doi.org/10.26565/2220-637X-2017-28-02

УДК 544.777 + 547.864.51 + 547.264 + 54-128.4 + 543.42.062

INFLUENCE OF THE IONIC AND NON-IONIC ADDITIVES ON THE ACID STRENGTH OF NEUTRAL RED IN THE AQUEOUS SOLUTIONS OF POLY (SODIUM 4-STYRENESULFONATE)

A.Yu. Kharchenko, O.G. Moskaeva

Polyions of poly (sodium 4-styrenesulfonate) in aqueous solution may be considered as colloidal pseudophase. Analogously to micelles, some species can be bind by the charged polyelectrolyte coils. In this paper, the colored acid-base indicator dyes were used for studying the penetration of ionic and non-ionic solution components in polyelectrolyte coils. Such analysis relies on alteration of the acid strength of dyes. The aim of this work was to determine the dependences of the apparent ionization constants of neutral red, K_a^{app}, on the ionic strength of solution, I, in different mixed systems containing poly (sodium 4-styrenesulfonate) (NaPSS) and tetraethylammonium bromide, tetra-*n*-butylammonium iodide, or 1-butanol with NaCl. Neutral red is fixed in the polyelectrolyte coils due to electrostatic and hydrophobic interactions. The polyelectrolyte : dye concentration ratio, P : D, an important parameter for spectophotometrical measurements, equals 100. It was found that tetra-*n*-alkylammonium salts display a stronger influence on the acid strength of neutral red as compared with that of NaCl. For instance, in the case of tetraethylammonium bromide pK_a^{app} = 7.90 ± 0.07 at I = 0.02 M whereas pK_a^{app} = 8.45 ± 0.04 with NaCl at the same ionic strength. It can be explained by specifical adsorption tetra-n-alkylammonium cations on polyions ‘surface’. Introduction of 1-butanol significantly increases the acid strength of neutral red too, however its influence isn’t monotonic with change of ionic strength. The dependences of pK_a^{app} on log I were discussed in terms of regularities which are well-known for surfactant micellar systems. All mentioned systems were also examined by dynamic light scattering measurements using Zetasizer Nano ZS Malvern Instruments apparatus. As it turned out, when the ionic strength is 3×10^{-3} M or more the size (by number) of polyions in the presence of NaCl is of about 7 nm. Introduction of the additives results in somewhat higher size: in the case of 1-butanol the size of NaPSS is 10 nm.

Keywords: polyelectrolyte, poly (sodium 4-styrenesulfonate), neutral red, apparent ionization constant, butanol-1, tetra-*n*-alkylammonium cation.

Introduction

Nowadays, thermodynamically stable colloidal systems such as surfactant micellar solutions, microemulsions, and aqueous polyelectrolyte solutions are used in many technologically processes, particularly, in drug delivery [1,2] or water treatment [3]. The penetration of some compounds, including alcohols, dyes, biological molecules, into micelles is scrutinized [4,5]. Also, the surface properties of micelles are well known [6-8]. In particular, indicator dyes are used as molecular probes whose acid-base properties are changed in micellar microenvironment [4,9,10].

Some charged species, especially dyes, can be also concentrated around polyions. It is widely used in the creation of biosensors [11,12] or the polyelectrolyte titration [13]. Moreover, Baumgartner et al. [14] reported the decreasing in the indices of the apparent ionization constant of neutral red, pK_a^{app}, by 1.7 units in NaPSS solution on adding aprotic solvent dioxane (2.0 M). Thus, the non-ionic additives influence on the structure of NaPSS coils, and, simultaneously, on the properties of such molecular probes (dyes) fixed to the coils. Polyions’ structure may be changed by specific adsorption of organic counterions, particularly tetra-*n*-alkylammonium cations. It was confirmed by increase in solubility of oil-soluble dyes in such solution as compared with individual solutions of NaPSS or tetra-*n*-alkylammonium salts [15].

The degree of counterion binding is important parameter of colloidal particles. In micellar systems, this parameter is usually determined by conductivity or potentiometry methods [16-19]. Equally with these methods, the acid-base indicator method is known for a long time [10,20]. The counterion binding by polyions is also the object of research. For instance, Böhme and Scheler have determined the fraction of charged of poly (sodium 4-styrenesulfonate) (NaPSS) as a model for a flexible polyelectrolyte [21] using diffusion and electrophoresis NMR. Böhme and Scheler have examined the influence of methanol on the fraction of charge of NaPSS. In addition, small angle X-ray scattering method was used for studying the structure of salt free polyelectrolytes solutions containing monovalent and diva-

buka_nana@ukr.net

lent counter-ions [22], binding of Cd^{2+} and Na^+ ions by poly (sodium 4-styrenesulfonate) was also analyzed by ultrafiltration [23]. In most cases the investigation of counterion condensation based on Manning's theory [24,25].

So, the aim of present work is to determine of acid strength of neutral red, NR, in NaPSS-based solution and to find the degree of counterion binding by the polyions under different conditions by indicator method. It is of important to verify this method to NaPSS coils and to determine values of the degree of counterion binding when tetra-*n*-alkylammonium salts or 1-butanol are added.

