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Cationic electrolyte copolymers of diallyldimethylammonium chloride with carboxybetaine 2-(diallyl(methyl) ammonio) acetate of various compositions in water solutions of different ionic strengths

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Abstract

Random copolymers of diallyldimethylammonium chloride (DADMAC) and carboxybetaine 2-(diallyl(methyl)ammonio) acetate (DAMA) with different compositions (10%/90%), (50%/50%) and (70%/30%), as well as poly(DAMA) and poly(DADMAC) homopolymers, were synthesized. Molecular characteristics of poly(DADMAC–co–DAMA) copolymers and homopolymers were determined in water solutions in the presence of 0.1 M NaOH and a low molecular weight salt (NaCl in various concentrations) by viscometery, dynamic and static light scattering. Dependences of several important conformational parameters, such as swelling coefficient α, the Huggins constant k_H, and the second virial coefficient A_2, on copolymer composition (charge asymmetry) and NaCl concentration in solution were analyzed. It was shown that growth of charge asymmetry leads to sharp increase in copolymer size.

Keywords Polyelectrolyte · Polybetaine · Conformation · Solution

Introduction

In recent years, cationic polyelectrolyte poly(diallyldimethylammonium chloride) (poly (DADMAC)) has attracted increasing interest of researchers due to its unique chemical structure and a variety of current and possible applications [1–5]. The processes that allow for commercial production of poly(DADMAC) have been developed. The materials based on this polymer show high thermal stability and can function even under extreme environmental conditions [6, 7]. Polycarboxybetaine poly(2-(diallyl(methyl)ammonio)acetate (poly(DAMA)) is similar to poly(DADMAC) in chemical

structure of the main chain. DAMA monomer contains a carboxylic group bonded to nitrogen through a methylene group. Carboxylic groups are ionizable in neutral and alkaline media, which allows obtaining negative charge within a single monomer unit, together with positive charge. Copolymerization of DADMAC with DAMA provides an opportunity to combine properties of polyelectrolyte (poly(DADAMAC)) and polybetaine (poly(DAMA)) in one macromolecule, and to control the effect of environment on polymer properties by varying the ratio of monomer units. It should be noted that the copolymer almost completely retains useful properties of these two homopolymers (such as solubility and thermal stability [8–10]).

It is rather difficult to provide quantitative theoretical description of properties of multiply charged macromolecular systems; moreover, such theories give only qualitative predictions for limiting cases. Therefore, it is most convenient to study influence of composition and environmental conditions on the properties of such macromolecules by experimental methods used in polymer physics.

Recently, we have obtained random poly(DADMAC-co-DAMA) copolymers containing 28% of cationic units and 72% of betaine units [11]. After dissociation, DADMAC units acquired positive charges, while DAMA units carried both

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positive and negative charges. Molar masses and hydrody-namic properties of the synthesized copolymers were studied in alkaline media of different ionic strengths. It was established that at insignificant concentrations of low molec-ular weight salt, the copolymer exhibits properties typical of polyelectrolyte, while at higher salt concentrations, intrinsic viscosity of the polymer practically does not depend on salt concentration (which is characteristic of polybetaines). Hence, varying copolymer composition makes it possible to change behavior of macromolecules in solution in the presence of a low molecular weight salt. To gain the detailed insight into this process, it is necessary to study a series of copolymers over a wider composition range.

In the present work, samples of poly(DADMAC-co-DAMA) copolymers of different compositions (10%/90%, 50%/50%, and 70%/30%), as well as samples of DAMA and DADMAC homopolymers, were synthesized. Molar masses and hydrodynamic characteristics of the synthesized copolymers and homopolymers were studied in water, in the presence of 0.1 M NaOH and low molecular weight salt NaCl (at various concentrations) using dynamic (DLS) and static (SLS) light scattering as well as viscometry.
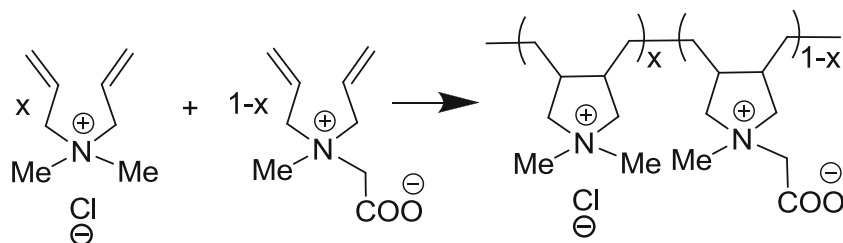
Experimental

Materials

Polymers of DADMAC [12] and DAMA [13], as well as their copolymers [11], were prepared according to the conventional procedure (see Fig. 1). The monomers were polymerized in aqueous solution (C = 4.0 M) after removal of oxygen; 4,4′-azobis-(4-cyanovaleric acid) was used as an initiator; the po-lymerization proceeded at 60 °C for 4 h. The product was precipitated into propanol-2, purified by dialysis against de-ionized water in Spectra/Por 1 membrane, concentrated in vacuum and isolated by lyophilization.

