Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2025;20(4):357–371

ISSN 2686-7575 (Online)

Analytical methods in chemistry and chemical technology

Аналитические методы в химии и химической технологии

UDC 54.04, 544.032.72, 544.032.76, 544.353.21
https://doi.org/10.32362/2410-6593-2025-20-4-357-371
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RESEARCH ARTICLE

Interaction of poly(diallyldimethylammonium chloride) with inorganic acids

Yaroslava N. Golubeva✉, Alexander V. Krylov✉, Tatyana A. Chebotareva

MIREA – Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119454 Russia

✉ *Corresponding authors, e-mail: Yaroslava N. Golubeva, golubeva.ya.n@gmail.com; Alexander V. Krylov, allylnmr@yandex.ru*

Abstract

Objectives. The study set out to investigate the state of poly(*N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride) (polyDADMAC) in aqueous solutions and the exchange reactions of polyelectrolyte anions with anions of inorganic acids, as well as to assess the effect of the acidity, basicity, and nature of H_nX_m acids on the state of the polymer-colloidal complex (PCC) in aqueous solutions.

Methods. Potentiometry, dynamic light scattering, infrared spectroscopy, and nuclear magnetic resonance spectroscopy methods were used.

Results. The main factors affecting the state of the polyDADMAC polyelectrolyte in aqueous solutions were determined along with the characteristics of exchange processes involving anions of inorganic acids. The polymer electrolyte polyDADMAC is shown to exist in an aqueous solution in the form of impermeable polymer coils, representing polymer solvent-separated ion pairs. The Cl^- anion of the polyelectrolyte is exchanged for the OH^- ion of water or the X^{n-} anions of inorganic acids to form PCCs with polymer chain links and various counteranions. The exchange of the anions takes place mainly on the surface of the polymer coil, which limits the degree of substitution of anions and depends on the strength, nature, and basicity of the H_nX_m acids. A relationship was found between the degree of substitution of the X^{n-} anions of the polymer coil and the strength of the resulting PCC with the enthalpy of solvation of inorganic acids H_nX_m.

Conclusions. The polymer electrolyte polyDADMAC exists in an aqueous solution in the form of impermeable polymer coils, which are represented by polymer solvent-separated ion pairs. The exchange of the Cl^- anion of the polyelectrolyte for the OH^- ion of water or the X^{n-} anions of inorganic acids results in the formation of PCCs with polymer chain links and various counteranions. The exchange of the anions, which takes place on the surface of the polymer coil, mainly involves the OH^- anion of the polyelectrolyte. A relationship was identified between the state of polymer coils of polyDADMAC, the degree of substitution of anions with different pK_a, and the degree of acid solvation. The degree of substitution of the X^{n-} anions of acids, which decreases with a decrease in the strength of the H_nX_m acid and the charge of the resulting anion in the series $HClO_4 > HCl > HNO_3 > HBF_4 > HSO_4^-, H_2PO_4^-$, is characterized by a significant change in the size of the coil of the slow mode of motion of the PCC polyelectrolyte. Here, the increased diffusion coefficient from $3.0 \cdot 10^{-13}$ to $1.3 \cdot 10^{-10}$ cm^2/s corresponds to a decrease in the degree of association of the links of the polymer coil of PCC in the same series. The degree of substitution of the X^{n-} anions of the polymer coil and the strength of the forming PCC decrease symbatically with a decrease in the degree of solvation of inorganic acids in water.

Keywords

polyDADMAC, potentiometric titration, IR spectroscopy, NMR spectroscopy, dynamic light scattering, polyelectrolyte chlorine anion exchange, inorganic acids, polymer-colloidal complexes, diffusion of polymer coils

Submitted: 26.10.2024
Revised: 27.03.2025
Accepted: 16.06.2025

For citation

Golubeva Ya.N., Krylov A.V., Chebotareva T.A. Interaction of poly(diallyldimethylammonium chloride) with inorganic acids. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2025;20(4):357–371. https://doi.org/10.32362/2410-6593-2025-20-4-357-371

НАУЧНАЯ СТАТЬЯ

Взаимодействие полидиметилдиаллиламмоний хлорида с неорганическими кислотами

Я.Н. Голубева✉, А.В. Крылов✉, Т.А. Чеботарева

МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119454 Россия

✉ *Авторы для переписки, e-mail: Я.Н. Голубева, golubeva.ya.n@gmail.com; А.В. Крылов, allylnmr@yandex.ru*

Аннотация

Цели. Исследовать состояние поли-*N*,*N*-диметил-*N*,*N*-диаллиламмоний хлорида (ПДМДААХ) в водных растворах и реакции обмена анионов полиэлектролита с анионами неорганических кислот; оценить влияние кислотности, основности и природы кислот H_nX_m на состояние полимер-коллоидного комплекса в водных растворах.

Методы. Использовались методы потенциометрии, динамического светорассеяния, инфракрасной спектроскопии и спектроскопии ядерного магнитного резонанса.

Результаты. Установлены основные закономерности, влияющие на состояние полиэлектролита ПДМДААХ в водных растворах и характеристики обменных процессов с участием анионов неорганических кислот. Показано, что полимерный электролит ПДМДААХ находится в водном растворе в форме непротекаемых полимерных клубков, представляющих собой полимерные сольватно-разделенные ионные пары. Установлено наличие обмена аниона Cl^- полиэлектролита на ион OH^- воды или анионы X^{n-} неорганических кислот с образованием полимер-коллоидных комплексов (ПКК) со звеньями полимерной цепи, содержащих различные противоанионы. Обмен анионов протекает преимущественно на поверхности полимерного клубка, что ограничивает степень замещения анионов и зависит от силы, природы и основности кислот H_nX_m. Установлена связь степени замещения анионов X^{n-} полимерного клубка и прочности образующегося ПКК с энтальпией сольватации неорганических кислот H_nX_m.

Выводы. Установлено, что полимерный электролит ПДМДААХ находится в водном растворе в форме непротекаемых полимерных клубков, представляющих собой полимерные сольватно-разделенные ионные пары. Результатом обмена аниона Cl^- полиэлектролита на ион OH^- воды или анионы X^{n-} неорганических кислот является образование ПКК со звеньями полимерной цепи, содержащих различные противоанионы. Обмен анионов протекает на поверхности полимерного клубка и преимущественно с участием аниона OH^- полиэлектролита. Установлена связь между состоянием полимерных клубков ПДМДААХ, степенью замещения анионов с различным pK_a и степенью сольватации кислот. Степень замещения анионов кислот X^{n-} уменьшается с понижением силы кислоты H_nX_m и зарядом образующегося аниона в ряду $HClO_4 > HCl > HNO_3 > HBF_4 > HSO_4^-, H_2PO_4^-$ и характеризуется существенным изменением размеров клубка медленной моды движения полиэлектролита ПКК, для которых величина коэффициента диффузии увеличивается от $3.0 \cdot 10^{-13}$ до $1.3 \cdot 10^{-10}$ см^2/с, что соответствует уменьшению степени ассоциации звеньев полимерного клубка ПКК в том же ряду. Степень замещения анионов X^{n-} полимерного клубка и прочность образующегося ПКК симбатно уменьшается с понижением степени сольватации неорганических кислот в воде.