Experimental section

Materials. NaPSS was purchased from Sigma-Aldrich as a powder. The molecular weight of NaPSS was around 70×10^3 g mol^{-1}. The polyelectrolyte was used as received. The stock solutions of NaPSS were prepared with concentration either 0.05 or 0.10 M by placing of the sample in pure water without stirring during one week. Hereafter, the concentrations of NaPSS are expresses in monomer mol dm^{-3} (monomol dm^{-3}). The stock solution of NR was prepared in distilled water and filtrated before measurements using filter papers 'Filtra acido hydrochlorico extracta' (Specialpapierfabric Niederschlag, Germany). The precise dye concentration was ascertained by spectrophotometric method using molar absorptivity value, 1.72×10^4 $M^{-1}cm^{-1}$ at 530 nm [26]. The dye concentrations in work solutions was about 3×10^{-5} M. Hereafter, 1 M = 1 mol dm^{-3}.

The pH values of the solutions were adjusted using HCl for pH < 4, or buffer solutions: phosphate (pH 5.8 – 8.5) or borate (pH 7.8 – 10.0). The pH values around 11 – 12 were adjusted by diluted sodium hydroxide. Aqueous NaOH solution was prepared from saturated stock solution using CO_2-free water and kept protected from the atmosphere. The total ionic strength of the bulk (aqueous) phase has been maintained by appropriate NaCl, tetraethylammonium bromide (Et_4NBr), or tetra-*n*-butylammonium iodide (But_4NI) additions. Hydrochloric and phosphoric acids, borax, sodium chloride, tetraethylammonium bromide, and tetra-*n*-butylammonium iodide used for preparation of working solutions were of analytical grade (Reakhim, Russia). 1-Butanol was purified by the standard procedure via rectification.

Methods. The ionization of a cationic acid in solution can be described by the below equation:

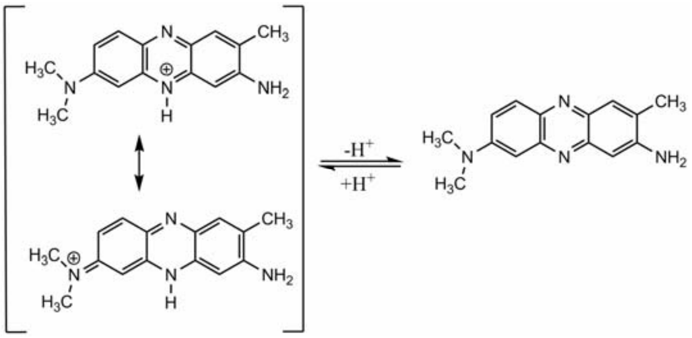
$$\mathrm{HB}^+ \rightleftarrows \mathrm{B} + \mathrm{H}^+, K_a \tag{1}$$

Therefore, the apparent ionization constant should be expressed as:

$$\mathrm{p}K_{\mathrm{a}}^{\mathrm{app}} = \mathrm{pH}_{\mathrm{w}} + \log\frac{\left[\mathrm{HB}^+\right]_t}{\left[\mathrm{B}\right]_t} = \mathrm{pH}_{\mathrm{w}} + \log\frac{A_{\mathrm{B}} - A}{A - A_{\mathrm{HB}}} \tag{2}$$

The acid-base couple HB^+/B is assumed to be (partly) located within the polyelectrolyte microenvironment and equilibrated with the pH value of the continuous (aqueous) phase, pH_w. Such apparent ionization constant was input by analogy with micellar systems [27]. The subscript *t* (total) denotes that the concentration is expressed in moles per dm^3 of the whole solution. If it deals with the acid-base indicator, the equilibrium concentrations ratio $[HB^+]_t/[B]_t$ can be determined via spectrophotometry. Absorption spectra were measured with Hitachi U-2000 spectrophotometer against pure water as blanks, at 25°C. The ionization of neutral red is shown in Scheme 1.

Basing on our previous study [28], we consider both acidic and basic forms of NR as almost bound by the polyelectrolyte coils.



Scheme 1. The ionization of neutral red in aqueous solutions.

The pH_w value may be maintained by buffer solutions. The pH determinations were performed by using R 37-01 potentiometer and pH-121 pH-meter (Russia) with an ESL-43-07 glass electrode (Gomel, Belarus) in a cell with liquid junction (3.0 M KCl). An Ag|AgCl electrode was used as a reference electrode. The glass electrode was calibrated with standard buffer solutions: pH 9.18, 6.86, 4.01, and 1.68 at 25°C.

In addition, the NaPSS particle size distribution and zeta-potentials, ζ, were determined via dynamic light scattering, DLS, using Zetasizer Nano ZS Malvern Instruments apparatus. The equilibration time of each probe was 120 s, the number of size measurements of each probe was 10, every measurement consisted of 12 to 30 runs (automatic choice). In the case of zeta-potential, the number of measurements was 5, the number of runs was chosen automatically (up to 100 runs). Distilled water wasn't filtrated. For assign the viscosity value was used solvent builder, which calculated the viscosity of dispersant depending on NaCl concentration.

Results and discussion

DLS measurements. As demonstrated in our previous work [28], the determination of the polyions size via the DLS method is difficult because of the non-sphericity of particles, which results in the apparent polydispersity. Nevertheless, the DLS method is widely used for determination of diffusion coefficients of NaPSS in water [29-32]. So, we consider that comparison of the size distributions by intensity, volume, and number, at the different conditions is reasonable. The data of cumulants analysis (Z-average values – hydrodynamic diameter) are given in Table 1 too, but only in the case of good quality of such calculation algorithms.

