \quad (6)$$

The oxygen exchange rate  $r^\delta$  is related to  $k^\delta$  via the formula

$$k^\delta = r^\delta \frac{M_r}{n_{\text{O}}^{\text{ox}} N_A \rho}, \quad (7)$$

wherein  $M_r$  is the molar mass of the oxide;  $n_{\text{O}}^{\text{ox}}$  is the oxygen content in the oxide, including the oxygen species on the surface;  $N_A$  is the Avogadro constant; and  $\rho$  is the crystallographic density.

The exponent of the dependence of  $k^\delta$  on oxygen pressure thus correlates with the exponent of the dependence of  $[\theta_j]$  on oxygen pressure. Thus, at the exponent  $n \approx 0.5$  for the BSCF and BSCFTa15 oxides, the dominant species were shown to be peroxide ions, whereas at the exponent  $n \approx 0.25$  for BSCFW2, the dominant species are ionized adatoms. This is apparently due to the defective surface structure of these oxides, which determines the difference in the rates of the stages observed in the equilibrium tracer oxygen exchange experiment for the BSCF and BSCFTa15 oxides. The stages of dissociative adsorption and oxygen incorporation for these oxides are competing. At the same time, for the BSCFW2 oxide, the rate-limiting stage is dissociative adsorption [17], and the dominant species on the surface are dissociated adatoms.

In order to analyze the differences between the absolute values of the chemical oxygen exchange coefficients  $k^\delta$ , let us compare the tracer ( $k^*$ ) and chemical ( $k^\delta$ ) exchange coefficients for the BSCF, BSCFTa15, and BSCFW2 oxides (Fig. 4).

Figure 4 shows that the oxides under study are divided into two groups: for the BSCF and BSCFTa15 oxides, the difference between  $k^\delta$  and  $k^*$  is more than three orders of magnitude, while for BSCFW2 this difference is significantly smaller. As we previously noted in [17], the kinetics of oxygen exchange with the BSCF and BSCFTa15 oxides studied by equilibrium and nonequilibrium methods differs from that with BSCFW2, namely, in the rate of the stages and the degree of surface coverage by ionized oxygen species participating in the stage that determines the rate of oxygen exchange. In addition, it was shown in [38] that the atomicity of the oxygen particle participating in the stage that determines the rate of oxygen exchange with BSCFW2 differs from that for BSCF and BSCFTa15.

Table presents the surface thermodynamic factor  $w_0|_{x=\pm L}$  calculated using Eq. (3) and the bulk thermodynamic factor  $w_0$  calculated using Eq. (5) from the linear region of the dependence of oxygen content in the oxide on the temperature and partial pressure of oxygen.

Table shows that the bulk thermodynamic factors for all oxides have similar values of the order of a hundred and do not exceed  $1.4 \cdot 10^2$ , which may indicate a similarity in the mechanism of point defect formation. An increase in temperature and concentration of the alloying element leads to a decrease in the bulk thermodynamic factor  $w_0|_{x=0}$  in the order from BSCF to BSCFW2 to BSCFTa15. This trend is consistent with the observed dependence of the Gibbs free energy of oxygen vacancy formation in these oxides on the oxygen content. Thus, the Gibbs free energy of oxygen formation increases in the order from BSCF to BSCFW2 to BSCFTa15 at the same concentration of oxygen vacancies [17]. In other words, the higher the concentration of the alloying element, the higher the energy required to form oxygen

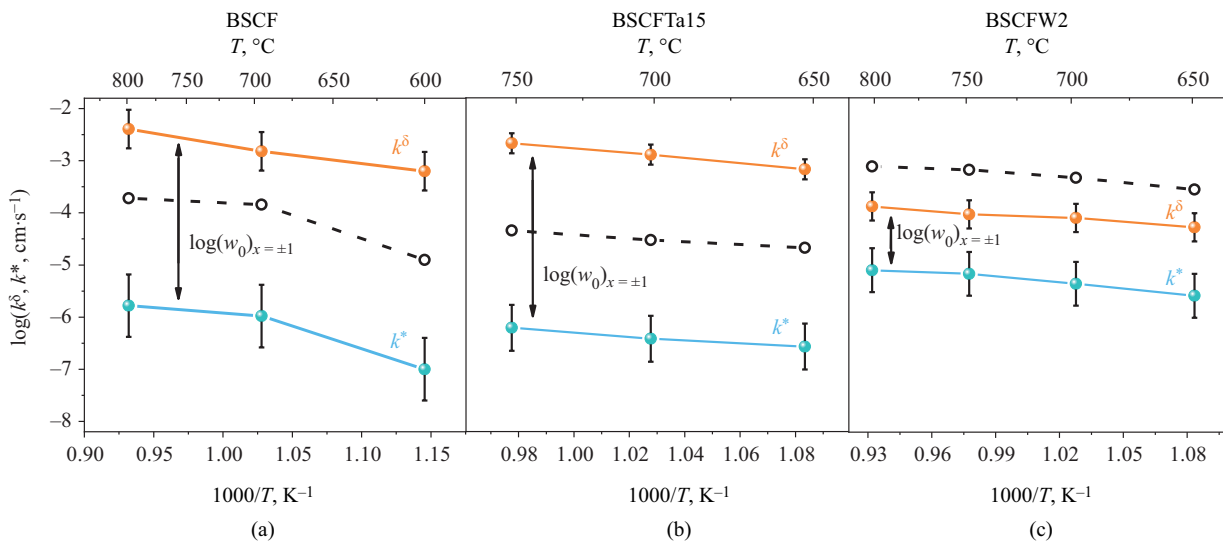


**Fig. 4.** Comparison of the tracer and chemical oxygen exchange coefficients for (a) BSCF, (b) BSCFTa15, and (c) BSCFW2 at an oxygen pressure of 6.7 mbar. The open circles connected by dashed lines represent the chemical oxygen exchange coefficients  $k^{\delta'}$  calculated from the bulk thermodynamic coefficient  $w_0|_{x=0}$  under the assumption  $w_0|_{x=0} = w_0|_{x=\pm L}$  [38]

**Table.** Calculated values of the bulk ( $w_0|_{x=0}$ ) and surface ( $w_0|_{x=\pm L}$ ) thermodynamic factors

| Oxide    | $T, ^\circ\text{C}$ | Thermodynamic factor        |                                 |
|----------|---------------------|-----------------------------|---------------------------------|
|          |                     | Surface<br>$w_0 _{x=\pm L}$ | Bulk<br>$w_0 _{x=0}$            |
| BSCF     | 600                 | $(6.3 \pm 0.9) \cdot 10^3$  | $(1.3 \pm 0.1) \cdot 10^2$ [26] |
|          | 700                 | $(1.5 \pm 0.4) \cdot 10^3$  | $(1.4 \pm 0.1) \cdot 10^2$ [26] |
|          | 800                 | $(2.4 \pm 0.6) \cdot 10^3$  | $(1.2 \pm 0.1) \cdot 10^2$ [26] |
| BSCFTa15 | 650                 | $(2.5 \pm 0.7) \cdot 10^3$  | $(0.8 \pm 0.1) \cdot 10^2$      |
|          | 700                 | $(3.4 \pm 0.8) \cdot 10^3$  | $(0.8 \pm 0.1) \cdot 10^2$      |
|          | 750                 | $(3.5 \pm 0.8) \cdot 10^3$  | $(0.7 \pm 0.1) \cdot 10^2$      |
| BSCFW2   | 650                 | $(2.0 \pm 0.5) \cdot 10^1$  | $(1.1 \pm 0.1) \cdot 10^2$      |
|          | 700                 | $(1.8 \pm 0.5) \cdot 10^1$  | $(1.1 \pm 0.1) \cdot 10^2$      |
|          | 750                 | $(1.3 \pm 0.5) \cdot 10^1$  | $(1.0 \pm 0.1) \cdot 10^2$      |
|          | 800                 | $(1.6 \pm 0.5) \cdot 10^1$  | $(0.9 \pm 0.1) \cdot 10^2$      |

vacancies. This is confirmed by the fact that oxygen content increases in the same series of oxides [17]. Thus, the bulk thermodynamic factor is directly determined by oxygen deficiency in the oxide.