Table 1 presents the percentage values of components in the synthesized copolymers. The obtained samples were de-noted by two letters (*pe* = polyelectrolyte; *pb* = polybetaine; *co* = copolymer). For copolymers this letters are followed by a number in brackets that represents the percentage of DADMAC (x) monomer units in copolymer.

Methods

Dynamic (DLS) and static (SLS) light scattering experiments were carried out using a "PhotoCor-Complex" apparatus (Photocor Instruments Inc., Moscow, Russia) equipped with a real-time correlator (288 channels, minimal $\tau = 10$ *ns*). Laser ($\lambda = 405$ nm) was used as an excitation source; the experiments were carried out at scattering angles (ϑ) ranging from 30° to 140° at a temperature of 25 ± 0.1 °C. Autocorrelation functions of scattered light intensity $G^{(2)}(t) = \langle I(t_0)I(t_0 + t)\rangle/\langle I(t_0)\rangle^2$ were processed using DynaLS software. It provides distributions $I(\tau)$ of scattered light intensities by relaxation times τ in accor-dance with the relation: $G^{(1)}(t) = \int I(\tau) e^{-t/\tau} d\tau$, where $G^{(1)}(t)$ is related to $G^{(2)}(t)$ by Siegert relation $G^{(2)}(t) = B + \beta|G^{(1)}(t)|^2$, here B is base line, and β is coherence factor.

The distributions $I(\tau)$ of scattered light intensities by relaxa-tion times τ contain two main peaks (see Fig. 2b, e, h). The first one corresponds to the diffusion of individual macromolecules; the second peak may be attributed to the presence of some number of high molar mass species in solutions. The nature of this species may be related to the presence of cross-linked polymers, appeared during storage or isolation of polymer, due to radical oxidation. Mass fractions of the high molar mass species, were estimated using relations from [14–17]. They do not exceed 1–2%, this makes impossible an observation of this fraction by NMR and viscometry. It should be noted that the presence of the slow mode in polyelectrolyte solutions is a famous problem, it was discussed particularly in [18, 19].

The dependence between $1/\tau$ (where τ is the maximum position of $I(\tau)$ distribution) and the scattering vector squared $q^2 = (4\pi n/\lambda \sin(\vartheta/2))^2$ for all studied samples was a straight line passing through the origin, this indicating diffusional character of the observed processes [20–22]. Translational diffusion coefficients D at fixed concentrations were calculat-ed from the slope of this line according to the following rela-tionship: $1/\tau = Dq^2$. The diffusion coefficients D_0 were deter-mined by extrapolation of $D(c)$ dependence to infinite dilution in accordance with equation: $D(c) = D_0(1 + c2A_2M)$.

Hydrodynamic radius R_h was calculated using the Stokes – Einstein equation [23].

$$R_h = kT/(6\pi\eta_0 D_0) \qquad (1)$$

Fig. 1 Preparation of poly(DADMAC-co-DAMA) copolymers

Table 1 Studied copolymers notation, percentage values of components and percentage values of charges

Sample	Composition		Charges	
	DADMAC %	DAMA %	(+), %	(−), %
pb	0	100	50	50
co(10)	10	90	53	47
co(50)	50	50	67	33
co(70)	70	30	77	23
pe	100	0	100	0

Weight-average molar masses M_W of the studied samples were determined from the static light scattering data according to the following equation:

$$Hc/R_\vartheta|_{\vartheta \to 0} = 1/M_W + 2A_2 c \qquad (2)$$

where $H = 4\pi^2 n_0^2 (\partial n/\partial c)^2 / (\lambda^4 N_A)$, R_ϑ is the Rayleigh relationship, A_2 is the second virial coefficient, $\frac{\partial n}{\partial c}$ is the refractive index increment, and N_A is the Avogadro number [24]. Rayleigh relationship was calculated from the equation $R_\vartheta = \left(\frac{n_0}{n_T}\right)^2 \frac{I_s(\vartheta) - I_0(\vartheta)}{I_T(\vartheta)} \left(R_T \cdot I_p(\vartheta)\right)$, where $I_s(\vartheta)$, $I_0(\vartheta)$, $I_T(\vartheta)$ are scattered light intensities of studied solution, solvent and toluene at fixed angle, R_T is toluene Rayleigh ratio, n_T is toluene refractive index, $I_p(\vartheta)$ is an area of the peak on I(τ) distribution which corresponds to individual macromolecules [14, 15, 18].