Using the DLS method, we studied the size distributions in system: NaPSS + NaCl, NaPSS + But_4NI, NaPSS + Et_4NBr and NaPSS + 1-butanol. In Figure 1, the typical size distribution of NaPSS with 0.05 M NaCl, and the dependence of polyions size (by number), d, on NaCl concentration at 0.001 M NaPSS are shown (see also Table 1). When the ionic strength is 3×10^{-3} or more, the size (by number) of polyions becomes constant (7–8 nm). The sizes obtained by intensity slightly decrease with ionic strength. Such a difference may result from the non-sphericity of polyions and interactions between polyions. More extended polyions move slower, so the size by intensity is large. When polyions coil to more compact conformation, they move faster, so the size by intensity is smaller. So, at low ionic strength the polyions are elongated that results in observation 'smaller' sizes, at higher ionic strength the polyions become more spherical and average size increases.

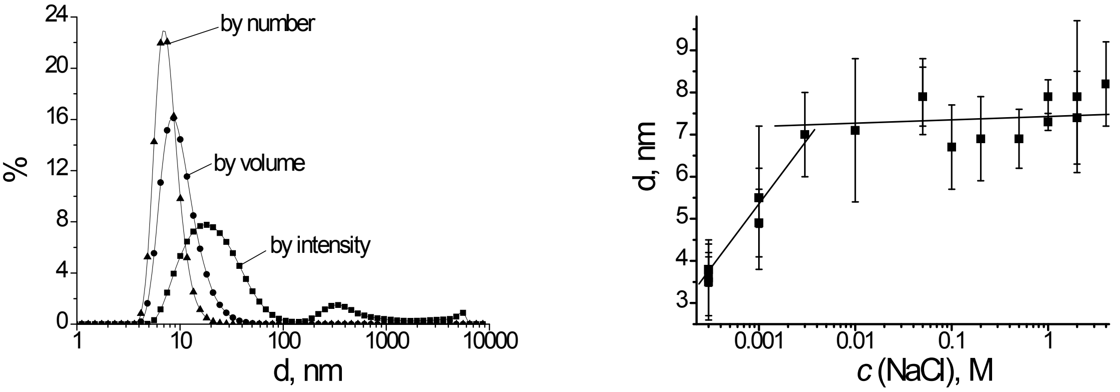


Figure 1. The macromolecules size distribution by intensity, by volume, and by number in 0.001 M NaPSS solution with 0.05 M NaCl, d (by intensity) = 25 ± 5 nm, d (by volume) = 13.3 ±2.7 nm, d (by number) = 7.9 ±0.7 nm (a); the dependence of polyions size (by number), d, on NaCl concentration, *c* (NaPSS) = 0.001 M (b).

The addition of the tetra-*n*-alkylammonium ions leads to some changes in the polyelectrolyte state. The DLS measurements of the 0.001 M NaPSS solution with 0.02 M But_4NI and Et_4NBr were carried out (Figure 2). In this case, the cumulant analysis is of higher quality, than in polyelectrolyte solutions with NaCl. Also, no particles with size of about 200 – 300 nm were observed in the case of But_4NI. This observation confirms that in other NaPSS-based systems, particles of such size are aggregates of polyions, which collapse at absorption hydrophobic tetra-*n*-butyl ammonium cation on the polyelectrolyte ‘surface’. The sizes of polyions by number in the presence of tetra-*n*-alkylammonium salts are similar to those observed with NaCl, but in the case of distribution by intensity tetraethylammonium bromide causes increase in polyions size. Such an alteration of size distribution character indicates strong absorption of tetra-*n*-alkylammonium ions on NaPSS surface. Probably, it occurs analogously to micellar systems where the selectivity parameters of But_4N^+ and Et_4N^+ were found equal to 125±5 and 22±3, respectively (the selectivity parameter of Na^+ is 1) [6].

The influence of 1-butanol on the NaPSS size distributions is non-expressed (Figure 3). The size of NaPSS in the presence of 1-butanol is somewhat higher either by intensity or by number. In these systems, the quality of cumulants analysis is good, which may indicate more spherical conformation of the polyions. Obviously, some kind of interaction between polyions and alcohol molecules takes place.