A different picture is observed for the surface thermodynamic factor  $w_0|_{x=\pm L}$ . Higher values of  $(1.5\text{--}6.3) \cdot 10^3$  are characteristic of the BSCF and

BSCFTa15 oxides, while the values for BSCFW2 do not exceed 20. This discrepancy is unlikely to be related to the nature and concentration of the highly charged dopant. Apparently, these differences should be interpreted through a significant difference in the defective surface structure in the series of isomorphic oxides. This is confirmed by the results we obtained

by X-ray photoelectron spectroscopy of the surface of these oxides [17]. Thus, the surface layer at a depth of 5–10 nm for the BSCF and BSCFTa15 oxides consists of a Ba- and Co-containing phase with an undefined stoichiometry, and the surface layer at a depth of 1–5 nm comprises exclusively  $\text{BaCO}_3$ . Conversely, the surface of BSCFW2 is completely covered with  $\text{BaCO}_3$ .

Therefore, the observed difference in the values of surface thermodynamic factors for the BSCF, BSCFTa15, and BSCFW2 oxides clearly correlates with the difference in the slope of the dependence of  $k^\delta$  on  $p_{\text{O}_2}$ . This observation reflects the difference in the mechanism of surface oxygen exchange. Specifically, for the BSCF and BSCFTa15 oxides, for which the dissociative oxygen adsorption stage and the oxygen incorporation stage compete and the dependence of the surface coverage with peroxide ions  $\text{O}_{2,\text{ad}}^{2-}$  on  $p_{\text{O}_2}$  is proportional to the oxygen exchange rate under nonequilibrium conditions, high values of the surface thermodynamic factor exceed the bulk thermodynamic factor by 1.5–2.0 orders of magnitude. On the other hand, for the BSCFW2 oxide, for which the dissociative oxygen adsorption is the rate-limiting stage and the dependence of the surface coverage with single charged adatoms  $\text{O}_{\text{ad}}^-$  on  $p_{\text{O}_2}$  is proportional to the surface oxygen exchange rate, the values of the surface thermodynamic factor are 0.5–1.0 times the bulk thermodynamic factor, being significantly smaller than the surface factor for the BSCF and BSCFTa15 oxides. However, this does not allow a conclusion about the generality of the observed correlations for oxides with mixed conduction to be drawn. Literature data on  $k^\delta$  and  $k^*$  for different oxide compositions can hardly be compared, since they were obtained under widely varying conditions for different oxides with different histories (e.g., synthesis method, experimental conditions, etc.). Further research is needed to identify general patterns concerning the oxygen exchange mechanism under equilibrium and nonequilibrium conditions.

The relationship between the thermodynamic factor and kinetic parameters was noted previously [33, 40–42]. It should be emphasized that the thermodynamic factor reflects the activity of an oxide system in response to changes in oxygen pressure and, thus, is directly related to the concentration of oxygen vacancies in the bulk or surface layers of the oxide material. In general, it is quite obvious that the structure of defects, which determines the oxygen exchange mechanism (including the concentration of point defects), differs significantly in the surface layers and in the bulk of the material. This was confirmed in numerous studies [17–19, 34–36, 43]. Given this “inequality” in the structure and composition of the bulk and surface, it becomes clear that the generally accepted [1, 20, 26, 30, 44–50] relationship

between the tracer oxygen exchange coefficient  $k^*$  and the chemical oxygen exchange coefficient  $k^\delta$  via the bulk thermodynamic factor  $w_0|_{x=0}$  is inaccurate. A more accurate approach would be to introduce the surface thermodynamic factor  $w_0|_{x=\pm L}$ , which is described by Eq. (3).

It can be concluded that when selecting an oxide material for high-temperature electrochemical devices operating under a gradient of the electrochemical potential of oxygen, it is recommended to use oxides with the highest values of surface thermodynamic factors, represented by the difference between the surface tracer oxygen exchange coefficients and the chemical exchange coefficients, measured under the same experimental conditions.

## CONCLUSIONS

The surface thermodynamic factor  $w_0|_{x=\pm L}$  was calculated from the ratio of the chemical ( $k^\delta$ ) to the tracer ( $k^*$ ) oxygen exchange coefficients for the BSCF, BSCFTa15, and BSCFW2 oxides. For the BSCF and BSCFTa15 oxides, the values of the surface factor exceed those of the bulk factor by 1.5–2.0 orders of magnitude. Conversely, for the BSCFW2 oxide, the surface thermodynamic factor was found to be 0.5–1.0 times the bulk thermodynamic factor. This difference was explained by differences in the defect structure of the oxide surfaces.

For identifying a more active material under electrochemical potential gradient conditions, we proposed a criterion represented by the ratio between the chemical and tracer oxygen exchange coefficients.

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## Authors' contributions

**A.R. Akhmadeev**—writing the text of the article, conducting experiments.

**V.A. Eremin**—conducting experiments.

**M.V. Ananyev**—conceptualization, editing the text of the article.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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RESEARCH ARTICLE

## Technologies for production and treatment of powder materials in thermal plasma of electric arc discharge

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### Abstract

**Objectives.** To summarize the results from studies of plasma processes for the production of specified composition powder materials; to implement plasma processes: plasma-chemical synthesis of nanopowders, granulation of nanopowders, plasma spheroidization of microgranules and micropowders in order to perform nanotechnologies and additive technologies tasks.

**Methods.** Thermal plasma generation was used at the A.A. Baikov IMET RAS by means of direct-current electric arc plasmatrons with a rated power up to 45 kW with self-adjusting arc length and gas stabilization of discharge, as well as plasmatrons with an interelectrode insert. In order to carry out the processes of nanopowders synthesis and metal powders spheroidization, the plasma reactor design with confined jet flow using thermal plasma of reducing, oxidizing, and inert media was used.

**Results.** The use of electric arc plasmatron in the processes of plasma chemical synthesis of nanopowders and plasma spheroidization of powders enabled productivity of 0.5 and 10 kg/h, respectively, to be achieved for various metals, alloys, compounds, and their compositions. In the case of the implemented processes of producing nanopowders, where the formation of particles depends on various macro-mechanisms, it was established that the average size of the particles obtained is controlled. This also depends on the synthesis parameters—the initial concentration of the precursor, enthalpy, and flow rate of the plasma jet, cooling rate and vapor condensation. The study shows the results of examining the processes of producing spheroidized powders in thermal plasma flows. These include (Ti, Ta, Fe, Ni, Mo, W), alloys (based on Fe, Ti, Ni, Co, Nb, W, Mg, including stainless, heat-resistant, refractory, hard), compounds (borides, oxides) and compositions (W–Ni–Fe, ZrB<sub>2</sub>–SiC, Ni–TiCN, etc.). The possibility of obtaining nonporous spherical powders of various dispersity was also shown: for particles of about 10–100 μm and for granules having a particle size of less than 1 μm. The study described the main process parameters determining the quality of spheroidization, including dispersity of precursor, plasma enthalpy, gas composition, characteristics of plasma flow, and their mixing with initial powders.

**Conclusions.** The research and development results presented here show the possibilities of plasma processes and apparatuses for producing nanopowders of various metal, inorganic compounds and compositions with given properties. The study also confirmed that powders of metals and alloys, compounds and compositions obtained by a variety of methods can be spheroidized in a plasma reactor with confined jet flow in a wide range of melting points, particle sizes, and morphology. The demonstrated approach using successive stages of plasma-chemical synthesis of nanopowders, their granulation and subsequent plasma spheroidization of microgranules enables tungsten-based composite micropowders with dense spherical particles and submicron structure to be obtained.

### Keywords

thermal plasma, plasma-chemical synthesis, granulation, plasma spheroidization, spherical micropowders, nanopowders

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## НАУЧНАЯ СТАТЬЯ

# Технологии получения и обработки порошковых материалов в термической плазме электродугового разряда

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## Аннотация

**Цели.** Обобщить результаты исследований плазменных процессов, обеспечивающих получение порошковых материалов заданного состава; осуществить плазменные процессы: плазмохимический синтез нанопорошков, грануляцию нанопорошков, плазменную сфероидизацию микрогранул и микропорошков для выполнения задач в области нанотехнологий и аддитивных технологий.