Ключевые слова

ПДМДААХ, потенциометрическое титрование, ИК-спектроскопия, ЯМР-спектроскопия, динамическое светорассеяние, обмен анионов хлора полиэлектролита, неорганические кислоты. полимер-коллоидные комплексы, диффузия полимерных клубков

Поступила:	26.10.2024
Доработана:	27.03.2025
Принята в печать:	16.06.2025

Для цитирования

Голубева Я.Н., Крылов А.В., Чеботарева Т.А. Взаимодействие полидиметилдиаллиламмоний хлорида с неорганическими кислотами. *Тонкие химические технологии*. 2025;20(4):357–371. https://doi.org/10.32362/2410-6593-2025-20-4-357-371

INTRODUCTION

As an ionic liquid, the polymer electrolyte poly(*N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride) (polyDADMAC) (Fig. 1) has wide practical, including biological, applications as a coagulant/flocculant in water treatment facilities (for example, in polyelectrolyte VPK-402), or as part of polymer inorganic hybrid materials based on it [1, 2].

The transition to the use of gel or polymer inorganic hybrid materials [3–5] leads to the demand for coagulants having higher molecular weights and larger molecular sizes for increasing treatment efficiency in comparison with conventional inorganic coagulating salts [5]. Polymer inorganic hybrid materials are also noted to be more resistant to temperature and pH in wastewater treatment technology [4].

Polyelectrolytes based on polymeric quaternary ammonium compounds (QACs) are used as effective biocidal agents in medicine, biology [6], and the food industry [1], as well as in the method of layer-by-layer assembly of polymer layers on the surface of metal hydroxides [1].

The water-soluble cationic polyelectrolyte VPK-402, which is used for natural and waste water treatment, is currently the only polyDADMAC-based product currently manufactured in the Russian city of Sterlitamak. This is a fairly viscous, opaque substance with a relatively high molecular weight of 250–350 kDa. Any addition of acids or salts to the solution of the polymer leads to its salting out, as confirmed experimentally in the present work. The product used in this work, which has a molecular weight of 20–70 kDa and offers high biocidal and penetrating activity, is recommended for use in medicine, disinfectology (disinfectant VOLAVELA) and agriculture (*Matritsa Rosta* agent, protected by a patent of the Russian Federation [7]). The manufacturer of the agents is *Penta Tekhnologii* (Russia), a developer and manufacturer of biologically active environmentally friendly high-molecular compounds, in partnership with and under the direction of whom this work was carried out.

PolyDADMAC is widely used in agriculture as an effective surfactant that exhibits structuring and moisturizing effects on the soil. This beneficial effect is due to the ability of the polyelectrolyte to dissociate to increase osmotic pressure and, consequently, the filling of soil capillaries with water. PolyDADMAC also exhibits good transport properties for the delivery of nutrients and salts along plant stems [8].

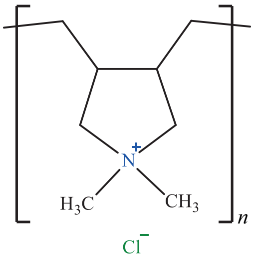


Fig. 1. Structure of poly(*N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride) (polyDADMAC)

An important role in the efficiency of coagulants/flocculants is played by the size of counteranions. It is asserted [9, 10] that the replacement of the small ions Cl^- and SO_4^{2-} with a bulky inorganic anion (for example, the silicate ion SiO_3^{2-}) in the composition of polymer inorganic hybrid materials leads to the formation of an inorganic polymer-colloidal complex (PCC) having a larger molecular structure. This leads to an increase in the aggregation capacity of the coagulant along with a simultaneous decrease in its concentration. The inclusion of polyDADMAC [8] or polyacrylamide [9] in the composition of organic–inorganic hybrid materials improves the ability of dispersed particles to aggregate via a bridge mechanism.

Apart from studies into the use of styrene–divinylbenzene copolymer anion-exchange resins AN-31, AV-17-8chS, and AV-2-8chS with grafted ammonium groups (NH_3^+, $N(CH_3)_3^+$) to remove a number of inorganic anions from aqueous media [11, 12], there are virtually no literature data on the effect of the size and nature of counteranions X^{n-} on the degree of substitution of Cl^- anions in polymeric QACs.

Many more studies have investigated the exchange of anions in mono-ammonium compounds, which are widely used in the anion-exchange extraction of nonferrous and rare-earth metals [11–13]. The efficiency of extraction is largely determined by the accessibility of the cationic center N^+. For example, it was determined that anion-exchange extraction of hydrophilic double charged anions with higher QACs, such as trinonyl octadecylammonium bromide (TNODA), occurs insignificantly, which is due to the steric accessibility of the exchange center [13–15].

The values of the constants for the exchange of X^{n-} anions for the standard Cl^- anion in a two-phase water–toluene system were determined [15–17], which made it possible to expand the Hofmeister series for anions:

$$\begin{gathered}ClO_4^- > SCN^- > BF_4^- > I^- > NO_3^- > Br^- > Cl^- > \\ > Ac^- > SO_4^{2-} > F^- > H_2PO_4^- > C_2O_4^{2-} > HCO_3^- > \\ > HPO_4^{2-} > CO_3^{2-} > PO_4^{3-} > OH^-.\end{gathered} \tag{1}$$

The obtained series of exchange efficiency shows confirms that the exchange constant in the series for a multiply charged anion decreases with increasing ion charge. This has been explained in terms of a change in the solvation of X^{n-} by water molecules and, as a consequence of this, a decrease in pK_a for anions with the same name at the central atom [13, 18]:

$$H_2PO_4^- > HPO_4^{2-} > PO_4^{3-}. \qquad (2)$$

A study into the ion-exchange equilibria of X^{n-} anions at the ammonium center of TNODA in reactions of extraction from an aqueous medium into toluene confirms that the position of anions in the exchange series is determined not only by the strength pK_a of the corresponding acids H_nX_m, but also by the energies of hydration of the acid anions [13, 18]. For strong and medium-strength mineral acids, the difference in the free energies of hydration of anions dominates over the difference in the free energies of solvation of the nitrogen center N^+. This is confirmed by the linear correlation of the dependence of the ion exchange constant $\ln K(X^{n-}/2Cl^-)$ in the two-phase water–toluene system on the energy of hydration of X^{n-} anions in water.

The noticeable difference of the absolute values of the equilibrium constants from those calculated using the Eigen–Dancy–Ramsey–Fuoss theory is explained by the difference in ion association [19]. More specifically, this proceeds according to the formation of solvent-separated ion pairs (SSIPs) in the aqueous and organic phases [14]. An increase in the strength of SSIPs with a decrease in the anion size leads to an increase in the ion exchange constants $K(An^{2-}/2Cl^-)$.

The reactivity of organic electrolytes can be varied by combining different cations or anions. Electrolytes have been developed that consist of large organic asymmetric cations such as 1,3-dialkylimidazolium, 1-alkylpyridinium, 1-alkylpyrazolium, and tetraalkylammonium cations and the anions HF_2^-, $HCOO^-$, CH_3COO^- [20], BF_4^-, PF_6^-, $CF_3SO_3^-$ or $N(SO_2CF_3)_2^-$ [21, 22], 1-ethyl-3-methylimidazoline chloroaluminate (EMImAICl$_4$) [20].

However, despite their wide practical application, fewer studies have been carried out into aqueous solutions of QACs and polymeric QACs as compared to the exchange of anions at ammonium centers in organic solvents.

The high hydrophilicity of charged quaternary ammonium groups of polyDADMAC promotes high solubility of the polymer in water; moreover, its solutions exhibit properties of strong polyelectrolytes [1].