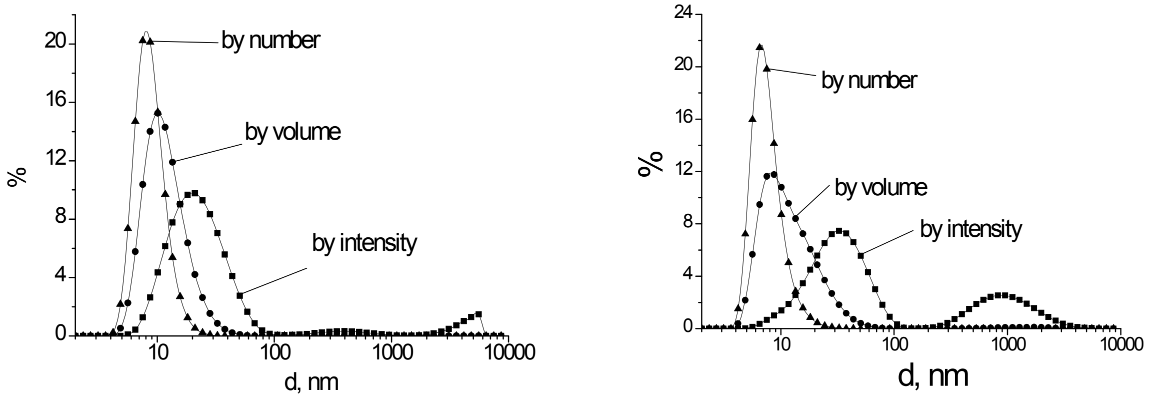


Figure 2. The macromolecules size distribution by intensity, by volume, and by number in 0.001 M NaPSS solution with 0.02 M But_4NI addition (a) and with 0.02 M Et_4NBr addition (b).

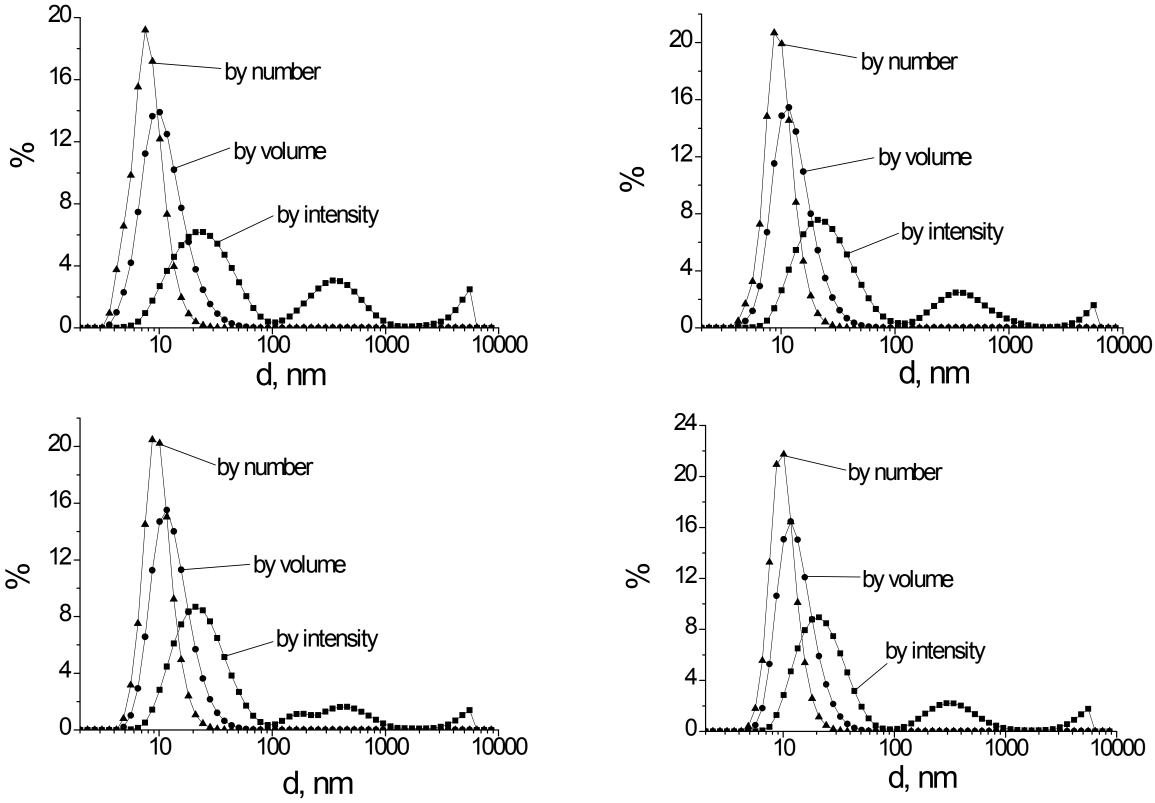


Figure 3. The macromolecules size distribution by intensity, by volume, and by number in 0.003 M NaPSS solution with 0.8 M 1-butanol: (a) 0.01 M NaCl; (b) 0.045 M NaCl; (c) 0.05 M NaCl; (d) 0.20 M NaCl.

Table 1. The results of size (d, nm) determination of NaPSS in aqueous solution with ionic and non-ionic aditives. Results of cumulants analysis (hydrodynamic diameter, d_{hd}, and diffusion coefficient, D) are shown only in the case of its good quality.

