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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 ^{1}H nuclear magnetic resonance spectroscopy (500 MHz, dimethyl sulfoxide-d_6).

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 K и атмосферном давлении. Определены составы равновесных жидких фаз методом спектроскопии ядерного магнитного резонанса ^{1}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 ±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}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	*Vekton*	0.990	No	GC
TBA	*Vekton*	0.990	No	GC
Glutaric acid	*Vekton*	0.990	No	NMR
Malonic acid	*Vekton*	0.990	No	NMR
Urea	*Vekton*	0.990	No	NMR
Glycerol	*Vekton*	0.980	No	NMR
Choline chloride	*AppliChem*	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 ±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}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 (β_i) and selectivity (S), calculated according to equations (1) and (2):

$$\beta_i = \frac{\omega_i^{\mathrm{II}}}{\omega_i^{\mathrm{I}}}, \tag{1}$$

$$S = \frac{\omega_i^{\mathrm{I}}}{\omega_i^{\mathrm{II}}}\frac{\omega_j^{\mathrm{II}}}{\omega_j^{\mathrm{I}}}, \tag{2}$$

wherein ω_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 ω_1, ω_2, and ω_3 are the mass fractions of TBA, MTBE, and choline chloride, respectively; β_1 is the distribution coefficient of the alcohol; β_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			β_1	β_2	S
ω_1	ω_2	ω_3	ω_1	ω_2	ω_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: ω_1, ω_2, and ω_3 are the mass fractions of TBA, MTBE, and choline chloride, respectively; β_1 is the distribution coefficient of alcohol; β_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			β_1	β_2	S
ω_1	ω_2	ω_3	ω_1	ω_2	ω_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			β_1	β_2	S
ω_1	ω_2	ω_3	ω_1	ω_2	ω_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			β_1	β_2	S
ω_1	ω_2	ω_3	ω_1	ω_2	ω_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			β_1	β_2	S
ω_1	ω_2	ω_3	ω_1	ω_2	ω_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			β_1	β_2	S
ω_1	ω_2	ω_3	ω_1	ω_2	ω_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 (ω_3) is minimal (close to zero) across all experimental points, which minimizes extractant loss and simplifies the subsequent purification of the final products.

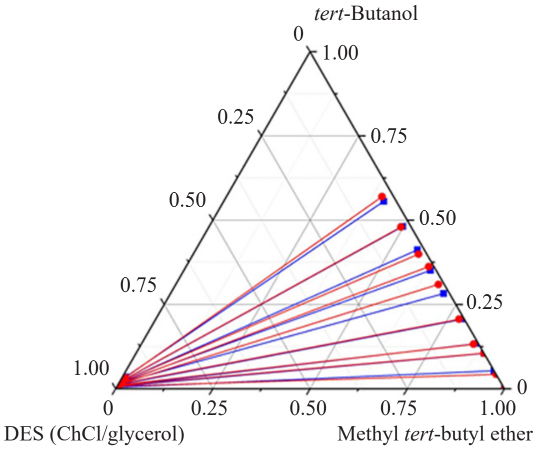

Fig. 1. Phase diagram of the TBA–MTBE–DES system based on choline chloride and glycerol at temperatures of 293.15 K (■) and 313.15 K (●) and atmospheric pressure

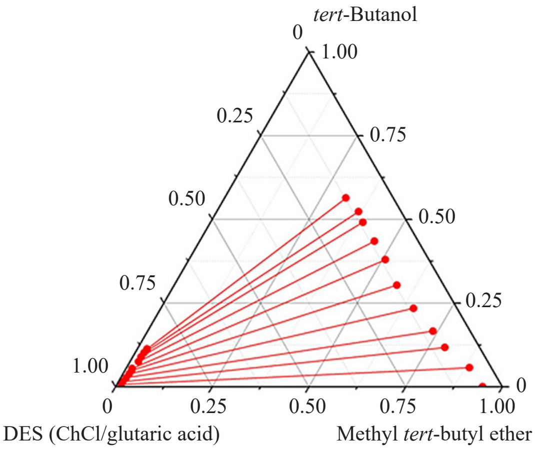

Fig. 2. Phase diagram of the TBA–MTBE–DES system based on choline chloride and glutaric acid at a temperature of 313.15 K and atmospheric pressure

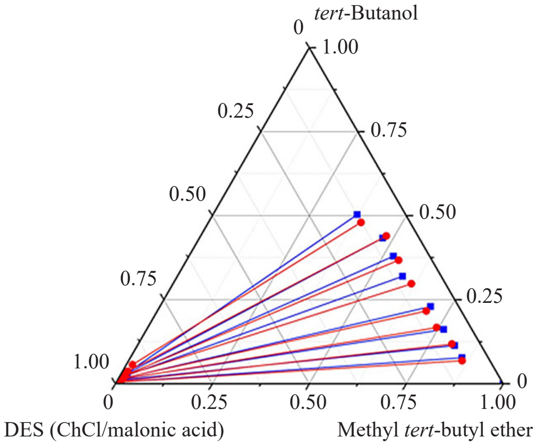

Fig. 3. Phase diagram of the TBA–MTBE–DES system based on choline chloride and malonic acid at temperatures of 293.15 K (■) and 313.15 K (●) and atmospheric pressure

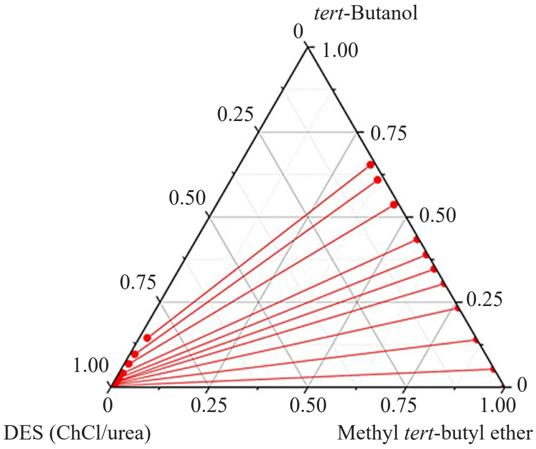

Fig. 4. Phase diagram of the TBA–MTBE–DES system based on choline chloride and urea at a temperature of 313.15 K (●) and atmospheric pressure

The efficiency of TBA extraction from its mixture with MTBE was evaluated using TBA distribution coefficients (β_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.

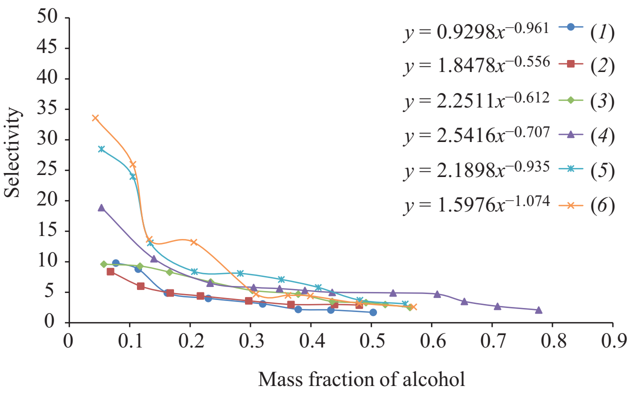

Fig. 5. Selectivity values *vs* alcohol mass fraction: (*1*) malonic acid at 293.15 K; (*2*) malonic acid at 313.15 K; (*3*) glutaric acid at 313.15 K; (*4*) urea at 313.15 K; (*5*) glycerol at 293.15 K; (*6*) glycerol at 313.15 K

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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