**Методы.** Генерация термической плазмы осуществлялась разработанными в ИМЕТ РАН электродуговыми плазматронами постоянного тока мощностью до 45 кВт с самоустанавливающейся длиной дуги и плазматронами с межэлектродной вставкой. В процессах плазмохимического синтеза нанопорошков и плазменной сфероидизации металлических порошков была использована конструкция плазменного реактора с ограниченным струйным течением с использованием термической плазмы восстановительных, окислительных и инертных сред.

**Результаты.** Использование электродугового плазматрона позволило в процессах плазмохимического синтеза нанопорошков и плазменной сфероидизации порошков достигнуть производительности 0.5 и 10 кг/ч соответственно для различных металлов, сплавов, соединений и их композиций. Для реализованных процессов получения нанопорошков, формирование частиц в которых происходит по различным макромеханизмам, установлено, что средний размер получаемых частиц управляется и зависит от параметров синтеза — начальной концентрации прекурсора, энтальпии и скорости истечения струи плазмы, скорости охлаждения и конденсации паров. Показаны результаты исследования процессов получения сфероидизированных порошков в потоках термической плазмы, включая металлы (Ti, Ta, Fe, Ni, Mo, W), сплавы (на основе Fe, Ti, Ni, Co, Nb, W, Mg, в том числе нержавеющие, жаропрочные, тугоплавкие, твердые), соединения (бориды, оксиды) и композиции (W–Ni–Fe, ZrB<sub>2</sub>–SiC, Ni–TiCN и др.). Показана возможность получения беспористых сферических порошков различной дисперсности: для частиц с размерами 10–100 мкм и для микрогранул, состоящих из частиц с размерами менее 1 мкм. Описаны основные параметры процесса, влияющие на качество сфероидизации, среди которых дисперсность прекурсоров, энтальпия плазменной струи, состав используемых газов, характеристики плазменного потока и его смешения с исходным сырьем.

**Выводы.** Продемонстрированные результаты исследований показывают диапазон возможностей плазменных процессов и аппаратов для получения нанопорошков различных металлов, неорганических соединений и композиций с необходимыми характеристиками. Подтверждено обеспечение возможности сфероидизации порошков металлов и сплавов, соединений и композиций, полученных различными методами, в плазменном реакторе с ограниченным струйным течением в широком диапазоне температур плавления, размеров и морфологии частиц. Представленный подход с использованием последовательных стадий плазмохимического синтеза нанопорошков, гранулирования полученных нанопорошков и последующей плазменной сфероидизации микрогранул позволяет получать композитные микропорошки на основе вольфрама с плотными сферическими частицами и субмикронной структурой.

## Ключевые слова

термическая плазма, плазмохимический синтез, грануляция, плазменная сфероидизация, сферические микропорошки, нанопорошки

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## INTRODUCTION

This work presents the results of applying thermal plasma generated by electrical discharges to the processes of producing and processing various powder materials. These results were obtained on the basis of research and developments carried out at the A.A. Baikov Institute of Metallurgy and Materials Science of the Russian Academy of Sciences (IMET RAS), in the aims of creating technologies and equipment for the nano- and additive technologies (ATs) fields.

Nanopowders serve as the basis for creating nanostructured materials for a variety of applications, including ceramic materials and hard alloys with enhanced mechanical properties, dispersion-strengthened and modified structural alloys, nanostructured coatings with improved thermal, corrosion, and wear resistance, as well as composites containing fillers and modifiers based on inorganic nanoparticles, among others [1–4].

Nanopowders can be synthesized by a variety of methods, including gas-phase, liquid-phase, solid-phase, and combined processes, such as mechanical milling, gas-phase deposition, precipitation from solutions, and others. Plasma-chemical synthesis is a gas-phase process and can serve as a universal method for producing nanopowders of elements, compounds, and composites when carried out in different gaseous environments—inert, reducing, or oxidizing [5, 6].

Numerous studies on the plasma-chemical synthesis of nanopowders in thermal-plasma flows generated by plasma torches of various types have confirmed the efficiency of producing nanopowders of various metals, oxides, carbides, nitrides, borides, and diverse compositions [7–12].

Various types of electrical discharges can be used to generate thermal plasma, including direct current (DC) arc, radio frequency (RF), microwave (MW), as well as combined discharges [13]. The leading company in the field of nanopowder production is *Tekna* (Canada) which employs plasma reactors based on RF plasma torches.<sup>1</sup> Modern high-power plasma torches with capacities of up to 2400 kW have a thermal efficiency of 70–85%, enabling highly energy-efficient operation. They can be used for the implementation of high-temperature processes on an industrial scale.<sup>2</sup>

At the present time, IMET RAS is actively conducting research into the production of nanopowders in thermal-plasma flows generated by DC arc plasma torches. The main focus of these studies is the implementation

of plasma-chemical synthesis of nanopowders with predetermined physicochemical properties, defined according to their specific applications in the creation of corresponding materials. This can be achieved by controlling the dispersity, phase and chemical compositions of the nanopowders during their synthesis, as well as through subsequent additional thermochemical and/or thermo-vacuum treatment.

Over the past decades, ATs have been rapidly developing worldwide. This is due to their ability to encompass all stages of the production cycle—from design to final product manufacturing [14–18]. ATs significantly reduce production time, quickly introduce design modifications, manufacture complex-shaped components, and substantially reduce the amount of industrial waste.

The most versatile and widely used variant of ATs for manufacturing metal and alloy components is implemented by the sequential layering of the part according to a specified geometry. A laser or electron beam acting on a powder layer 20–60 μm thick is used, ensuring local melting of the powder particles due to intense energy exposure. The properties of the metallic powders largely determine the efficiency of the processes, as well as the quality of the produced components. Consequently, one of the key challenges in the development of AT is the creation of efficient methods for producing metal and alloy powders with the required properties and their subsequent successful application [19–21].

Technologies have already been implemented on an industrial scale to produce spherical powders of various metals and alloys (based on iron, aluminum, titanium, chromium, copper) with the ability to achieve the desired particle size distribution. These include processes such as inert gas atomization of molten metal and melt film atomization using centrifugal forces. However, these processes have several significant limitations (for example, low yield of product with the required particle size) which substantially increases the cost of the resulting powders. In addition, the molten metal atomization method does not allow for the production of powders of refractory metals and alloys.

An alternative to the atomization method for producing spherical powders is the spheroidization of irregularly shaped metal particles by melting them in a high-temperature gas flow generated by electric-discharge thermal plasma generators. The leading technology is the spheroidization processes carried

<sup>1</sup> TEKNANO Nanopowder synthesis systems. 2016. <http://www.tekna.com/nanopowder-synthesis-systems>. Accessed November 21, 2025.

<sup>2</sup> Nyun A. Plasma Torches by Westinghouse Plasma Corporation. 2005. [https://www.academia.edu/24044626/Plasma\\_Torches\\_by\\_Westinghouse\\_Plasma\\_Corporation](https://www.academia.edu/24044626/Plasma_Torches_by_Westinghouse_Plasma_Corporation). Accessed November 21, 2025.

out in thermal plasma flows generated by RF and MW discharges, using equipment from *Tekna*<sup>3</sup> and *6K Inc.*<sup>4</sup> (USA).

At present, IMET RAS is conducting research into the field of plasma spheroidization of powder materials using DC arc plasma torches, including the following directions:

- investigation and development of technologies for spheroidizing metallic powders in thermal plasma flows generated by arc discharges;
- creation of foundational technologies for the recycling of spent metallic powders used in ATs;
- development and production of efficient powder spheroidization systems based on arc plasma torches.

This article presents a review of the results of experimental studies conducted at IMET RAS on plasma-chemical synthesis of nanopowders and spheroidization of powder materials, with particle sizes ranging from 10 to 100  $\mu\text{m}$ , in thermal DC arc plasma jet flows.