c(NaPSS), M	c(NaCl), M	$d_{Intensity}$	d_{Volume}	d_{Number}	d_{hd}	$D \times 10^7$, cm²/s
0.001	0	30 ± 6	5.2 ± 1.2	3.7 ± 0.9	—	—
	0.001	27 ± 4	9 ± 3	5.3 ± 1.5	20.0	2.5
	0.01	23 ± 4	12 ± 3	7.1 ± 1.7	20.7	2.4
	0.05	19.1 ± 1.8	11.9 ± 1.7	7.9 ± 0.9	20.5 ± 0.1	2.39 ± 0.01
	0.20	16.6 ± 2.1	9.5 ± 1.0	7.1 ± 1.0	—	—
	2	12.2 ± 0.2	10.7 ± 0.8	7.4 ± 1.1	—	—
0.003 +0.8 M 1-butanol	0.013	27.5 ± 0.98	19 ± 4	8.3 ± 1.4	—	—
	0.045	27.5 ± 2.7	19.1 ± 3.5	10.1 ± 1.5	27.3 ± 2.0	1.80 ± 0.12
	0.05	26 ± 3	18.5 ± 2.6	10.2 ± 1.4	25.5 ± 1.2	1.92 ± 0.09
	0.20	24.2 ± 1.7	19.8 ± 2.3	10.5 ± 1.0	25.5 ± 1.5	1.90 ± 0.11
0.001	0.02 (But_4N^+)	24.1 ± 0.8	15.9 ± 1.6	9.0 ± 1.0	20.4 ± 0.5	2.42 ± 0.06
0.001	0.02 (Et_4N^+)	34.7 ± 1.5	28 ± 5	7.9 ± 1.0	37.0 ± 1.0	1.33 ± 0.04

The acid strength of neutral red in presence of ionic additives. Firstly, it should be noted that all $\mathrm{p}K_a^{app}$ values reported in this paper were obtained at polyelectrolyte : dye concentration ratio, P : D, equals 100. It allows avoiding polyelectrolyte-induced metachomatic effects [28,33,34]. The corresponding concentration of NaPSS was of about 0.003 M.

The study of influence of ionic additives was carried out in terms of the salt effects on $\mathrm{p}K_a^{app}$ values of NR. As reported earlier [20,35], in micellar solution the dependences of $\mathrm{p}K_a^{app}$ on log I (or more precisely log $c_{counterion}$) are linear up to several mol per liter. The slope of dependences, b, is in fact very similar to the degree of counterion binding, β, by colloidal particles:

$$\mathrm{p}K_a^{app} = B - b \times \log [Na_w^+] \tag{3}$$

$$\beta = -\frac{\partial\, \mathrm{p}K_a^{app}}{\partial \log [Na_w^+]} \tag{4}$$

When the molecular weight of polyelectrolyte becomes high enough (degree of polymerization $N > 10$), the counterion condensation becomes apparent according to the measurement of poly (4-styrenesulfonate) electrophoretic mobility [36]. For higher molecular weight ($N > 100$) at $I = 0.02$ M NaPSS is in random coil conformation and the degree of counterion binding becomes independent of the average molecular mass. Also, according to Manning [24], the number of bound counterions doesn't depend on the ionic strength or the concentration of free counterions. Nevertheless, when the ionic strength increases, the effective charge on polyions decreases [21] (analogously to the shrinking of diffuse part of ionic atmosphere of micelles). Hereupon polyions assume less extended conformation that leads to a higher density of the nominal charges, leading to a further condensation of counterions. Finally, at given ionic strength the equilibrium state appears.

So, in terms of mentioned properties of polyions we have suggested that Eq. (3) and (4) may be applied to polyelectrolyte coils too. In our previous paper, the dependences of $\mathrm{p}K_a^{app}$ on log I for a set of indicator dyes were obtained in the presence of NaCl [28]. Indeed, these dependences are linear in the sufficient range of the ionic strengths. In Table 2 the $\mathrm{p}K_a^{app}$ data for system water – NaPSS – NaCl are shown for comparison.

Then, the aim of this work was the study of influence of tetra-*n*-alkylammonium cations on NR bound to NaPSS polyions. It should be mentioned that tetra-*n*-alkylammonium salts significantly influenced the acid strength of dyes in sodium dodecyl sulphate (NaDS) solutions [6,10]. For instance, $\mathrm{p}K_a^{app}$ of methyl yellow in 0.02 M NaDS and 0.05 M But_4N^+ equals 1.61, whereas when NaCl used, it is 4.81. So, the obtained $\mathrm{p}K_a^{app}$ values in the system water – NaPSS – tetra-*n*-alkylammonium salts are represented in Table 2. The NR spectra are exemplified in Figure 4. It was found experimentally that freshly prepared stock solution of tetraethylammonium bromide results in somewhat lower $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ values. These values are mentioned in Table 2, but they aren't used in further discussion because of their non-systematic character.

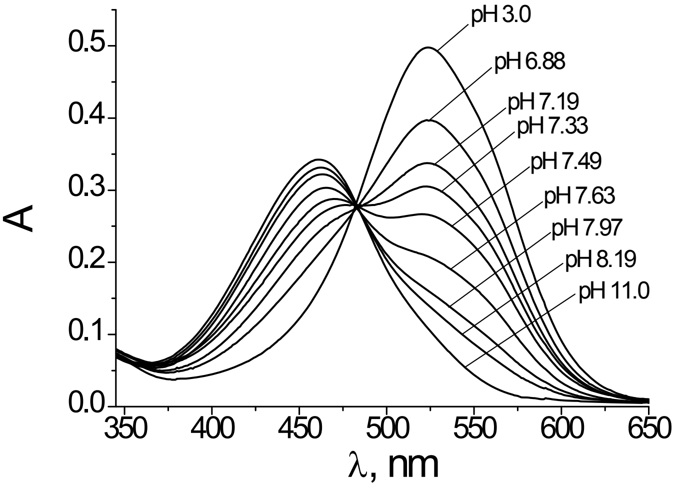


Figure 4. The spectra of NR in ternary system water – NaPSS – Et_4NBr at I = 0.10 M, c (Et_4NBr) = 0.08 – 0.09 M; $c_\mathrm{dye} = 3.48 \times 10^{-5}$ M; phosphate buffer solutions except pH 3.0 (HCl solution), pH 11.0 (NaOH solution), and pH 7.6 – 8.2 (borate buffer).