Refractive indices of the solutions and the solvents were determined using an RM-40 automatic refractometer (Mettler Toledo, Switzerland). The following values of refractive indices were obtained: $n_0 = 1.3335$ for aqueous solution of 0.1 M NaOH; $n_0 = 1.3346$ for (0.1 M NaOH +0.1 M NaCl) solution, and $n_0 = 1.3433$ in the case of (0.1 M NaOH +1 M NaCl) solution.
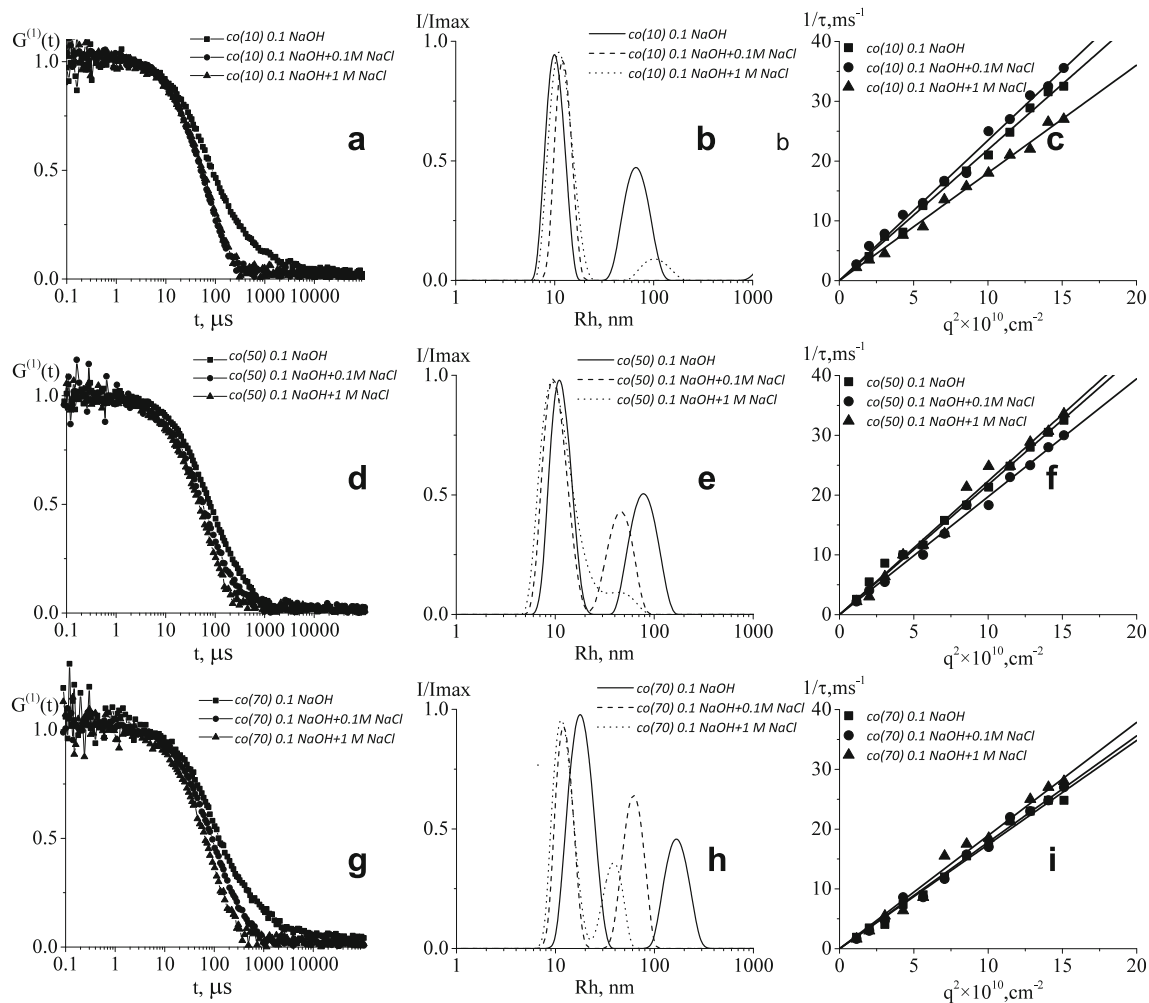
Fig. 2 Autocorrelation functions of scattered light intensity $G^{(1)}(t)$ of copolymers *co(10)* (**a**); *co(50)* (**d**); *co(70)* (**g**) at different NaCl concentrations. Normalized distributions of hydrodynamic radii R_h derived from the data on scattered light intensity I/I_{max} for *co(10)* (**b**); *co(50)* (**e**); *co(70)* (**h**). The dependence between $1/\tau$ and the scattering vector squared q^2 for *co(10)* (**c**); *co(50)* (**f**); *co(70)* (**i**)