## METHODS AND EQUIPMENT

DC arc plasma torches with a nominal power of up to 45 kW, featuring a self-adjusting arc length, as well as plasma torches with an interelectrode insert, were used (Fig. 1) for the generation of thermal plasma in laboratory and pilot-scale setups at IMET RAS. These plasma torches enabled the stable generation of thermal plasma flows in reducing, oxidizing, and inert atmospheres, with equilibrium mean mass temperatures of  $2\text{--}10 \cdot 10^3 \text{ K}$ . They also enabled plasma-chemical synthesis of nanopowders and plasma spheroidization processes.

The design of a plasma reactor with a confined jet flow for plasma-chemical synthesis of nanopowders [22] and plasma spheroidization of powder materials [23], developed at IMET RAS, is protected by patents of the Russian Federation. Figure 2 shows general views of a plasma system based on a 35 kW DC arc plasma torch for nanopowder synthesis and plasma spheroidization of powder materials.

The following methods were used for characterization and study of the main properties of the powders produced. The specific surface area  $S_{\text{sp}}$  ( $\text{m}^2/\text{g}$ ) of nanopowders was measured by means of the Brunauer–Emmett–Teller method using a TriStar 3000 surface area analyzer (*Micromeritics*, USA). Particle size distribution and related parameters were determined by laser diffraction using a Mastersizer 2000M particle size analyzer with an automatic Hydro 2000S dispersion and sample delivery module (*Malvern*, United Kingdom). The total contents

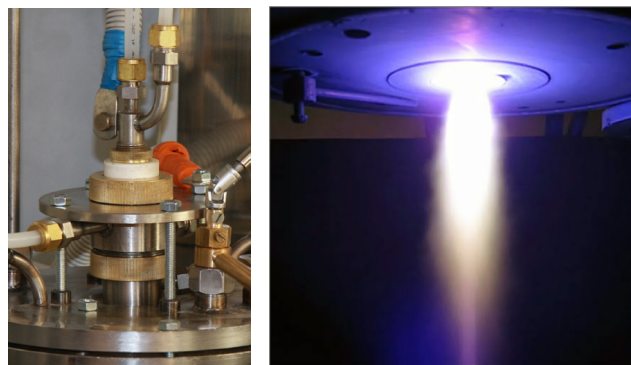


**Fig. 1.** Electric arc plasma torches of A.A. Baikov Institute of Metallurgy and Material Science at the Russian Academy of Sciences (IMET RAS) with rated power up to 45 kW

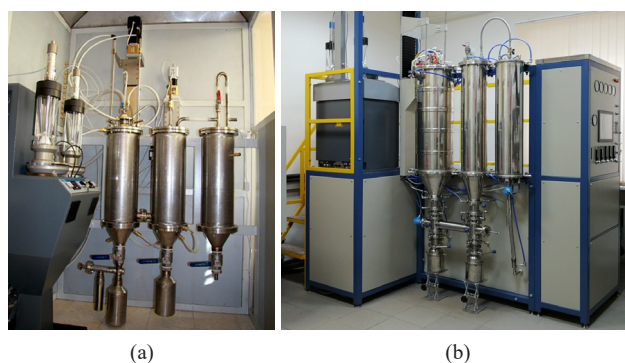


**Fig. 2.** General view of a plasma setup with restricted jet flow reactor based on 35-kW DC arc plasma torch for plasma chemical synthesis of nanopowders (a) and for plasma spheroidization of powders materials (b)

of oxygen, nitrogen, and hydrogen were measured on an RNH-836 analyzer (*Leco*, USA). This was achieved by heating samples in a graphite crucible under a helium flow and detecting the evolved gases using infrared (IR) and thermal conductivity sensors. The total carbon content was measured using a CS-600 analyzer (*Leco*, USA) by combusting the sample in an oxygen flow and detecting the evolved gases with an IR sensor. The morphology and characteristic particle size were studied by scanning electron microscopy using a Scios instrument (*FEI*, USA) and by transmission electron microscopy using an Osiris instrument (*FEI*, USA) with elemental energy-dispersive microanalysis performed on an EDAX Elite attachment (*EDAX*, USA). Phase composition analysis was carried out using Ultima-4 (*Rigaku*, Japan) and XRD-6000 (*SHIMADZU*, Japan) X-ray diffractometers with monochromatized copper radiation at room temperature ( $20^\circ\text{C}$ ).

<sup>3</sup> TEKSPHERO. Spheroidization Systems. 2023. <http://www.tekna.com/spheroidization-systems>. Accessed November 21, 2025.

<sup>4</sup> 6K Production of Breakthrough Materials. 2023. <https://www.6kinc.com>. Accessed November 21, 2025.

## RESULTS AND DISCUSSION

### Plasma-chemical synthesis of nanopowders

The plasma-chemical synthesis of nanopowders is governed by a complex of physicochemical processes in turbulent gas-disperse non-isothermal flows. Reactors with confined jet flow are widely used to implement plasma processes for nanopowder production. Here the plasma jet is discharged into a reactor volume bounded by reactor walls with the ratio of the reactor diameter to the plasma torch nozzle diameter significantly exceeding 10. The formation of nanoparticles in the plasma reactor takes place through condensation of components from the gas phase followed by their deposition onto the water-cooled reactor walls.

The evolution of nanoparticles within the reactor volume leads to changes in their particle-size distribution as a result of condensational and coagulation growth. Changes in their chemical and phase composition may also occur. Parameters can vary in the plasma-chemical process of nanopowder production: composition, enthalpy, and velocity of the plasma jet; reagent concentrations and their delivery characteristics; as well as the size of the initial particles of the dispersed precursor. In this context, not only the technological implementation of the plasma-chemical synthesis process is important, but also the method of collecting and storing the nanopowders. This is essential to prevent physicochemical transformations in the layer of deposited particles, including sintering and possible phase transformations. In order to achieve this, the thickness of the nanoparticle layer must not exceed a specified limit. This requires periodic removal of deposited particles from the reactor walls and their collection in hermetically sealed containers.

In order to carry out the plasma-chemical synthesis of nanopowders, a reactor with confined jet flow was used. Some syntheses were performed in a combined reactor equipped with a unit for preliminary evaporation of the dispersed raw materials in a thermally insulated channel and the subsequent use of gas chemical quenching.

Table 1 presents nanopowders of metals and their inorganic compounds produced at IMET RAS in a confined-jet-flow plasma reactor using a 25 kW DC arc plasma torch [22, 24]. Various individual gases and their mixtures (with a purity of at least 99.98%) were used as plasma-forming gases. The initial raw material consisted of powders of elements and their compounds with particle sizes not exceeding 25–40  $\mu\text{m}$ ; liquid reagents were pre-evaporated before being fed into the reactor. Commercial chemical reagents (manufactured in Russia) with a purity of no less than 99.9% were used as starting materials.

### Particle-size distribution of the obtained nanopowders and particle morphology

One of the most important characteristics of nanopowders, which determines the feasibility of their use in scientific tasks and practical applications, is their particle-size distribution. In the process of plasma-chemical synthesis, the formation of nanoparticles occurs via three macromechanisms:

- vapor–liquid–crystal (VLC);
- vapor–crystal (VC);
- a mixed mechanism which combines the above processes (VLC and VC).

The formation of nanoparticles and the corresponding mechanism in the plasma-chemical process can be assessed using thermodynamic calculations of nanopowder yield as a function of temperature. If the material exists in both liquid and solid states, its yield will depend on temperature. In this case,  $T^*$  is the minimum temperature corresponding to the maximum yield of the nanoparticle material.  $T_{\text{cond}}$  is the maximum temperature at which the nanoparticles remain in the condensed state, while  $T$  is the temperature at which melting of the nanoparticle material occurs.