Table 2. The indices of the apparent ionization constants of NR in the NaPSS-based aqueous systems.

I, M	NaCl[a]	Et_4NBr, borate buffer	Et_4NBr, phosphate buffer
0.01	8.62 ± 0.06 (borate buffer)	8.24± 0.12 7.93± 0.04[b]	—
0.02	8.45 ± 0.04 (borate buffer)	7.90 ± 0.07	—
0.03	—	—	7.86 ± 0.04
0.05	8.10 ± 0.08 (phosphate buffer)	7.38 ± 0.07	7.66 ± 0.04 7.50 ± 0.04[b]
0.10	7.91 ± 0.03 (borate buffer)	7.16 ± 0.02	7.34 ± 0.02
0.50	7.50 ± 0.03 (phosphate + borate buffer)	—	—

[a] – Ref. [28].

[b] – Freshly made prepared solution of tetraethylammonium bromide.

We used borate and phosphate buffer systems. It should be noted that the concentration of tetra-*n*-alkylammonium salts doesn't equal the ionic strength because of buffer system using (Na^+ counterions). Besides, the $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ values obtained by means of borate buffer are found somewhat lower than that ones which were obtained with phosphate buffer. Thus, in the presence of But_4NI $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ = 7.69 ± 0.04 when borate buffer were used or 7.89 ± 0.07 in the case of phosphate buffer at I = 0.02 M and c (But_4NI) = 0.01 M. The decrease in $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ value as compared with $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ in water – NaPSS – NaCl system is considerable even at low salt concentration. Due to low solubility of But_4NI in water, we have examined the binding of counterions using tetraethylammonium bromide.

In Figure 5, the data obtained with the same buffer systems are compared. So, in water – NaPSS – NaCl – $Na_2B_4O_7$ system the dependences of $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ on logarithm of ionic strength are linear and are characterized by slope of 0.67. It means that actually the degree of counterion binding is 0.67. In the case of water – NaPSS – Et_4NBr – Na^+ system, the dependence is also sufficiently linear and the degree of counterion binding is of about 1.0. This value indicates that the association of the tetraethylammonium cations with the SO_3^- groups of the polyelectrolyte is almost complete. So, the specific adsoption of tetra-*n*-alkylammonium cations results in more compact disposition of polyelectrolyte chain that has been confirmed by improvement of size measurement quality as mentioned above.

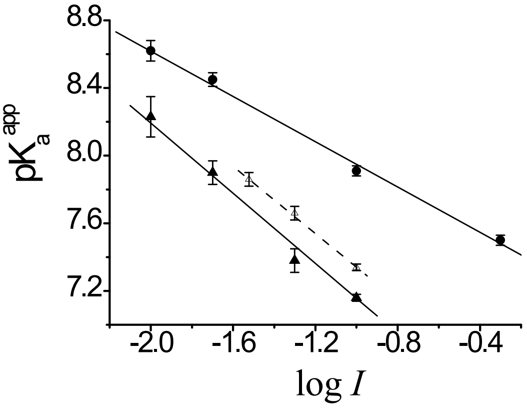


Figure 5. The dependence of pK_a^{app}s on logarithm of ionic strength (Et_4NBr or NaCl) in NaPSS-based systems. The characteristics of dependences are:
circles (NaCl): $pK_a^{app} = (7.28 \pm 0.03) - (0.67 \pm 0.03) \times \log I$, n=4, R^2=0.9973;
full triangles (Et_4NBr, borate buffer): $pK_a^{app} = (6.12 \pm 0.09) - (1.04 \pm 0.08) \times \log I$, n=4, R^2=0.9949;
empty triangles (Et_4NBr, phosphate buffer): $pK_a^{app} = (6.33 \pm 0.09) - (1.01 \pm 0.08) \times \log I$, n=3.

Influence of 1-butanol. Besides ionic additives, we have determined the influence of 1-butanol on the ionization of NR in the presence of NaCl. Firstly, the pK_a^{app} value of 7.27 ± 0.04 in NaPSS solution at P : D = 100 and I = 0.05 M, with 0.80 M 1-butanol, was obtained. So, 1-butanol increases the acid strength of the dye by 0.8 pK_a^{app} units in NaPSS solutions. Similar effects have been observed in the NaDS–1-butanol system [4]. Therefore, strong influence on the acid strength of NR and mentioned above 1-butanol-induced changes in DLS measurements have pointed that 1-butanol makes the micro-environment more non-aqueous. In this case, the term $\log \gamma_B / \gamma_{HB}$ becomes more negative [Eq. (5)] due to decrease in ε:

$$\log \frac{\gamma_R}{\gamma_{HR}} = \frac{e^2 N_A}{8\pi\varepsilon_0 2.303RT} \times \left[\frac{(z-1)^2}{r_B} - \frac{z^2}{r_{HB}}\right] \times \left[\frac{1}{\varepsilon_{eff}} - \frac{1}{\varepsilon_w}\right] + \frac{\Delta G_{tr}^{solv}(B^{z-1}) - \Delta G_{tr}^{solv}(HB^z)}{2.303RT} \quad (5)$$