Viscosities of the investigated samples were measured with the use of a Lovis 2000 M rolling-ball microviscometer (Anton Paar, Austria) at 25 °C; the capillary inclination angle was varied from 55° to 35° at 5° intervals. The obtained values of dynamic viscosity of a solution η were averaged over a series of angles and used in calculations of reduced viscosity ($\eta_r = (\eta - \eta_0)/(\eta_0 c)$), where c is the concentration of a solution. After extrapolation of reduced viscosity to infinite dilution, intrinsic viscosity $[\eta]$ of the polymer under study was determined using the relationship $\eta_r = [\eta] + ck_H[\eta]^2$ [24]; here, k_H is the dimensionless Huggins constant [25]. The k_H constant, which characterizes a polymer - solvent system, depends on solvent quality. In θ-solvents, it is close to 0.4–0.7; in good solvents, $k_H = 0.2 - 0.4$ [26]. The following solvent viscosity values η_0 were obtained: $\eta_0 = 0.92$ cP for aqueous solution of 0.1 M NaOH; $\eta_0 = 0.93$ cP for (0.1 M NaOH +0.1 M NaCl)

solution, and $\eta_0 = 1.01$ cP in the case of (0.1 M NaOH +1 M NaCl) solution.

Density measurements were performed using a DM40 densitometer (Mettler Toledo, Switzerland).

Results and discussion

Molecular properties of DADMAC-co-DAMA copolymers

Concentration dependences of reduced viscosity and translation diffusion coefficient of copolymers are presented in Fig. 3. For all solvents and samples, these dependences were approximated by straight lines. The values of translation diffusion coefficients D_0 and intrinsic viscosities $[\eta]$ of the
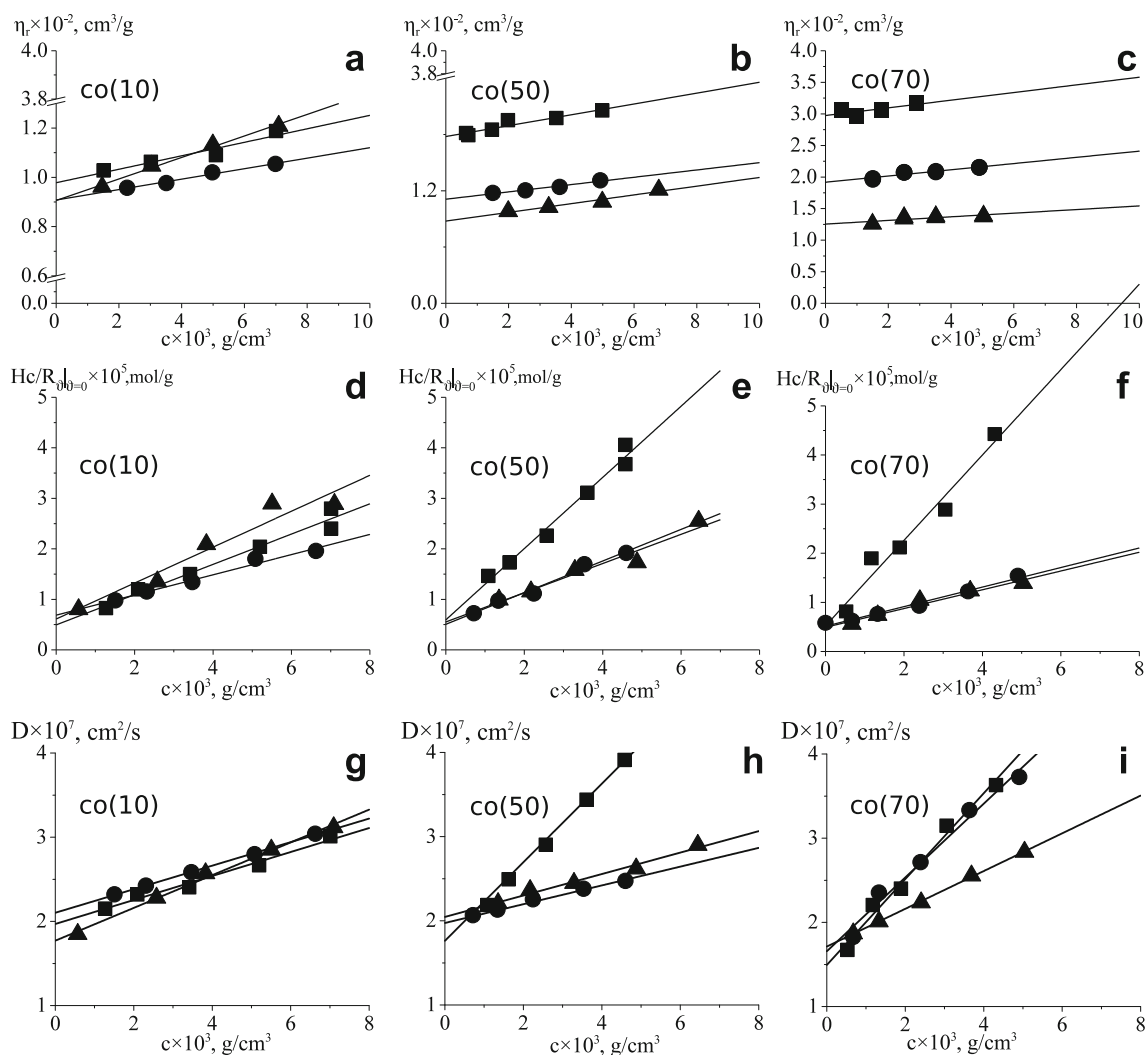