The plasma process occurs at a temperature initially exceeding  $T_{\text{cond}}$ , which gradually decreases. Accordingly, the temperature conditions for nanoparticle formation via the specified macromechanisms can be described as follows:

- VLC mechanism:  $T < T^* < T_{\text{cond}}$ , all nanoparticles have a spherical shape;
- VC mechanism:  $T^* < T_{\text{cond}} < T$ , all nanoparticles have a faceted shape;
- VLC–VC mixed mechanism:  $T^* < T < T_{\text{cond}}$ , nanoparticles exhibit both spherical and faceted shapes.

Under conditions of decreasing process temperature, the formation of predominantly spherical nanoparticles via the VLC mechanism occurs when the maximum particle yield is achieved at temperatures above the melting point of the substance (Fig. 3a). If nanoparticle formation occurs at temperatures below the melting point, or if the substance does not exist in a liquid state, the process follows the VC mechanism which primarily leads to the formation of faceted particles (Fig. 3b). When the substance crystallizes before reaching the maximum yield, a transition from the VLC to the VC mechanism occurs, resulting in a product containing both spherical and faceted particles (Fig. 3c).

Figure 4 shows the results of electron microscopy studies of nanopowders obtained by plasma-chemical synthesis. All powders are polydisperse and consist of particles with equiaxed rounded or faceted shapes. It is demonstrated that nanoparticle formation can occur via all three mechanisms—VLC, VC, and VLC–VC (corresponding to  $\text{Al}_2\text{O}_3$ , TiCN, and W nanopowders, respectively).

**Table 1.** Nanopowders produced in plasmochemical synthesis at IMET RAS

| No.                 | Produced nanopowder                              | Reagents                                                                             | Plasma-forming gas                                                  | Specific surface area, m <sup>2</sup> /g |
|---------------------|--------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------|------------------------------------------|
| Individual metals   |                                                  |                                                                                      |                                                                     |                                          |
| 1                   | W, Mo, Ni, Co, Re                                | Me <sub>x</sub> O <sub>y</sub> , H <sub>2</sub> , C <sub>3</sub> H <sub>8</sub> +air | H <sub>2</sub> +N <sub>2</sub> , C <sub>3</sub> H <sub>8</sub> +air | 2–30                                     |
| 2                   | Cu                                               | CuCl, H <sub>2</sub>                                                                 | H <sub>2</sub> +N <sub>2</sub>                                      | 2–5                                      |
|                     |                                                  | Cu(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O                               | N <sub>2</sub>                                                      | 5–35                                     |
|                     |                                                  | Cu                                                                                   | N <sub>2</sub>                                                      | 20–36                                    |
| Composite materials |                                                  |                                                                                      |                                                                     |                                          |
| 3                   | W–Ni–Fe (W = 95%)                                | WO <sub>3</sub> , NiO, Fe <sub>2</sub> O <sub>3</sub> , H <sub>2</sub>               | H <sub>2</sub> +N <sub>2</sub>                                      | 4–10                                     |
| 4                   | W–Cu (W = 80%)                                   | WO <sub>3</sub> , CuO, H <sub>2</sub>                                                | H <sub>2</sub> +N <sub>2</sub>                                      | 4–10                                     |
| 5                   | W–Y <sub>2</sub> O <sub>3</sub> (W = 95–99.7%)   | WO <sub>3</sub> , Y(CH <sub>3</sub> COO) <sub>3</sub> , H <sub>2</sub>               | H <sub>2</sub> +N <sub>2</sub>                                      | 4–10                                     |
| 6                   | W–B (W = 88–97%)                                 | WCl <sub>6</sub> , BCl <sub>3</sub> , H <sub>2</sub>                                 | H <sub>2</sub> , Ar+H <sub>2</sub>                                  | 13–20                                    |
| 7                   | Ag–SnO <sub>2</sub>                              | Ag, SnO <sub>2</sub>                                                                 | Air                                                                 | 5–12                                     |
| Anoxic compounds    |                                                  |                                                                                      |                                                                     |                                          |
| 8                   | TiN                                              | Ti, TiH <sub>2</sub> , N <sub>2</sub>                                                | N <sub>2</sub>                                                      | 12–18                                    |
|                     |                                                  | TiCl <sub>4</sub> , H <sub>2</sub> , N <sub>2</sub>                                  | H <sub>2</sub> +N <sub>2</sub>                                      | 11–39                                    |
| 9                   | AlN                                              | Al, NH <sub>3</sub> , N <sub>2</sub>                                                 | N <sub>2</sub>                                                      | 30–70                                    |
| 10                  | TiC                                              | TiCl <sub>4</sub> , H <sub>2</sub> , CH <sub>4</sub>                                 | H <sub>2</sub> +Ar                                                  | 15–30                                    |
| 11                  | TiCN                                             | TiCl <sub>4</sub> , H <sub>2</sub> , N <sub>2</sub> , CH <sub>4</sub>                | H <sub>2</sub> +N <sub>2</sub>                                      | 13–23                                    |
| 12                  | SiC                                              | SiCl <sub>4</sub> , H <sub>2</sub> , CH <sub>4</sub>                                 | H <sub>2</sub> +Ar                                                  | 15–30                                    |
| 13                  | WC                                               | WO <sub>3</sub> , CH <sub>4</sub> , H <sub>2</sub>                                   | H <sub>2</sub> +N <sub>2</sub>                                      | 20–40                                    |
| 14                  | ZrB <sub>2</sub>                                 | ZrCl <sub>4</sub> , BCl <sub>3</sub> , H <sub>2</sub>                                | H <sub>2</sub> +Ar                                                  | 10–50                                    |
| 15                  | HfB <sub>2</sub>                                 | HfCl <sub>4</sub> , BCl <sub>3</sub> , H <sub>2</sub>                                | H <sub>2</sub> +Ar                                                  | 5–30                                     |
| Oxides              |                                                  |                                                                                      |                                                                     |                                          |
| 16                  | Al <sub>2</sub> O <sub>3</sub>                   | Al, O <sub>2</sub>                                                                   | Air                                                                 | 15–35                                    |
| 17                  | Al <sub>2</sub> O <sub>3</sub> –MeO (Me: Mg, Co) | Al, Me, O <sub>2</sub>                                                               | Air                                                                 | 15–25                                    |
| 18                  | AlON                                             | Al, NH <sub>3</sub> , N <sub>2</sub> , O <sub>2</sub>                                | N <sub>2</sub>                                                      | 30–50                                    |
| 19                  | TiO <sub>2</sub>                                 | TiCl <sub>4</sub> , O <sub>2</sub>                                                   | O <sub>2</sub> +Ar                                                  | 30–120                                   |
| 20                  | SiO <sub>2</sub>                                 | SiCl <sub>4</sub> , O <sub>2</sub>                                                   | O <sub>2</sub> +Ar                                                  | 120–250                                  |
| 21                  | ZrO <sub>2</sub>                                 | ZrCl <sub>4</sub> , O <sub>2</sub>                                                   | O <sub>2</sub> +Ar                                                  | 18–32                                    |
| 22                  | ZrO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> | ZrCl <sub>4</sub> , Al, O <sub>2</sub>                                               | O <sub>2</sub> +Ar                                                  | 17                                       |
| 23                  | Y <sub>2</sub> O <sub>3</sub>                    | Y(CH <sub>3</sub> COO) <sub>3</sub> , O <sub>2</sub>                                 | O <sub>2</sub> +Ar                                                  | 12–25                                    |

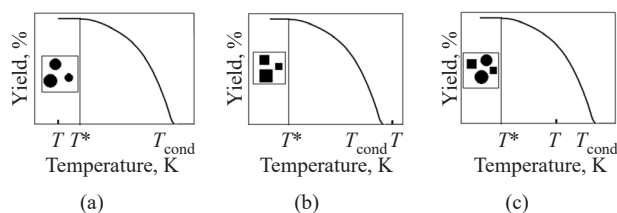


**Fig. 3.** Conditions for the formation of nanoparticles morphology at characteristic temperatures in various macromechanisms: (a) VLC, (b) VC, (c) VLC-VC