All solvents, which differ in their thermodynamic qualities in terms of their interaction with a polymer, can be divided into thermodynamically “good”, “ideal”, and “bad”. This determination is carried out according to the preferred polymer–solvent interaction in a “good” solvent or a polymer–polymer interaction in a “bad” solvent. In a thermodynamically “good” solvent, a linear macromolecule tends to adopt the conformation of the so-called swollen polymer coil (Fig. 2a): as the salinity of the medium increases, the coil contracts (Fig. 2b).

In “bad” solvents or in the presence of inorganic salts, polymer coils are observed to contract and adopt a more compact globule conformation [19, 23]. A similar effect of polymer coil contraction, which should also be observed upon introduction of low-molecular inorganic and organic salts (Me_nX_m) (Fig. 2b), will be determined by both the concentration of the polyelectrolyte and the acidity pK_a of the salt-forming acids (H_nX_m). An equally

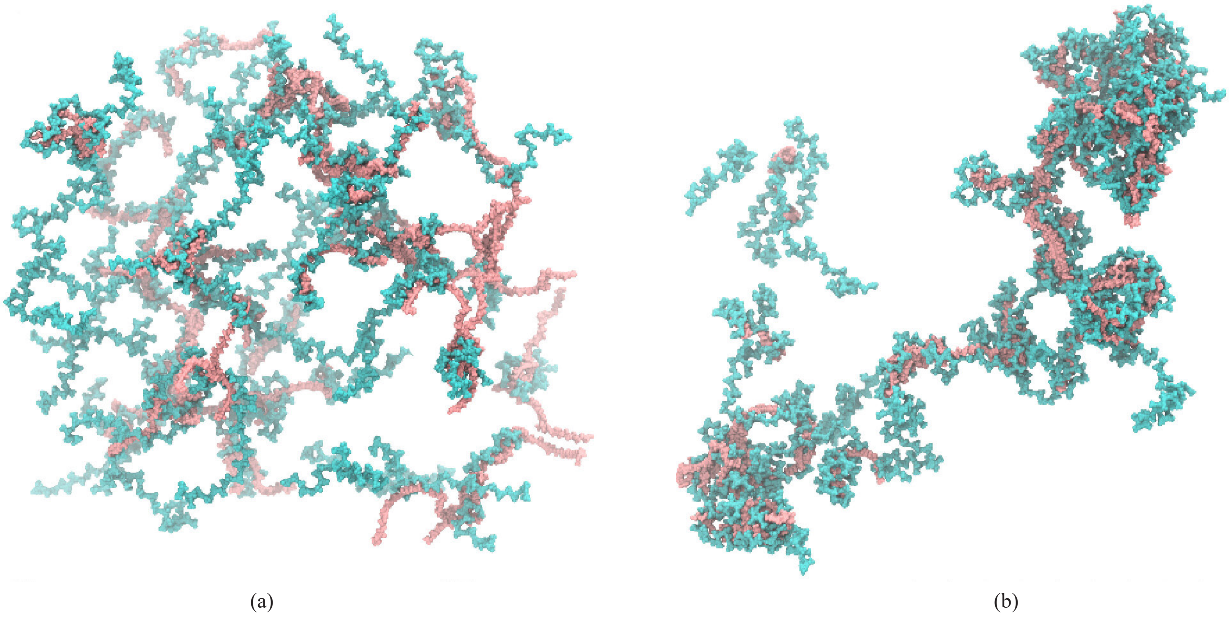
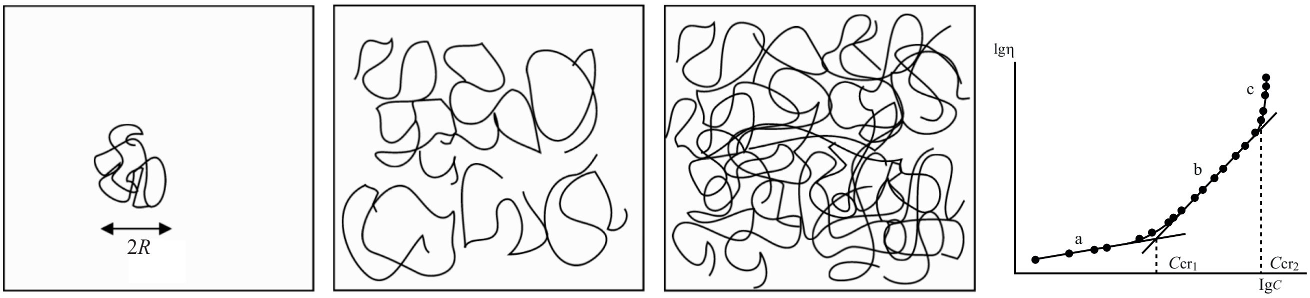

(a) (b)

Fig. 2. Conformation of the polyDADMAC coil (0.3 *M*) as determined by the molecular dynamics method in the OPLS (Optimized Potential for Liquid Simulations) force field (water molecules are omitted for clarity) (a) in a salt-free system or (b) with 2 *M* KBr [22]



(a) (b) (c) (d)

Fig. 3. Schemes of (a) dilute, (b) semi-dilute, and (c) concentrated solutions. (d) Dependence lgη = *f*(lg*C*). 2*R* is a hydrodynamic diameter of the folded polymer chain

important role in the conformation of the polymer coil is played by the ionic strength of the medium, as was described in the literature [20, 24–27] and confirmed in our work.

In "ideal" (theta) solvents, the coil has a conformation of a coil obeying Gaussian statistics.

It is reported [26] that a 1 *M* NaCl aqueous solution and the Mark–Kuhn–Houwink equation correspond to the conditions of the theta solvent according to the equation:

$$[\eta]=1.12\cdot10^{-4}M_{\mathrm{w}}^{0.82}, \qquad (3)$$

where [η] is the characteristic viscosity of the polymer chain with the molecular weight M_{w}.

It is also necessary to take into account the dependence of the state of the polymer molecule on its concentration [24]. The characteristic viscosity [η] determined in a given concentration range characterizes the density of filling the solution with segments (loops) of macromolecules or the concentration at which the overlap of polymer blobs occurs. The limiting concentrations of the transition from dilute (C^*) to semi-dilute (C^{**}) to concentrated (C^{***}) solution depend on the molecular weight M_{w}, the concentration of the polyelectrolyte, and the quality of the solvent, which in turn determine the volume of the polymer coil (Fig. 3). Thus when the solution is concentrated, the structure of the polyelectrolyte solution changes from the content of "polymer in water" to "water in polymer".

Since the polymer concentration is quite low in the case of dilute solutions, the polymer chains exist separately from each other. Here polymer–polymer interaction plays a minor role; thus, for such solutions the M_{w} of polyDADMAC is determined in most studies using Mark–Kuhn–Houwink equation (3).

It has been confirmed that the crossover points C^*, C^{**}, and C^{***} (Fig. 3d) are fairly well determined for this polyelectrolyte on the dependence lgη = *f*(lg*C*) and that the crossover point values shift toward higher values with increasing salt concentration [24, 26]. The size of the polymer coil also exhibits this tendency.

EXPERIMENTAL

Equipment and methods for sample preparation

Initial substances. The initial aqueous solution of polyDADMAC having a polymer mass fraction of ω = 52% and a viscosity of 25000 mPa·s was obtained by homoallylic condensation of *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride in the presence of analytical grade ammonium persulfate (*Scharlab*, Spain) in the Laboratory of the Department of Physical Chemistry at the MIREA – Russian Technological University according to the published procedure [7]. The M_{w} of the polyelectrolyte sample, which was estimated using equation (3) taking into account the content of inorganic salts, was approximately ~20–25 kDa. The estimated value of M_{w} can be considered approximate, since, as will be shown below, the state of the polymer in the solution changes as acids or salts of inorganic acids are added to the aqueous solution. PolyDADMAC solutions were prepared using distilled water H_2O of the first category with a specific electrical conductivity of 4–5 µS/cm in accordance with GOST R 58144-2018[1].