Here e is the elemental charge, N_A is Avogadro number, ε_0 = 8.854×10^{-12} F m^{-1}, r_i are the radii of B^{z-1} and HB^z species, ε_w is the relative permittivity of water, ε_{eff} is the effective relative permittivity of the polyelectrolyte pseudophase, and the ΔG_r^{solv} values reflect the changes in the Gibbs solvation energies of transfer, which are not included in the first (electrostatic) item.

Moreover, the study of the quaternary systems water – NaPSS – 1-butanol – NaCl from the viewpoint of influence on the acid strength of NR is of important. Firstly, it should be noted how alter the solubility of 1-butanol in water with NaCl addition. Thus, at 25 ^{0}C the solubility of 1-butanol is 7.41 % (wt) [37], 7.29 % (wt) [38], or according to data obtained by Stephenson [39] at 20.0^{0}C it is 8.03 % (wt) or at 30.8^{0}C it is 7.07 % (wt). The solubility of 1-butanol decreases with temperature rise up to 60^{0}C. When the solution is saturated by NaCl (of about 26 % (wt) NaCl), the solubility of 1-butanol is 0.59 – 0.7 % (wt) [37,38,40]. In 3.1 % (wt) NaCl solution 1-butanol solubility is 5.43 % (wt) [38]. In our investigation, we chose the concentration of 1-butanol as 0.80 M (5.9 % (wt) on conditions that the density of solution equals density of water), which is similar to 1-butanol solubility limit in water but somewhat lower. According to data obtained by Li [38], the given amount of 1-butanol can be dissolved in less than 2.2 % (wt) NaCl aqueous solution (of about 0.38 M NaCl). So, we have measured the pK_a^{app}s of NR in system water – NaPSS – 1-butanol – NaCl at salt concentration not exceeded 0.38 M.

On the other hand, the NaPSS-based quaternary system should be compared with system water – NaDS – 1-butanol – NaCl. As mentioned above, the last one is scrutinized. In our work [4] we have reported that the value of slope of linear dependence of pK_a^{app} of NR on log *I* in water – NaDS –

1-butanol – NaCl system is 0.39 at 0.8 M 1-butanol. This parameter may be equated to the degree of counterion binding, as it was demonstrated earlier [4,27].

The data obtained for the quaternary systems water – NaPSS – 1-butanol – NaCl are shown in Table 3 and Figure 7. The spectra of NR in the presence of 1-butanol are exemplified in Figure 6. Firstly, we have found out that the dependence of $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ of NR on log I is not linear in the range 0.01 – 0.20 M NaCl. Let us consider section I – III (see Figure 7) more thoroughly. At the ionic strength up to 0.04 M, introduction of 1-butanol significantly decreases the $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ of NR as compared with system water – NaPSS – NaCl. Nevertheless, the slope of the dependence (0.58) is similar to this one, obtained in the system without 1-butanol. On the contrary, at I = 0.04 – 0.05 M, the sharp additional decrease in $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ values is occurred (section II in Figure 7). When the ionic strength is further raised, the dependence becomes linear again, its slope is 0.44 that is substantially lower in comparison with non-1-butanol solutions of NaPSS. In micellar NaDS solution with the same concentration of 1-butanol, the slope is 0.39 as against 0.71 in non-1-butanol system in the all range of ionic strength under examination [4]. So, if we assume that the dye is completely bound by the coils, the sharp decrease in $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ at the range of I = 0.04 – 0.05 M is caused by additional penetration of 1-butanol in macromolecule coils and decrease effective charge density on the ‘surface’. By-turn, the additional penetration (or specific adsorption) may result from the decrease of solubility limit of 1-butanol with increase of ionic strength (the salting-out of 1-butanol from aqueous to polyelectrolyte phase). In the other hand, 1-butanol causes lowering of dielectric permittivity of solution. For instance, according to Böhme and Scheler [21], the addition of methanol results in decrease of fraction of charge (i.e. increase of counterion binding) on NaPSS. Our experiment has shown opposite effect that confirms the penetration of 1-butanol into coils and its influences as non-ionic component of coils.

Table 3. The indices of the apparent ionization constants of the NR in NaPSS-based aqueous systems contained 0.80 M 1-butanol, the ionic strength was maintained by NaCl, phosphate buffer was used.