Fig. 3 Concentration dependences of reduced viscosity η_r of copolymers co(10) (a); co(50) (b); co(70) (c). Concentration dependences of $Hc/R_\theta|_{\theta \to 0}$ for copolymer samples co(10) (d); co(50) (e), and co(70) (f). Concentration dependences of translation diffusion coefficient D for copolymer samples co(10) (g); co(50) (h), and co(70) (i). Solvents: 0.1 M NaOH (■); 0.1 M NaOH+ 0.1 M NaCl (●); 0.1 M NaOH+1 M NaCl (▲)

studied samples were determined by extrapolation of the above dependences to infinite dilution.

The values of weight average molar mass M_W and the second virial coefficients A_2 of copolymers were determined by static light scattering in three solvents: 0.1 M NaOH, (0.1 M NaOH +0.1 M NaCl) and (0.1 M NaOH +1 M NaCl) (see Table 2 and Fig. 3d, e, f).

The concentration dependence of the difference between refractive indices of solutions and solvents for all samples was a linear relationship (Fig. 4). The value of refractive index increment $\left(\frac{\partial n}{\partial c}\right)$ was equal to 0.18 cm^3/g for all the studied polymer solutions. Molecular characteristics of the studied copolymers are presented in Table 2.

Degree of polymerization Z of the studied samples was determined from the $Z = M_W/M_0$ ratio, where M_0 is the molar mass of a monomer unit. It was calculated using the following equation: $M_0 = M_{0DADMAC}x + M_{0DAMA}(1-x)$. Here M_{0DAMA} and $M_{0DADMAC}$ are the molar masses of the DAMA and DADMAC monomer units correspondingly.

The values of equilibrium rigidity A for the investigated copolymers were estimated from the relationship:

$$\frac{1}{A} = \frac{1}{A_{DADMAC}} x + \frac{1}{A_{DAMA}} (1-x) \qquad (3)$$

where A_{DADMAC} is the Kuhn segment length of the DADMAC macromolecule, and A_{DAMA} is the Kuhn segment length of the DAMA macromolecule [11–13]. The values of equilibrium rigidity A obtained from Eq. (3) were equal to 4 nm for sample *co(10)*, 4.7 nm for *co(50)*, and 5.2 nm for *co(70)*. Taking into account the length of the projection of a monomer unit on the direction of maximum elongation λ (that is equal to 0.28 *nm* [12, 13, 27] for polymers with DADMAC backbone), we

calculated the amount of the Kuhn segments per macromolecule $N = \frac{Z\lambda}{A}$ (see Table 2).

It can be concluded that all the studied samples consist of more than 20 Kuhn segments, and, therefore, draining effects do not make a decisive contribution into hydrodynamic behavior of macromolecules [23]. Note that k_H and A_2 demonstrate dependence on molar mass, although the A_2 and k_H values depend very slightly on molar mass of a sample [24, 28, 29] at fixed salt concentrations.