For the study, polyDADMAC solutions with concentrations in the range of 0.06–0.3 *M* (0.67–3.35 wt %) were selected, i.e., semi-dilute solutions, in which both small polymer coils without entanglement and large coils with entanglement can be expected [22, 23].

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[1] GOST R 58144-218. National Standard of the Russian Federation. Distilled water. Specifications. Moscow: Standartinform; 2018. https://meganorm.ru/mega_doc/norm/gost-r_gosudarstvennyj-standart/10/gost_r_58144-2018_natsionalnyy_standart_rossiyskoy.html. Accessed June 11, 2025.

Taking into account a high pH sensitivity of the polyelectrolyte, the initial polyelectrolyte solution was prestandardized by treatment with the solid anion exchanger AV-17-8chS (*Smoly*, Russia) in the OH form to pH 12. For brevity, let us denote the alkaline form polyDADMA–OH. To obtain polyDADMA–OH, the solid anion exchanger AV-17-8chS was initially treated with a 3 *M* NaOH solution in a glass beaker for 60 min. Next, the anion exchanger was repeatedly washed with water until a neutral pH to remove residual alkali and chlorine anion salts. To the obtained anion exchanger AV-17-8chS in the OH form, a solution of polyDADMAC was added and stirred for 60 min until reaching pH 12. The concentration of the obtained polyDADMA–OH solution was refined gravimetrically using the dried residue of the solution in a vacuum drying oven.

Reagents. The following acids were selected. Monoprotic acids: perchloric acid (pure, 60%); hydrochloric acid (chemically pure, 35%); nitric acid (chemically pure, 65%); tetrafluoroboric acid (pure, 40%); sulfamic acid (pure, 99.5%). Polyprotic acids: sulfuric acid (special pure, 93.5%); orthophosphoric acid (pure, 85%); periodic acid (pure, 98%); boric acid (pure, 99%) (all by *CHIMMED*, Russia). Acid titers were controlled by the titer of the alkali of the state standard sample (standard titer, 0.5 N, *CHIMMED*, Russia).

^{1}H nuclear magnetic resonance (NMR) spectra were recorded with an AVHD600 NMR pulsed broadband Fourier spectrometer with a superconducting magnet (*Bruker BioSpin AG*, USA). Strongly adsorbed water molecules in polyDADMAC make it difficult to record NMR due to requiring dissolution of the polymer in D_2O. A specially developed technique was used to transfer polyDADMAC from an aqueous solution to a D_2O solution. A solution of the polyDADMAC polyelectrolyte sample in H_2O (2 mL) was placed in a 15-mL glass vial and concentrated in a CentriVap 7310031 tabletop concentrator (*Labconco Corporation*, USA) with a built-in RV5 pump (*Edwars*, United Kingdom) with a gradient increase in temperature to 55°C. As evaporation proceeded, a new portion of the sample was added. After evaporation until the formation of a dry residue, the resulting polyelectrolyte was immediately dissolved in deuterated water (99.8 wt %) to record ^{1}H NMR spectra. At higher temperatures, the polyelectrolyte decomposed with the appearance of a characteristic odor of methylamines, which is consistent with the published data [27].

Infrared (IR) spectra of the samples in liquid and solid forms were recorded with an Agilent Cary 630 FTIR spectrometer (*Agilent*, USA) by the attenuated total internal reflection method in the range of 4000−350 cm^{-1} at a spectral resolution of <2 cm^{-1}. The IR spectra were processed using the Agilent MicroLab software.

The solid samples of polyDADMAC and polymer complexes based on it were obtained by drying in a BV-50 vacuum drying oven (*Being*, China) for 180 min at a temperature of 80°C. The use of solid samples after using the CentriVap concentrator is impossible due to the active absorption of water vapor by the dehydrated polyelectrolyte sample.

Dynamic light scattering (DLS) spectra were recorded with a Photocor Compact-Z analyzer (*Fotokor*, Russia). The power of the 638-nm thermostable semiconductor laser was 25 mW. The particle sizes in concentrated and low-transparency systems were measured by the backscattering method at an angle of 160° at a constant temperature of 25°C. The signals were analyzed by a built-in Photocor FC correlator for auto- and cross-correlation measurements. The DLS spectra were processed by the DynaLS software package (*Fotokor*).

Potentiometric titration was carried out in an ATP-02 automatic titrator (Russia) with an IT ESC 10601.7 combined glass electrode in the measurement range of pH 0–12. The limiting reference absolute error of measuring pH is 0.03. In all experiments, polyDADMA–OH solutions were titrated, and acid solutions were titrants. The corresponding PCCs were conventionally denoted as polyDADMA–X, where X is a fully substituted anion of the titrant acid.

Data of **polyDADMAC** analyses. ^{1}H NMR (600 MHz, D_2O) δ, ppm: 3.91–3.77 (2H, $N^+(CH_2)_2$), 3.40–3.10 (6H, $N^+(CH_3)_2$), 2.67–2.24 (2H, *cis*/*trans*-CH), 1.57–1.00 (4H, iso/sindio/a $CH\underline{CH_2}$). IR (1 wt %, H_2O): 3328, 2357, 2327, 2115, 1995, 1632, 706, 674 cm^{-1}. IR (52 wt %, H_2O): 3360, 2950, 2871, 2322, 2096, 1997, 1917, 1634, 1472, 1420, 1101, 1000, 959, 875, 674 cm^{-1}. IR (96 wt %, H_2O): 3362, 3019, 2933, 2866, 2706, 2113, 1995, 1636, 1472, 1457, 1418, 1386, 1252, 1093, 989, 961, 911, 877, 836 cm^{-1}.

RESULTS AND DISCUSSION

The state of polyDADMAC in D_2O was analyzed by ^{1}H NMR spectroscopy. The symmetry of the relatively flat five-membered heterocyclic rings of the polymer component gives rise to *cis*- and *trans*-isomers of polymeric QAS as confirmed by a double set of broadened signals of proton-containing groups. The ratio of *cis*/*trans*-isomers is 4.5 : 1.