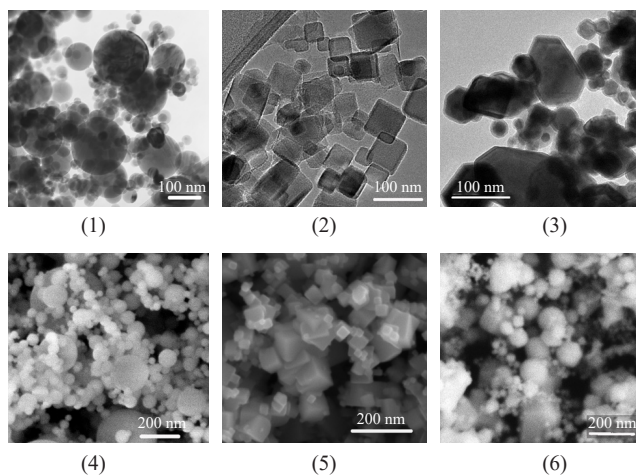


**Fig. 4.** Transmission electron microscopy (1–3) and scanning electron microscopy (4–6) micrographs of nanopowders formed in a plasma reactor by various macromechanisms: (1), (4) Al<sub>2</sub>O<sub>3</sub> (VLC); (2), (5) TiCN (VC); and (3), (6) W (VLC-VC)

Figure 5 presents the results of particle size distribution analysis for Al<sub>2</sub>O<sub>3</sub>, TiCN, and W nanopowders [25]. It was noted that all nanopowders are reliably described (with a correlation coefficient greater than 0.95) by a log-normal particle size distribution function:

$$p(d) = \frac{1}{d\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{\ln d - m}{\sigma}\right)^2\right),$$

where  $d$  is the particle diameter,  $\sigma$  is the standard deviation, and  $m$  is the median of the distribution. The conformity to a log-normal particle size distribution has been confirmed for nanopowders produced via the coagulation-driven VLC mechanism [26]. In the absence of coagulation growth [4], a log-normal distribution of particle residence times in the growth zone can also result in a log-normal distribution of particle sizes, as observed in experimental studies of plasma-chemical synthesis of nanopowders.

In the case of nanopowder production processes, in which particle formation occurs via different macromechanisms, it was established experimentally

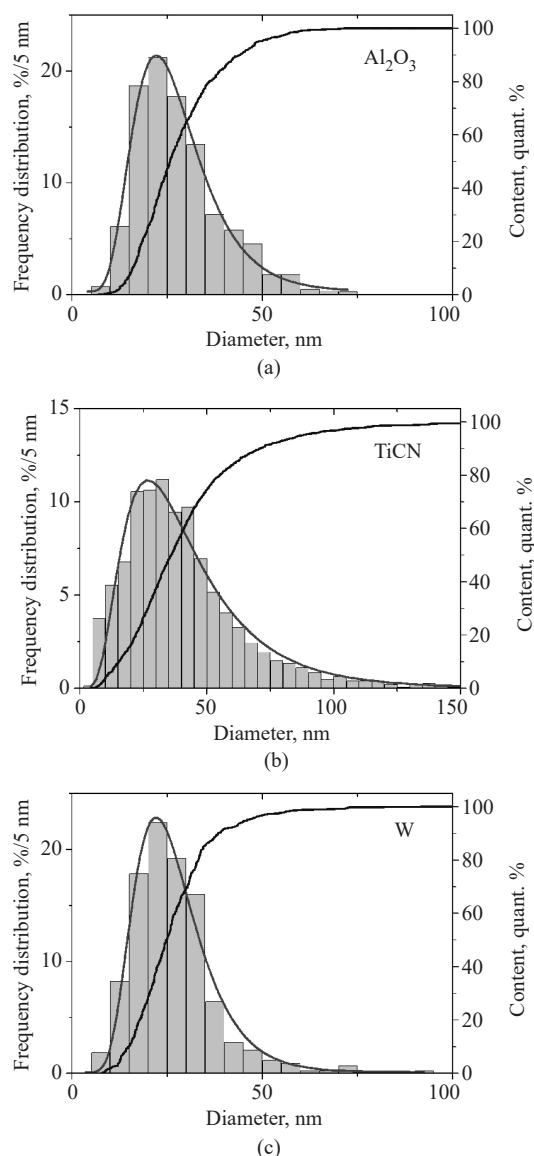


**Fig. 5.** Histograms of particle size distributions for nanopowders formed by various macromechanisms: (a) Al<sub>2</sub>O<sub>3</sub> (VLC), (b) TiCN (VC), and (c) W (VLC-VC) [25]

that the average size of the resulting nanoparticles increases with an increase of the precursor concentration in the gas components. The results also showed that the average particle size depends on synthesis parameters: initial precursor concentration, plasma jet enthalpy, and the jet velocity in the reactor volume. The nanoparticle size decreases with a reduction in the concentration of the condensing component in the gas or with an increase in the plasma jet velocity. However, lowering the concentration reduces productivity, while increasing the jet velocity is subject to technical and physical limitations. The use of gas quenching allows for forced suppression of coagulation growth of particles, thereby controlling the particle size formed via the VLC

mechanism. The results demonstrate the feasibility of producing a variety of nanopowders and controlling their particle-size distribution using plasma-chemical synthesis in a confined-jet-flow reactor.

Plasma spheroidization of metal powders

Spherical powders with particle sizes on the order of tens microns are used for the production of metal and alloy components using modern additive manufacturing methods. The formation of spherical micropowders is achieved by treating irregularly shaped particles in thermal plasma. Their morphology changes as the particles are heated and melted. They form liquid droplets with a rounded shape due to surface tension forces. Upon subsequent cooling within the reactor volume with water-cooled walls, the droplets solidify and crystallize into metallic microspheres.

Experiments conducted on plasma spheroidization of powder materials established that micropowders of various metals and alloys with particle sizes ranging from 10 to 100 μm, predominantly with a spherical shape, can be produced. The degree of spheroidization of plasma-treated particles can reach up to 99 vol %.

The particle roundness coefficient ranges from 1 to 1.4, with an average value of 1.01. The spherical shape of the powder particles ensures high bulk density and good flowability, which are essential for their further use in ATs.

For the production of spheroidized powders of various metals (Ti, Ta, Fe, Ni, Mo, and W), alloys (stainless, heat-resistant, and refractory), compounds, and composites (Table 2), their treatment in a thermal plasma jet at IMET RAS is currently accompanied not only by intensive research on the processes but also by the development of technologies and the necessary equipment.

The results of plasma treatment and the characteristics of certain spheroidized powders are presented in Figs. 6–12: spheroidization of titanium powders [27] (Figs. 6 and 7); spheroidization of iron powders [28] (Figs. 8 and 9); spheroidization of Ti–Al–V alloy VT6 powders (Fig. 10); and spheroidization of Ni–Al–Cr–Co alloy CompoNiAl-M5-3 powders [29] (Fig. 11). Experimental studies demonstrated the feasibility of producing pore-free spherical powders of multicomponent metal alloys with particle sizes

Table 2. Powders produced by spheroidization in thermal plasma at IMET RAS

| Metals     | W, Mo, Ta, Fe, Ti                                                                                                                                                                                                                                                                                                                                                                      |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Alloys     | 316L, 12Kh18N10T, Kh15N5D4B, AISI321 (stainless steel)<br>Inconel (718, 625), VKM, VZh159, VNL14 (Ni alloys)<br>VPr27-50 (Ni solder)<br>VT6, VT14 (Ti–Al–V alloys)<br>CCM (Co–Cr–Mo alloys)<br>CuCrZr (bronze)<br>Nb–Si, Nb–C, Nb–Al, Nb–Mo (Nb alloys)<br>Ni–Al, Ti–Al, Nb–Al, Ni–Al–Co–Cr, Ti–Ni, CompoNiAl-M5-3 (intermetallic compounds)<br>WC–Co (hard alloy)<br>27KKh (Mg alloy) |
| Composites | W–Ni–Fe, W–Cu, W–Y <sub>2</sub> O <sub>3</sub> , W–B, W–C–Co, ZrB <sub>2</sub> –SiC, Ni–TiCN                                                                                                                                                                                                                                                                                           |
| Oxides     | Ta <sub>2</sub> O <sub>5</sub> , Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>                                                                                                                                                                                                                                                                                                     |
| Compounds  | ZrB <sub>2</sub> , HfB <sub>2</sub><br>Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>                                                                                                                                                                                                                            |