Dependence of conformational properties on charge asymmetry of DADMAC-co-DAMA copolymers

It was shown in [11, 13] that the decisive contribution into conformational changes of the DAMA macromolecules and the DADAMC-co-DAMA copolymer with 28% DADMAC units was made by interactions between the units widely separated along the chain. This fact, as well as relatively high degrees of polymerization of the samples under study, makes it possible to use the Flory ratio:

$$[\eta] = \Phi_\infty \alpha^3 \langle h_0^2 \rangle^{3/2} / M \qquad (4)$$

where Φ_∞ is the Flory constant, $\langle h_0^2 \rangle$ is the mean square vector connecting ends of a chain in ideal conditions, α is the macromolecule swelling ratio, which is equal to the ratio of the coil size $\langle h^2 \rangle^{1/2}$ to the coil size in θ-solvent $\langle h_0^2 \rangle^{1/2}$.

Figure 5a shows the dependence of the $[\eta]/[\eta]_{0.1M\ NaOH + 1M\ NaCl}$ ratio on concentration of the used low molecular weight salt (NaCl). The decrease in viscosity with increase in ionic strength of a medium is characteristic of all samples, but this effect is most pronounced in

Table 2 Molar masses and hydrodynamic characteristics of DADMAC-co-DAMA copolymers studied in 0.1 M NaOH at different NaCl concentrations (c_{NaCl})

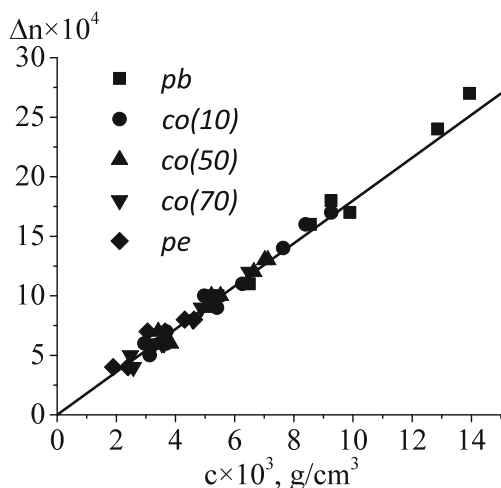| Sample	c_{NaCl}, M/L	$D \times 10^7$, cm^2/s	R_h, nm	$[\eta]$, cm^3/g	k_H	$M_W \times 10^{-5}$, g/mol	$A_2 \times 10^3$, mol × cm^3/g^2	Z	N
pb	0	2.4	9.9	78	0.43	1.4	1.5	732	31
	0.1	2.3	10.2	89	0.22	1.3	1.7	659	28
	1	2.1	10.3	95	0.26	1.3	1.6	642	27
co(10)	0	2.0	11.9	98	0.28	1.8	1.5	1029	47
	0.1	2.1	11.2	91	0.25	1.5	1.0	741	34
	1	1.8	12.0	91	0.54	1.6	1.8	823	38
co(50)	0	1.8	13.2	166	0.31	1.7	3.5	872	50
	0.1	2.0	11.7	111	0.32	2.0	1.6	1024	58
	1	2.0	10.8	88	0.61	1.8	1.4	937	54
co(70)	0	1.5	15.8	290	0.07	1.9	4.3	999	63
	0.1	1.7	13.8	190	0.13	1.9	1.1	1014	64
	1	1.7	12.7	120	0.41	2.0	1.0	1062	67
pe	0	2.4	9.9	127	0.08	0.7	8.9	384	28
	0.1	2.7	8.7	92	0.07	0.8	7.5	422	30
	1	2.9	7.5	54	0.31	0.6	2.7	325	23

Fig. 4 The concentration dependence of the difference $\Delta n = (n - n_0)$ between refractive indices of solutions n and solvents n_0 for studied samples

the case of copolymer with the maximum number of DADMAC units. When ionic strength of the medium changes by an order of magnitude (from $1M/L$ to $0.1\ M/L$), viscosities of solutions of this copolymer do not vary significantly. Sample *co(10)* exhibits noticeable swelling only if salt concentration remains below $0.1\ M/L$. This behavior agrees with the results obtained in [9].

The dependence between $[\eta]$ of a sample and NaCl concentration may be caused by changes in hydrodynamic sizes

of the macromolecules. This assumption is confirmed by the data of dynamic light scattering (Table 2). In addition, the values of the second virial coefficient A_2 for samples *co(50)* and *co(70)* in the absence of NaCl significantly exceed the corresponding values obtained in 0.1 M and 1 M NaCl (Table 2). For sample *co(10)*, increase in the second virial coefficient at decreasing salt concentration is less pronounced. This is most likely related to the fact that DAMA betaine units (that exhibit anti-polyelectrolyte behavior) predominate in this macromolecule. Sample *pb* showed typical anti-polyelectrolyte behavior (swelling of polymer coils) with increasing ionic strength of the medium. This phenomenon results from screening opposite charges along the chain, and hindering attraction between them. It will be recalled that this phenomenon is characteristic of carbobetaines in neutral environments and the media with pH approaching the alkaline values (i.e., when carboxyl groups are deprotonated [13, 30]).