IR spectroscopy was carried out for solutions with different concentrations of polyDADMAC from 1 to 52 wt % and dried samples with a content of 96 wt %. The IR spectrum of dilute aqueous solutions of polyDADMAC (Fig. 4) presents mainly broadened

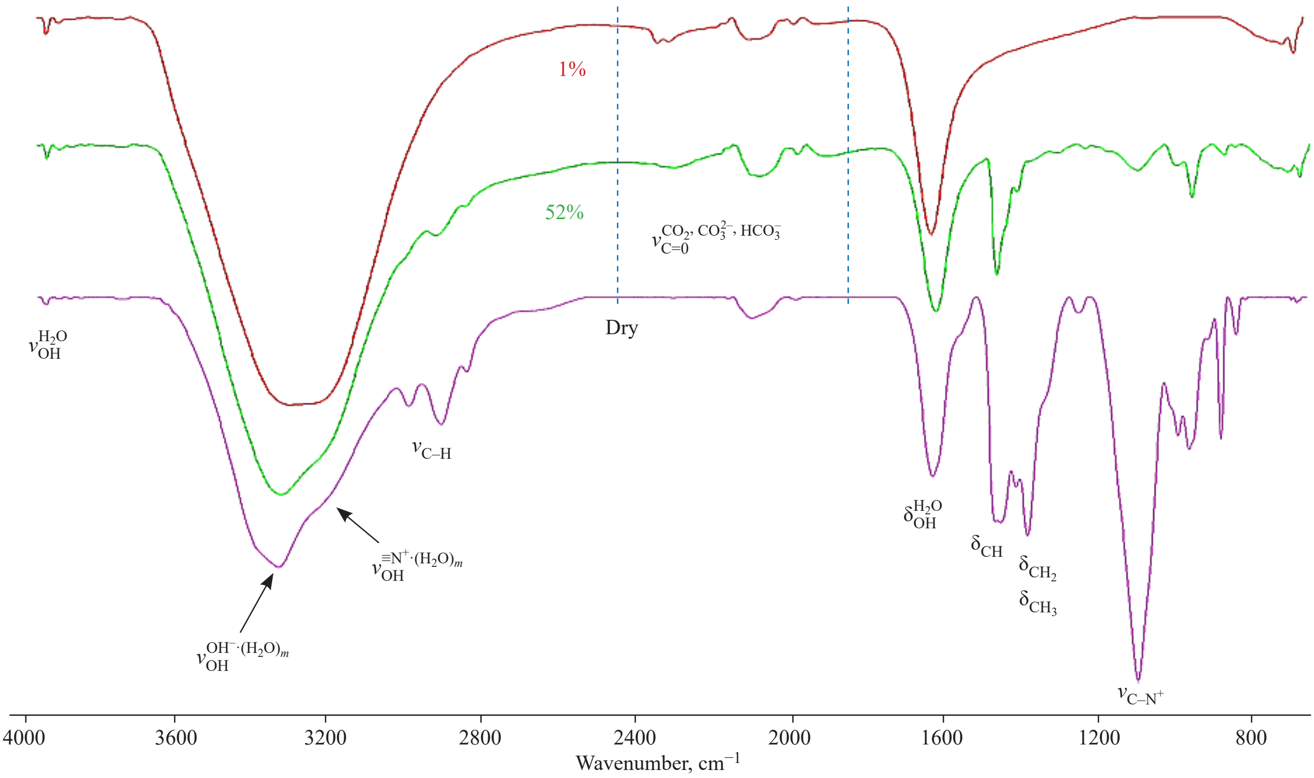


Fig. 4. IR spectra of polyDADMAC solutions of various concentrations from 1 to 96 wt %

overlapping signals of stretching vibrations in the range of ν = 3650–3050 cm^{-1} and bending vibrations of water $\delta_{\mathrm{H_2O}}$ = 1635–1640 cm^{-1} shows almost no polyDADMAC vibration bands due to the overlap with the H_2O bands.

It should be noted that, even for a virtually completely dried sample, the IR spectrum is dominated by the vibration bands of adsorbed water. As can be seen from Fig. 4, the band of stretching vibrations is divided into two signals characteristic of a strongly adsorbed phase in the form of SSIP and free water, which agrees with the published data [19].

The vibration bands of the polyelectrolyte become clearly distinguishable for a concentrated aqueous sample (52 wt %), i.e., in the region of the "water-in-polymer" system, or for dried samples (≈96 wt %).

The stretching vibrations of the C–H bond occur at ν = 2937 cm^{-1} and δ = 1470 and 1370 cm^{-1} in the CH_2 groups and the terminal CH_3 groups of the polymer chain. The stretching vibrations of the C–N$^+$ bond are characterized by an intense vibration band with a maximum at ν = 1080 cm^{-1}.

We may also note the occurrence of vibration bands in the range of 2100–2200 cm^{-1} due to the presence of carbonate and bicarbonate ions bound to the polyelectrolyte, which agrees with the previously obtained data [28] and confirms the possibility of using polyDADMAC solutions for gas treatment.

The results obtained suggest that the exchange of Cl$^-$ anions for OH$^-$ ions of water for the monomer and polymer occurs according to the schemes shown in Figs. 5 and 6, respectively, which should be manifested in both monomeric and polymeric QASs.

According to the proposed scheme and as confirmed in the present work, monomeric and polymeric QASs are pH-sensitive and can be titrated in both acidic and alkaline media.

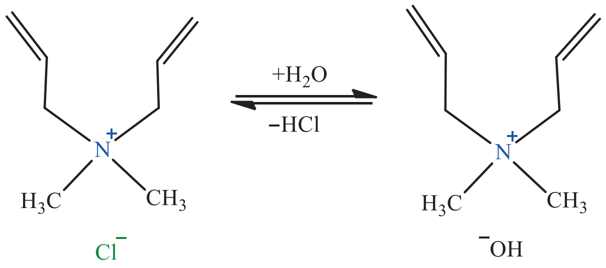


Fig. 5. Scheme of anion exchange at ammonium N$^+$ centers in polyDADMAC in water

Figure 7 illustrates the results of acid–base titration of monomeric and polymeric QASs separately with hydrochloric acid and sodium hydroxide. The curves of titration with acid and alkali at polyelectrolyte concentrations of 2.7, 5.4, and 10.8 wt % are combined

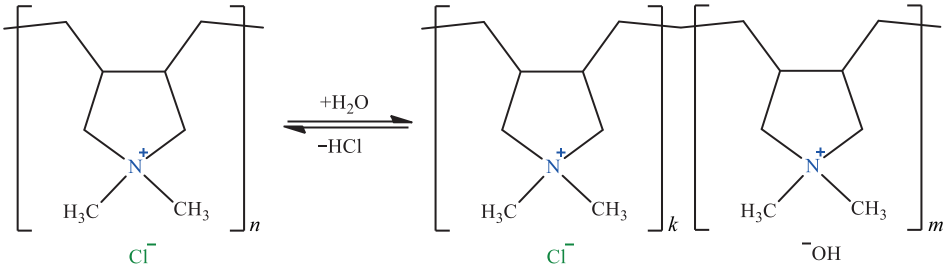


Fig. 6. Scheme of anion exchange at ammonium N^+ centers in polyDADMAC in water ($n = k + m$)

into a common graph (Fig. 7b). In contrast to the monomer, for which equilibrium between the chloride and hydroxide forms of QAS is observed (Fig. 5), in the case of polymeric QASs (Fig. 7), in the polyelectrolyte molecule, equilibrium is achieved between the polymer units containing different counterions Cl^- and OH^-.

As can be seen from Fig. 7, the titration curves have a typical sigmoid shape with a single pH step, which confirms the proposed anion exchange schemes (Figs. 5 and 6). The equivalence point (EP) for QASs virtually corresponds to a ratio of equivalents n_{eq} of ~1 and shows that all monomer anions are accessible for titration.

A different picture is observed in the case of polyDADMAC, for which the EP shifts from the alkaline to the acidic region: pH_{EP} = 7.75, 6.16, and 5.24 as the polymer concentration is increased from 2.7 and 5.4 to 10.8 wt %, respectively, which confirms the pH sensitivity of the polyelectrolyte according to the scheme (Fig. 6). At the same time, the number of HCl equivalents remains virtually unchanged after quadrupling the polyelectrolyte concentration and is $n_{eq} \approx 0.032$. This result confirms that the polyelectrolyte in the solution exists in the form of an impermeable polymer coil, and only a part of the anions located on the surface is accessible for exchange.