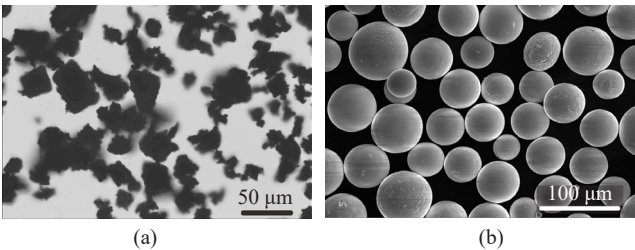


Fig. 6. Micrographs of particles for 20–50-μm fraction of titanium powder (a) before and (b) after plasma spheroidization

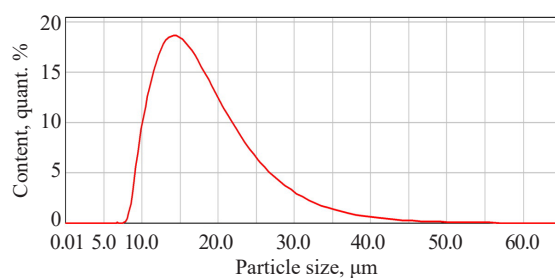


**Fig. 7.** Particle size distribution of spheroidized titanium powder

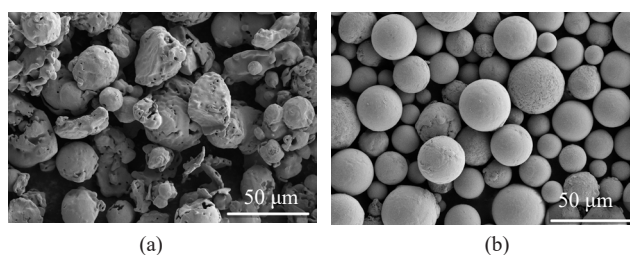


**Fig. 8.** Micrographs of 25–50-μm iron powder (a) before and (b) after plasma spheroidization

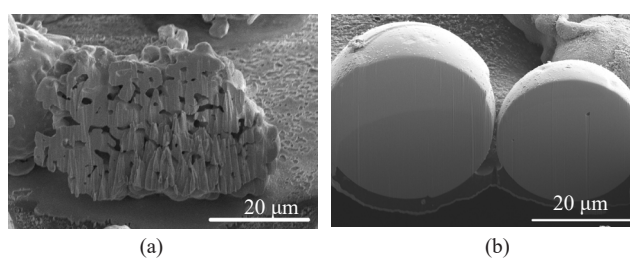


**Fig. 9.** Micrographs of iron powder particles in focused ion beam cross section (a) before and (b) after plasma spheroidization

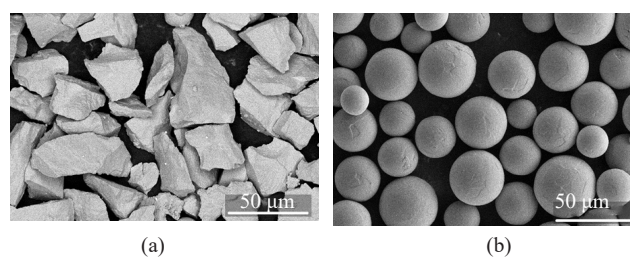


**Fig. 10.** Micrographs of particles for powder of Ti–Al–V alloy (VT6 grade) (a) before and (b) after plasma spheroidization

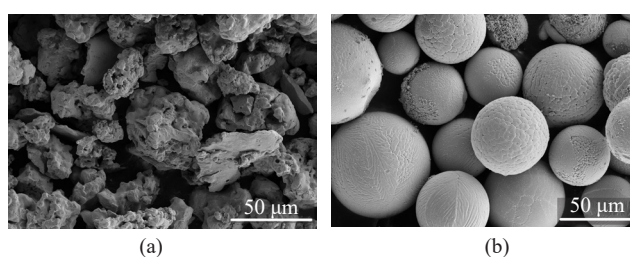


**Fig. 11.** Morphology of 20–50 μm powder particles of CompoNiAl-M5-3 alloy (a) before and (b) after plasma spheroidization

ranging from 10 to 100  $\mu\text{m}$  from initial powders of various dispersities composed of irregularly shaped particles. The experimental results indicate the possibility of producing spherical powders of metals and alloys from various initial powder materials in a confined-jet-flow plasma apparatus based on a DC arc plasma torch.

IMET RAS is also carrying out research on the use of plasma-based regeneration for the spheroidization of previously used powders and the reduction of gas impurities [30]. An example of spheroidization and regeneration of X-IN718 stainless steel powders is shown in Fig. 12.

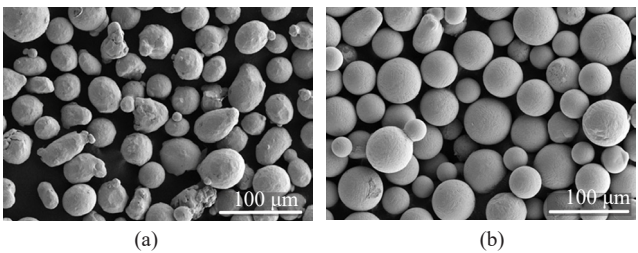


**Fig. 12.** Micrographs of particles for powder of Fe–Ni–Cr alloy (IN718 grade) (a) before and (b) after plasma regeneration

The use of a hydrogenous plasma jet during the regeneration of powders of Fe-, Ni-, Co-, W-, and Mo-based alloys allows gas impurities to be significantly reduced: oxygen by 1.5–6 times and nitrogen by 1.5–10 times (depending on the plasma enthalpy and hydrogen content). They also allowed for an improvement in particle morphology and a decrease in oxygen and nitrogen content (Table 3). Gas impurities (oxygen) are present in the surface layer of the particles in the form of metal oxides, which allows these oxides to be reduced to metals via reactions with hydrogen during the residence time of the particles in the high-temperature zone.

Factors which determine the quality of powders obtained in plasma spheroidization processes include: the thermophysical properties of the treated material and its particle size distribution; the characteristics of the thermal plasma flow; the arrangement of powder mixing with the plasma flow; as well as the organization of the high-temperature gas–disperse flow within the processing chamber. For each powder material, the

combination of process parameters which ensures optimal performance—high particle spheroidization, the desired particle size distribution, and maximum productivity—is determined experimentally.

The spheroidization process of particles by melting in a thermal plasma flow, where the gas temperature exceeds the boiling point of the treated material, is accompanied by its evaporation. Upon cooling of the gas-disperse flow, the vapor condenses, resulting in the formation of nanoparticles.

The presence of nanoparticles in plasma-spheroidized powders is highly undesirable, since it reduces powder flowability. Also due to the high chemical reactivity of metallic nanoparticles, it can lead to their oxidation upon exposure to air. A special classification method in a liquid medium is used, in order to remove nanoparticles from powders treated in a thermal plasma flow. This involves preliminary ultrasonic treatment to break up nanoparticle aggregates and remove them from the surfaces of the spheroidized microparticles.

In order to reduce the nanoparticle content in spheroidized metal and alloy powders, it has been proposed to separate the treated powder into narrower particle size fractions and then process each fraction under the corresponding optimal spheroidization parameters. After processing, the powder fractions are blended. This approach allows for a reduction in the nanoparticle content in the final product.

**Plasma spheroidization of composite powders**

The study of obtaining spherical micropowders of W–C–Co, W–Ni–Fe, W–Cu, W–Y<sub>2</sub>O<sub>3</sub>, and W–B composites from nanopowders of the corresponding systems, produced by plasma-chemical synthesis is new direction in the production of powders with spherical particle shapes.