It should be noted that all samples were studied under the conditions where polyelectrolyte effects do not manifest themselves explicitly (i.e., concentration dependences of reduced viscosity demonstrate the common linear character). In this case, conformation characteristics of the studied samples can be described in terms of volume effects [23]. Figure 5d shows dependences of the second virial coefficient A_2 on percentage of DADMAC units in a copolymer in 0.1 M NaOH and 0.1 M NaOH+1 M NaCl solutions. In the case of 0.1 M NaOH solution, increase in the fraction of DADMAC units in a copolymer leads to a sharp increase in its A_2 values. This indicates

Fig. 5 Dependence of $[\eta]/[\eta]_{0.1M\ NaOH + 1\ M\ NaCl}$ on concentration of low molecular weight salt NaCl (**a**); dependences of $(\alpha_{app}^5 - \alpha_{app}^3)$ (**b**), k_H (**c**), and A_2 (**d**) on DADMAC monomer fraction in a copolymer
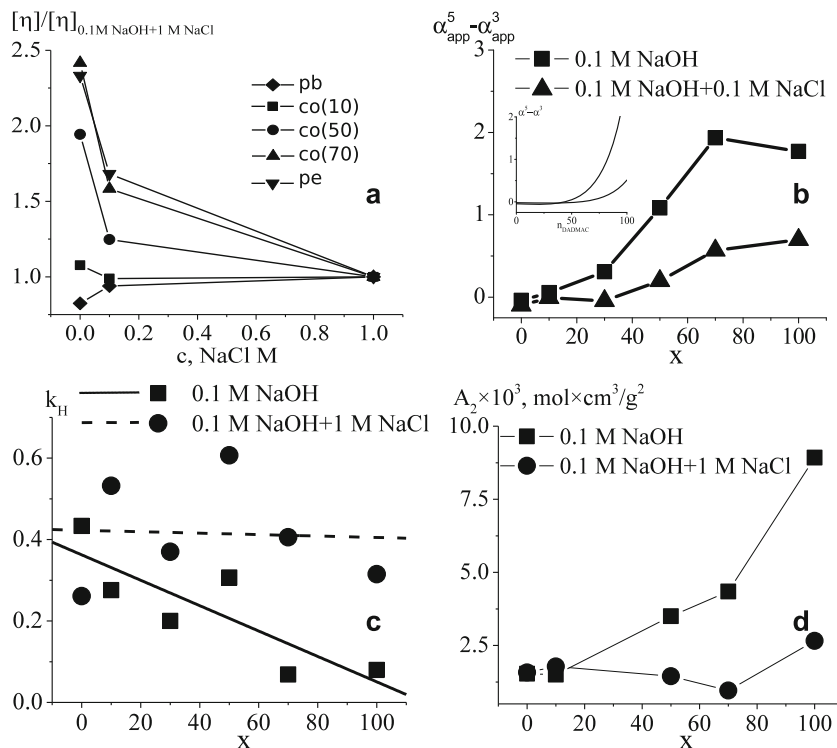
an increase in thermodynamic quality of the solvent. In the presence of 1 M NaCl, dependence between the second virial coefficient and the fraction of DADMAC units in samples is practically absent, which indicates screening of electrostatic attraction in the solution.

For the majority of samples, it was found that the Huggins constant decreases with decreasing concentration of a low molecular weight salt (NaCl), which also indicates rise in thermodynamic quality of solvent with decrease in the ionic strength of the medium. An exception is the **pb** sample that demonstrates the opposite behavior. The Huggins constant for this polymer in the absence of NaCl has a maximum value of 0.43. This is due to the fact that attraction between units of the polybetaine chain in the absence of NaCl is manifested as a decrease in thermodynamic quality of the solvent. The experimentally obtained dependences qualitatively agree with the theoretical results for conformational properties of polyampholytes and polyzwitterions in dilute solutions described in [31, 32]. Figure 5c shows dependences of the Huggins constants k_H measured in 0.1 M NaOH and (0.1 M NaOH +1 M NaCl) on contents of DADMAC units in copolymer. It was established that in 0.1 M NaOH, a decrease in k_H occurred with increasing percentage of DADMAC units. The obtained range of k_H values corresponds to the k_H values estimated for uncharged polymers in a good solvent [26], and thermodynamic quality of the solvent increases with increase in the fraction of DADMAC units in copolymer. In (0.1 M NaOH +1 M NaCl) solution, the dependence of k_H on DADMAC fraction (x) was not been observed; the k_H value averaged over all studied samples was close to 0.4, which corresponds to the k_H values observed in solutions of flexible chains in θ-solvents [26].