This state of the polyelectrolyte can be characterized as a PCC. Since the equilibrium distribution of counterions Cl^- or OH^- in the PCC between the polyDADMAC units or the ratio of units $k : m$ (Fig. 6) will depend on the nature of the exchanging anion, a change in the size of the polymer coil occurs, which we confirmed by the DLS method.

In the DLS spectra of the initial polyDADMAC (Fig. 8a) and the polymer treated with an anion exchanger (PDMDAA–OH) (Fig. 8b), three modes of polymer coil motion are observed: fast (F), intermediate (I), and slow (S).

Depending on the concentration of the polyelectrolyte, three to five modes of motion can appear in the DLS spectrum [22, 23]. The diffusion coefficients D of the fast and slow modes of motion of the macromolecular coils depend linearly on the polymer concentration C_p [23, 24]:

$$D = D_0(1 + K_D C_p), \tag{4}$$

where D_0 is the diffusion coefficient as $C_p \to 0$ and the diffusion coefficient constant K_D is determined by the balance of bulk and hydrodynamic interactions. Whereas

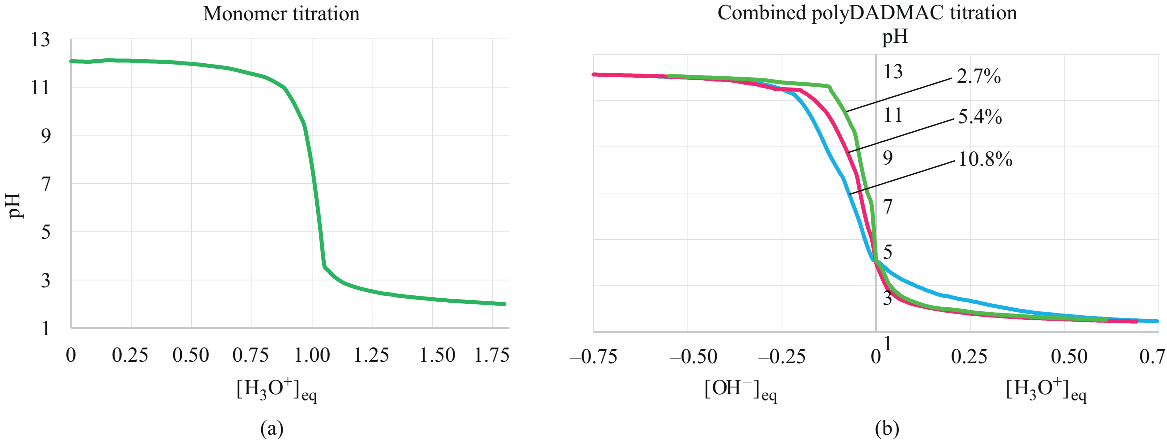
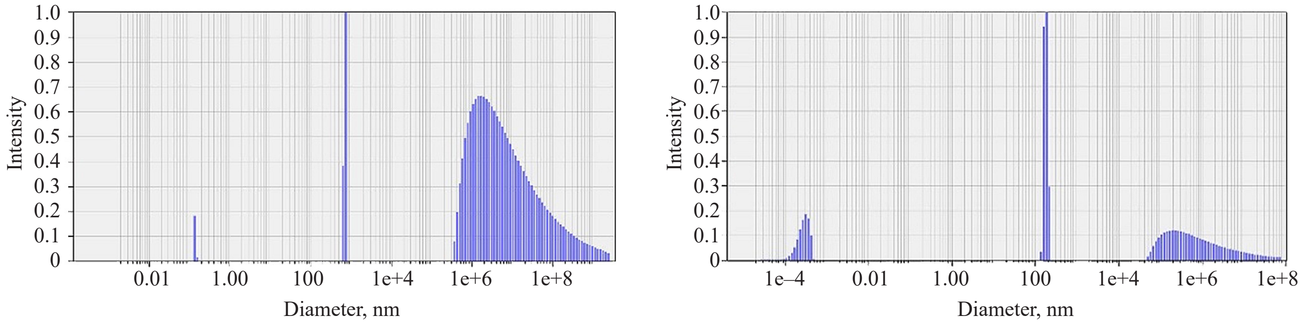


Fig. 7. (a) Titration curve of the monomer and (b) the full titration curve of the 0.3 *M* polyelectrolyte with 0.1 *M* NaOH and 0.1 *M* HCl. $[H_3O^+]_{eq} = n(HCl)/n(polyDADMAC)$; $[OH^-]_{eq} = n(NaOH)/n(polyDADMAC)$



(a)
$D = 1.8\cdot10^{-12}$ см^2/с (92%)
pH 3.96

(b)
$D = 4.8\cdot10^{-11}$ см^2/с (63%)
pH 11.83

Fig. 8. Dynamic light scattering (DLS) spectra of the initial 0.3 *M* polyDADMAC and the treated 0.3 *M* polyDADMA–OH

the slow mode characterizes the agglomeration or contraction of the polymer chain into a polymer coil, the nature of the fast mode remains somewhat unclear [23]. Table presents the diffusion coefficients of the slow mode of motion for PCCs with various inorganic acids. The slow mode of motion (S) is of the greatest interest since it reaches micron sizes and is contained in the maximum amount (Table).

As will be shown, the state of polyDADMAC and the number of modes of motion of polymer coils significantly depend on the nature of the X^{n-} anion.

The DLS spectra of the acidic form polyDADMAC and alkaline form polyDADMA–OH of the polyelectrolyte (Fig. 8) differ noticeably in content and diffusion coefficients of the slow mode S_1 of the polymer coils. This confirms the influence of the anion

Table. Results of potentiometric titration and DLS data on polyDADMA–OH + H_nX_m system

Acid	n_{eq}	pH_{EP}	F (EP), %	S (EP), %	D_S (EP)·10^{11}, cm^2/s	pK_a(H_nX)	ΔH_s, kJ/mol
–*	–	11.83*	8.2*	63.3*	4.80*	–	–
$HClO_4$ **	0.359	4.69	50.2	48.9	0.03	−15.20	−88.41
HCl	0.205	4.75	22.7	75.0	13	−5.60	−74.52
HNO_3	0.188	6.26	35.9	47.7	7.1	−1.64	−32.90
HBF_4	0.087	7.36	1.9	97.1	58	−0.44	–
NH_2SO_3H	0.250	5.65	3.1	77.6	15	1.00	–
H_2SO_4	0.048	7.67	66.3	28.6	0.68	−3.0 / 1.9	−76.73
H_3PO_4	0.067 / 0.162	8.89 / 4.43	17.4	74.8	3.3	2.14 / 7.20 / 12.37	−10.71
H_3BO_3	0.077 / 0.296	10.79 / 9.21	33.6	26.7	14	9.24 / 12.40 / 13.30	20.05
H_5IO_6	0.184 / 0.336	8.64 / 4.76	64.9	20.4	6.1	3.29 / 8.31 / 11.60	–

Note:
* Data for 0.3 *M* polyDADMA–OH solution.
** A white precipitate is formed.
$n_{eq} = n(H_nX)/n$(polyDADMA–OH).
ΔH_s is the heat of H_nX_m solvation in water.
pH_{EP} is the pH value at the EP of the titration curve.
D_S (EP) are the diffusion coefficients of the slow mode at the EP, cm^2/s.

nature and acidity on the aggregation of the polyelectrolyte.