The main stages of such processes are:

1. Production of nanopowders of the W–Ni–Fe and W–Cu systems by reduction of mixtures of metal oxide powders of the corresponding systems in a hydrogenous plasma flow generated by a DC arc plasma torch. For the W–C–Co system, the reaction is carried out in the presence of methane, while for

**Table 3.** Properties of IN718 powder alloy before and after plasma regeneration

| Sample                    | [O], wt % | [N], wt % | Flowability, s/50 g | Bulk weight, g/cm <sup>3</sup> |
|---------------------------|-----------|-----------|---------------------|--------------------------------|
| Initial powder            | 0.031     | 0.14      | 19                  | 4.6                            |
| After plasma regeneration | 0.019     | 0.071     | 18                  | 4.6                            |

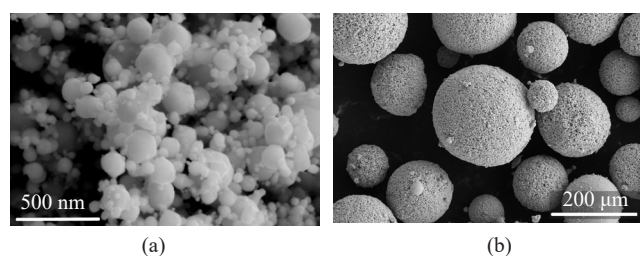


**Fig. 13.** Micrographs of nanopowder (a) and resulting nanopowder granules (b) for W–Ni–Fe composition

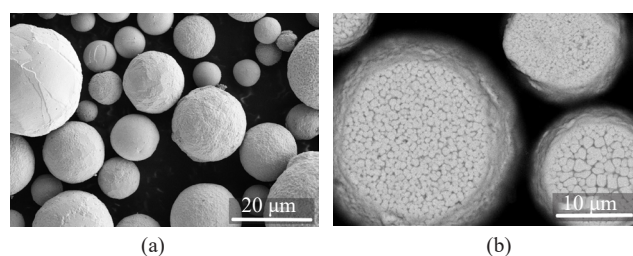


**Fig. 14.** Micrograph of particles (a) and grinding thin sections (b) for powder of W–Ni–Fe composition after plasma treatment of nanopowder granules

the W–Y<sub>2</sub>O<sub>3</sub> system, the raw materials consists of tungsten trioxide and yttrium acetate. Nanopowders of the W–B composition are produced by hydrogen reduction of a mixture of chlorides, or the W–B and other compositions can be obtained by mixing individual nanopowders produced via plasma-chemical synthesis.

2. Preparation of the corresponding liquid suspensions with an additionally introduced binder (e.g., sucrose).
3. Spray drying of the suspensions to obtain nanopowder porous microgranules.
4. Classification of the microgranules to isolate the required particle size fraction.
5. Densification and spheroidization of the microgranules by sintering and/or melting in a thermal DC plasma flow.

The synthesis of nanopowders in the considered systems in a plasma jet flow is achieved through reduction reactions in the gas phase, resulting in the formation of target metals as nanosized particles. One example of such composites is the W–Ni–Fe system nanopowder. As shown in Fig. 13a, these nanopowders predominantly consist of spherical nanosized particles with a “core-shell” structure, in which nickel and iron form an alloy in the near-surface layers of the nanoparticles, while the core consists of tungsten. The specific surface area of the nanopowders ranges from 4 to 10 m<sup>2</sup>/g.

The aqueous suspension prepared from the nanopowder, containing 2 wt % organic binder (sucrose), was granulated by spray drying using a laboratory Mini Spray Dryer B-290 (*Buchi*, Switzerland). The resulting microgranules were sieved on an AS 200 sieve machine (*Retsch*, Germany) to isolate particles smaller than 50 μm (Fig. 13b). The yield of microgranules within this size range was approximately 60%. The obtained nanopowder microgranules have a uniform structure, free of internal voids, with a homogeneous distribution of metals [31].

Spherical microparticles of the W–Ni–Fe system were obtained (Fig. 14a) as a result of processing the microgranules in an argon–hydrogen (up to 20 vol % H<sub>2</sub>) DC plasma flow, exhibiting a predominantly dense

structure without internal voids (Fig. 14b). Analysis of the microstructure of the plasma-treated powder particles revealed that the tungsten grain size falls within the micron and submicron range (Fig. 14b).

The micropowders obtained exhibited a low content of oxygen (up to 0.2 wt %) and carbon (up to 0.01 wt %). The bulk density of the powder was 10 g/cm<sup>3</sup>, and the flowability was 9 s/50 g.

The conducted studies demonstrated the feasibility of spheroidizing metal and alloy powders, produced by various methods, across a wide range of melting temperatures, particle sizes, and morphologies.

Particular attention is paid to the development and creation of plasma equipment and technologies. Plasma technologies for producing nanopowders with a productivity of up to 0.5 kg/h and spherical micron-sized powders with a productivity of up to 10 kg/h are implemented on IMET RAS installations with power ratings up to 45 kW. These installations enable powder production and can be used both for research purposes and for the fabrication of experimental batches of spherical micropowders and nanopowders.

Based on many years of accumulated experience in the research of powder spheroidization in thermal plasma flows, IMET RAS has developed a plasma installation based on a DC plasma torch with a nominal power of 30 kW for spheroidizing powders of metals, alloys, and metal-matrix composites, which it supplies to customers. The installation is included by the Ministry of Industry and Trade of the Russian Federation in the “Catalog of Additive Equipment Produced in the Russian Federation.” Since early 2024, this installation has been in operation directly at IMET RAS, as well as at *GIREDMET* (Russia), the Institute of Advanced Technology (Harbin, China), and the All-Russian Scientific Research Institute of Aviation Materials of the National Research Center “Kurchatov Institute” (Russia). At IMET RAS, the plasma spheroidization installation is used for processing batches of powders of various alloys in quantities up to 1000 kg under orders from Russian companies operating in the ATs field.

## CONCLUSIONS

The results of developments and experimental studies confirm the wide potential of plasma processes and equipment for producing metal nanopowders, their inorganic compounds, and composites. Powders obtained at plasma-chemical synthesis installations have been used in a large number of research studies in the aim of creating new materials with enhanced properties for specialized applications.

In addition to the production of various nanopowder materials, the confined-jet-flow reactor developed at IMET RAS enables plasma spheroidization of metal and alloy powders for their subsequent use in ATs. The study also demonstrated the feasibility of spheroidizing metal and alloy powders produced by different methods across a wide range of melting temperatures, particle sizes, and morphologies.

A new approach involving sequential stages of plasma-chemical synthesis of nanopowders, granulation of the obtained nanopowders, and subsequent plasma spheroidization of the microgranules enables the production of composite micropowders with dense spherical particles and a submicron structure.

The accumulated experience in the development and use of plasma apparatuses based on DC plasma torches serves as a foundation for establishing highly efficient industrial-scale production of powder materials.

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## Authors' contributions

**A.V. Samokhin**—conceptualization, supervision, funding acquisition, manuscript writing, data analysis and results.

**N.V. Alekseev**—manuscript writing, methodology, data analysis and results, references.

**M.A. Sinayskiy**—experimental studies and analyses, references, manuscript writing and editing, data analysis and results.

**A.A. Fadeev, A.G. Astashov, D.E. Kirpichev**—engineering and preparation of equipment for experiments, experimental research.

**A.A. Dorofeev**—experimental research and analysis.

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Erratum  
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## Erratum to the article “Influence of the structure of phosphorus(III)-containing oligoester(meth)acrylates on the physical and mechanical properties, thermal stability, and combustion mechanisms of cured polymers”

**Boris A. Buravov, Ali Al-Hamzawi, Rashid B. Gadzhiev, Svetlana A. Orlova, Lyubov Yu. Donetskova, Semyon M. Solomakhin, Sergey V. Borisov, Olga S. Fomenko, Stanislav A. Trubachev, Aleksander A. Paletsky, Andrey G. Shmakov, Oleg I. Tuzhikov, Oleg O. Tuzhikov**

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Page 595, the affiliation of Ali Al-Hamzawi<sup>2</sup>,  
instead of:

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The original article can be found under: <https://doi.org/10.32362/2410-6593-2025-20-6-594-611>

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