According to Eq. (4), the equality $[\eta]/[\eta]_{0.1NaOH+1NaCl} = \alpha^3/\alpha^3_{0.1NaOH+1NaCl}$ is true. The values of Φ_∞, M are mutually reduced. Suggesting that in $0.1\ M\ NaOH + 1\ M\ NaCl$ all the studied compounds (except for **pb**) have the lowest sizes and electrostatic interactions are screened, we can introduce the value of apparent swelling coefficient $\alpha^3_{app} = \alpha^3/\alpha^3_{0.1NaOH+1NaCl}$.

Figure 5b shows dependence of the $\alpha^5_{app} - \alpha^3_{app}$ difference on charge asymmetry in the studied macromolecules, and the inset in this figure shows the theoretical dependence obtained in [32]

$$\alpha^5 - \alpha^3 = \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2}\frac{N^{1/2}}{A^3}\left[B - \frac{\sqrt{\pi}l_b^{\frac{3}{2}}(f+g)^2}{2\sqrt{2}c_0} + \frac{(f-g)^2}{2c_0}\right]$$

Here f and g are the fractions of positive and negative charges in the chain, respectively, c_0 is the concentration of low molecular weight salt (NaCl) in solution, and l_b is the Bjerrum length. When plotting theoretical dependences, calculation of the equilibrium stiffness A in this relationship was carried out according to Eq. (3).

Note that there is qualitative agreement between theoretical and experimental data presented in Fig. 5b. In the absence of NaCl in solution, as well as in the presence of 0.1 M NaCl, an increase in the fraction of electrolyte units in the copolymer ultimately leads to an increase in the $(\alpha^5 - \alpha^3)$ value. However, it should also be emphasized that, according to the experimental data obtained, low charge asymmetry leads to noticeable changes in the $\alpha^5_{app} - \alpha^3_{app}$ value, which were not observed in the theoretical dependence.

The effect of distribution of positively or negatively charged monomers along the chain on properties of polyampholytes was theoretically studied in [33]. It was found that alternating polyampholytes demonstrate higher solubility in comparison to random copolymers of the similar composition. In our case, every negative charge on the polymer chain is always accompanied by a positive charge in the DAMA monomer unit, that is, we are dealing with a partially ordered polyampholyte. Theoretical dependence for the $\alpha^5 - \alpha^3$ value was obtained in [32] for random polyampholytes, and, therefore, it may not correctly describe the behavior of a partially ordered polyampholyte.

It was shown in [11] that poly(DADMAC-co-DAMA) samples obtained by radical copolymerization of a mixture of the corresponding monomers are random copolymers. Consequently, DAMA and DADMAC monomers are distributed randomly along the chain. However, this system is peculiar, since one unit of DAMA monomer contains two opposite charges. One of important properties of the resulting macromolecule is that each negative charge on the chain is adjacent to a positive one. That is, no local area of the chain contains the prevailing amount of negative charges. Copolymerization of DAMA and DADMAC monomers at different molar ratios results in copolymers where, depending on the x ratio, positively charged monomers predominate to varying degrees. It was shown in [34] that block co-polyampholytes are capable of forming intramolecular complexes between two oppositely charged "blocks" of a chain due to electrostatic forces, since in one fragment of this chain, positive charges prevail, and the other part contains mostly negative charges. In the case studied in the present work, this situation cannot be realized, and any change in charge asymmetry leads only to an increase in copolymer size.

Conclusions

Copolymerization of DADMAC with carboxybetaine monomer DAMA allows preparation of random copolymers whose properties can be controlled by varying the ratio of monomer units. Dependences of thermodynamic parameters of the solution, such as the second virial coefficient A_2 and the Huggins constant k_H, on charge asymmetry of the

copolymer, were obtained. It was established that an increase in charge asymmetry leads to an increase in thermodynamic quality of solvent (in the salt-free system). With increasing salt concentration in the solution, this dependence becomes less pronounced. Degree of sensitivity of the copolymer to environmental conditions can be changed by varying the DADMAC fraction in the copolymer. Thus, it was shown that varying composition of the copolymer may allow for fine adjustment of response of the resulting compound to environmental changes.

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