Whereas the fraction of the slow mode S decreases from 92.0 to 63.3%, the polyDADMA–OH solution is characterized by a narrower molecular weight distribution and an increase in the contribution of the fast mode of motion (F) from 1.0 to 8.2%. This is apparently due to a change in the size of the polymer coil involving an increase in the fraction of units containing OH^- anions. The diffusion coefficient of the mode S is observed to quadruple. At the same time, adsorption of some larger aggregates on the anion exchanger cannot be ruled out.

As inorganic acids and salts, substances differing in strength (pK_a) and heat of solvation of H_nX_m in water (ΔH_s) were selected. Table presents the results of potentiometric titration and DLS data on the polyDADMA–OH + H_nX_m system for EPs.

As can be seen from Table, the degree of substitution of polyelectrolyte anions for acid anions H_nX_m does not exceed n_{eq} = 0.184–0.336. This confirms that polyDADMAC in solution exists in the form of an impermeable polymer coil and that only a part of the anions located on the surface of the polymer coil is accessible for exchange. In this case, the result of exchange for the X^{m-} anion is the presence of 3 types of links in the polyelectrolyte structure (Fig. 9).

In the case of $HClO_4$, the titration of the system yields an insoluble white precipitate at the EP having an extremely low value of the diffusion coefficient of the slow mode of motion S with D_S (EP) = $3 \cdot 10^{-13}$ cm^2/s. While the EP on the titration curve symbatically shifts from the acidic to the alkaline region from pH_{EP} 4.69 to 7.36, the degree of substitution of anions of monoprotic strong acids (n_{eq}) increases with increasing strength of the H_nX_m acid: $HClO_4 > HCl > HNO_3 > HBF_4$. The obtained result from the point of view of acid–base equilibrium shows that the exchange reaction of the acid anion X^{n-} occurs predominantly with the participation of the OH^- anion of the polyelectrolyte. An exception is the amino-substituted acid NH_2SO_3H with a low $pK_a(H_nX)$ = 1 value in the series of inorganic acids; however, this is capable of additional protonation at the amino group during titration.

The low value of n_{eq} = 0.048 for the strong dibasic acid H_2SO_4 and simultaneous shift of the pH of 7.67 to the alkaline region can be explained in terms of an exchange reaction that predominantly forms the HSO_4^- anion with pK_a = 1.9. A similar effect is observed for other polyprotic acids.

The triprotic acids H_3PO_4 and H_3BO_3 and the polyprotic periodic acid H_5IO_6 are characterized by two pH steps; here, despite the inverse relationship $pK_a(H_2X^-) < pK_a(H_3X)$, the degree of substitution at the second stage increases ($n_{eq}(H_2X^{2-}) > n_{eq}(X^{3-})$) with a decrease in the ion charge. This observed phenomenon agrees with the published data [13, 18] on the efficiency of anion exchange in the Hofmeister series. Thus, a change in the nature of the anion affects not only the degree of substitution, but also the state of the polymer coil (Fig. 10).

With a decrease in the acid strength pK_a in the acid series, the diffusion coefficient D_S (cm^2/s) of the slow mode S increases: $3 \cdot 10^{-13}$ ($HClO_4$), $7.1 \cdot 10^{-11}$ (HNO_3), $1.3 \cdot 10^{-10}$ (HCl), and $5.8 \cdot 10^{-10}$ (HBF_4). This corresponds to a decrease in the degree of association of the units of the polymer coil of PCC in the same series. The high value of the diffusion coefficient D_S of the slow mode for HBF_4 (Table) can also be explained by its partial dissociation in the alkaline medium of polyDADMA–OH into H_3BO_3 and HF to form a PCC with the F^- anion.

A decrease in the strength pK_a was also found to lead to the occurrence of two to three additional intermediate (I) modes of motion, which are the modes of interaction between the cationic nitrogen N^+ centers and anions. This argues for the formation of the PCC in the form of SSIP with different values of the diffusion coefficients *D* of the modes of motion of polymer coils.

In this case, both a broadening and an increase is observed in the contributions of fast (F) and intermediate (I) modes of motion in the series $HNO_3 > H_2SO_4 > H_3PO_4$ (Fig. 10; Table), which can be explained by the presence of different forms of anions of acidic and neutral salts.

The obtained result confirms that the process of solvation of acid anions X^{n-} by water molecules represents an important additional factor in the exchange

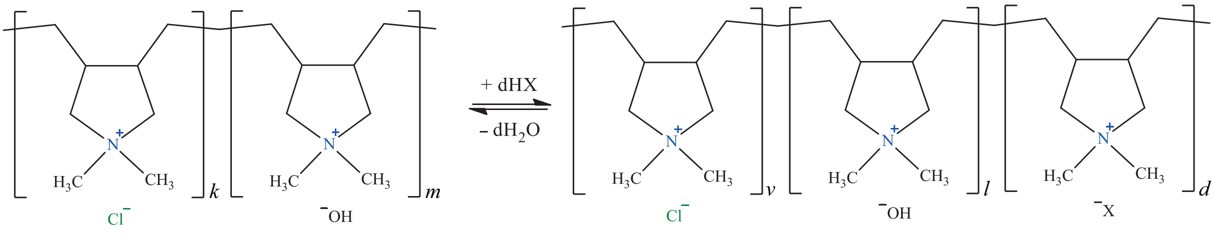
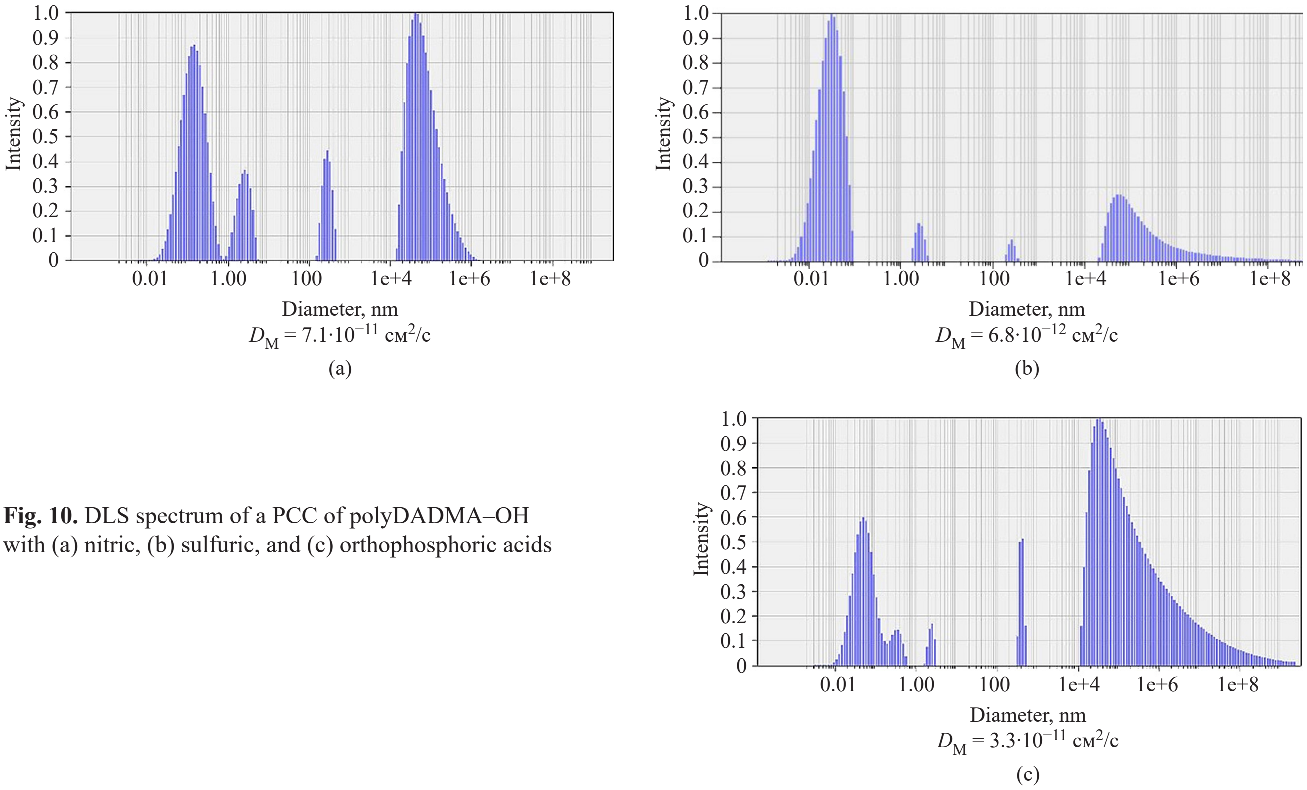


Fig. 9. Scheme of anion exchange at ammonium N^+ centers of polyDADMAC with H_nX ($k + m = v + l + d$)



$D_M = 7.1·10^{-11}$ см^2/с

(a)

$D_M = 6.8·10^{-12}$ см^2/с

(b)

$D_M = 3.3·10^{-11}$ см^2/с

(c)

Fig. 10. DLS spectrum of a PCC of polyDADMA–OH with (a) nitric, (b) sulfuric, and (c) orthophosphoric acids

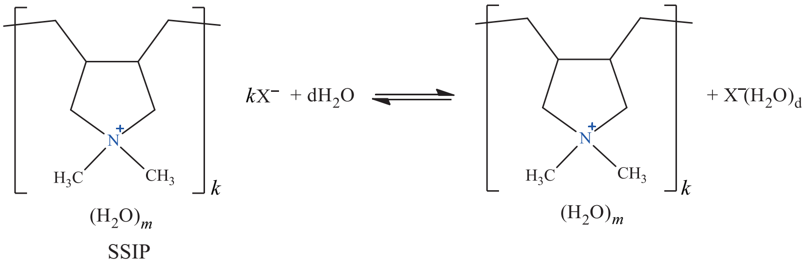


Fig. 11. Scheme of solvation of the solvent-separated ion pair (SSIP) anion: $X^- = ClO_4^-$, Cl^-, NO_3^-, BF_4^-, HSO_4^-, and $H_2PO_4^-$

(Fig. 11), which will affect both the strength of the PCC and the degree of dissociation of SSIP into a polymer cation and solvated anions $X^-(H_2O)_d$.

In this work, the degree of solvation of the X^{n-} anions is estimated using the heats of dissolution of the H_nX acids. A decrease in the exothermicity of the heat of dissolution of the inorganic acid from $\Delta H_s = -88.4$ to -10.71 kJ/mol of the H_nX acids (Table) leads to a symbatic decrease in the degree of substitution of the X^{n-} anions of the polymer coil from $n_{eq} = 0.359$ to 0.048, thus confirming that the solution contains not only SSIP aggregates, but also dissociated forms of the polyelectrolyte. The exceptions to this rule are sulfur-containing acids H_2SO_4 and NH_2SO_3H, which form HSO_4^- and $NH_2SO_3^-$ anions during titration.

CONCLUSIONS

The reported DLS, potentiometry, and IR spectroscopy studies confirm that the polymer electrolyte polyDADMAC exists in an aqueous solution in the form of impermeable polymer coils, which are made up of polymer solvent-separated ion pairs (SSIPs). Here, the Cl^- anion of the polyelectrolyte is exchanged for the OH^- ion of water or the X^{n-} anions of inorganic acids to form polymer chain links with various counteranions. The anion exchange, which mainly occurs on the surface of the polymer coil and depends on the strength, nature, and basicity of the H_nX_m acids, serves to limit the degree of anion substitution. The obtained forms of substituted polyelectrolyte can be classified as PCCs.

The substitution of the X^{n-} anions of strong acids in the series $HClO_4 > HCl > HNO_3 > HBF_4 > H_2SO_4$, H_3PO_4, which mainly involves the OH^- anion of the polyelectrolyte, decreases with decreasing strength of the HX acid from $n_{eq} = 0.336$ to 0.07. This also leads to significant changes in the sizes of the slow-mode PCC coil, for which the diffusion coefficient increases from $D = 3.0 \cdot 10^{-13}$ to $1.3 \cdot 10^{-10}$ cm^2/s, as well as corresponding to a decrease in the degree of association of the PCC polymer coil links in the same series.

The degree of exchange for polyprotic acids is limited by the formation of mainly monoprotic anions HSO_4^- and $H_2PO_4^-$ corresponding to the first stage of substitution. The fallout from the trend of the influence of the strength of the acids H_3BO_3 and H_5IO_6 is explained by their ability to form polymeric forms of anions in solution, which are stabilized by the polymer matrix of polyDADMAC.

The exchange of anions at the ammonium centers of polymeric QASs is established to be an important factor influencing the degree of solvation of acid anions X^{n-} by water molecules. A decrease in the degree of solvation (ΔH_s) of acids H_nX_m in water symbatically reduces the degree of substitution of X^{n-} anions of the polymer coil, as well as the strength of the forming PCC and its ability to dissociate into a polymer cation and solvated anions $X^-(H_2O)_d$.

Authors' contributions

Ya.N. Golubeva—conducting research, collecting and processing the material, and writing the text of the article.

A.V. Krylov—development of the concept of scientific work, critical revision with the introduction of valuable intellectual content.

T.A. Chebotareva—reviewing publications on the topic of the article.

The authors declare no conflict of interest.

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About the Authors

Yaroslava N. Golubeva, Postgraduate Student, Ya.K. Syrkin Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (78, Vernadskogo pr., Moscow, 119454, Russia). E-mail: golubeva.ya.n@gmail.com. https://orcid.org/0009-0008-2344-6933

Alexander V. Krylov, Cand. Sci. (Chem.), Associate Professor, Ya.K. Syrkin Department of Physical Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (78, Vernadskogo pr., Moscow, 119454, Russia). E-mail: allylnmr@yandex.ru. Scopus Author ID 57484351900, RSCI SPIN-code 5633-1360, https://orcid.org/0000-0002-2389-9026

Tatyana A. Chebotareva, Master Student, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (78, Vernadskogo pr., Moscow, 119454, Russia). E-mail: chiebotariova.t@mail.ru. https://orcid.org/0009-0008-8412-7098

Об авторах

Голубева Ярослава Николаевна, аспирант, кафедра физической химии им. Я.К. Сыркина, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119454, Россия, Москва, пр-т Вернадского, д. 78). E-mail: golubeva.ya.n@gmail.com. https://orcid.org/0009-0008-2344-6933

Крылов Александр Владимирович, к.х.н., доцент, кафедра физической химии им. Я.К. Сыркина, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119454, Россия, Москва, пр-т Вернадского, д. 78). E-mail: allylnmr@yandex.ru. Scopus Author ID 57484351900, SPIN-код РИНЦ 5633-1360, https://orcid.org/0000-0002-2389-9026

Чеботарева Татьяна Александровна, магистр, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119454, Россия, Москва, пр-т Вернадского, д. 78). E-mail: chiebotariova.t@mail.ru. https://orcid.org/0009-0008-8412-7098

Translated from Russian into English by V. Glyanchenko
Edited for English language and spelling by Thomas A. Beavitt