I, M	$\mathrm{p}K_\mathrm{a}^\mathrm{app}$
0.013	7.80 ± 0.04
0.018	7.68 ± 0.07
0.027	7.64 ± 0.03
0.040	7.50 ± 0.04
0.045	7.37 ± 0.06
0.05	7.27 ± 0.04
0.09	7.17 ± 0.06
0.20	6.99 ± 0.08

The displacement of NR in aqueous phase (the salting-out of NR from polyelectrolyte to aqueous phase) also can be results in decrease of $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ values. However, the last hypothesis is less probable since the transfer of NR in aqueous phase would cause a shift of absorption band to its aqueous values. On the contrary, we have observed that at low ionic strength, up to 0.04 M, λ_max = 530 nm, but at I = 0.20 M λ_max value reaches 534 nm. In the system water – NaPSS – NaCl within the whole range of ionic strengths, λ_max = 525±1 nm. It should be noted that in this case the equality of λ_max at low ionic strength in 1-butanol-contained system to its aqueous value (530 nm) is coincidence and doesn’t point on equality of dye states in those cases. Such a coincidence is caused by the dependence of NR spectra on the concentration of NaPSS that by-turn depends on additives to water – NaPSS system. Thus, at the increase of P : D from 10 to 1500 λ_max rises from 507 nm to 540 nm [28] in pure NaPSS solutions without salts. So, at some P : D values, which are different depending on the other compounds of solutions, λ_max value can be equals 530 nm, but such a spectrum will not be the spectrum of NR in water.

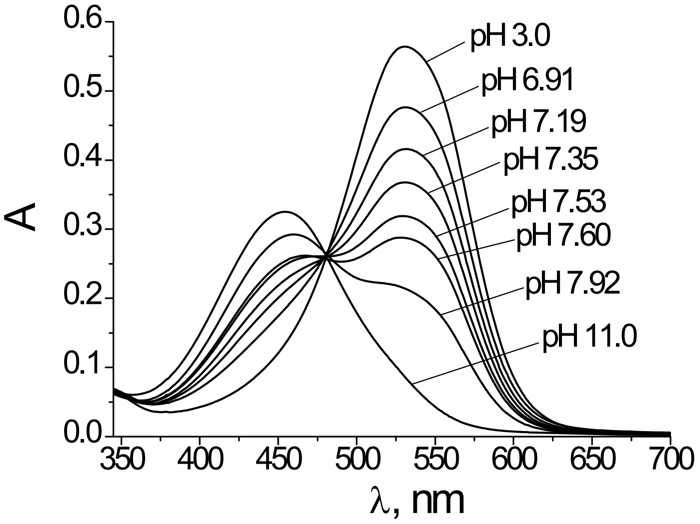


Figure 6. The spectra of NR in quaternary system water – NaPSS – 1-butanol – NaCl at I = 0.04 M; $c_{\text{dye}} = 3.44 \times 10^{-5}$ M; phosphate buffer solutions except pH 3.0 (HCl solution) and pH 11.0 (NaOH solution).

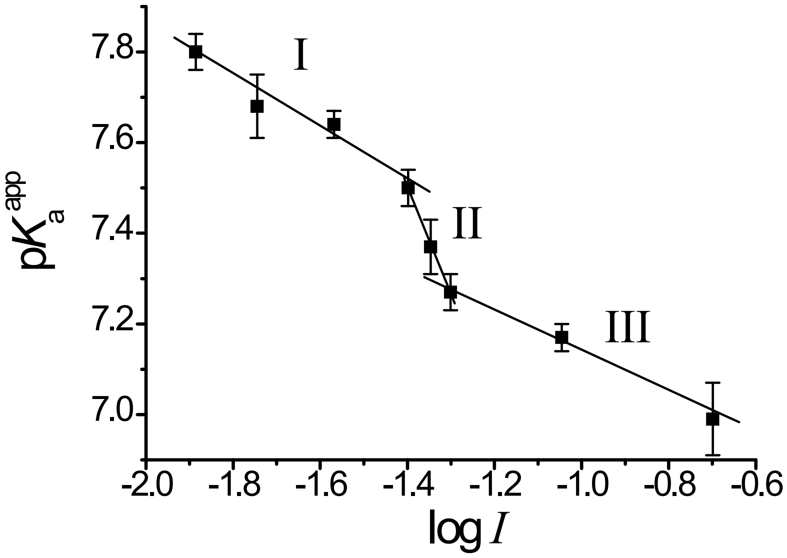


Figure 7. The dependence of $\mathrm{p}K_{\mathrm{a}}^{\mathrm{app}}$ s on logarithm of ionic strength (NaCl) in NaPSS-based systems contained 0.80 M 1-butanol. The characteristics of different sections of dependence are:

I: $\mathrm{p}K_{\mathrm{a}}^{\mathrm{app}} = (6.71 \pm 0.18) - (0.58 \pm 0.11) \times \log I$, n=4, R^2=0.981;

II: $\mathrm{p}K_{\mathrm{a}}^{\mathrm{app}} = (4.18 \pm 0.79) - (2.38 \pm 0.58) \times \log I$, n=3, R^2=0.9995;

III: $\mathrm{p}K_{\mathrm{a}}^{\mathrm{app}} = (6.70 \pm 0.15) - (0.44 \pm 0.14) \times \log I$, n=3, R^2=0.994.

Acknowledgment

The authors express their gratitude to Dr. L. V. Miroshnik (Materials Chemistry Department, V.N. Karazin Kharkiv National University, Ukraine) for her helpful advice on the methods of polyelectrolyte solutions preparation, and to Professor N. O. Mchedlov-Petrossyan (Department of Physical Chemistry, V.N. Karazin Kharkiv National University, Ukraine) for the discussions of the obtained results.

References

1. J. Y. Teo, W. Chin, X. Ke, S. Gao, S. Liu, W. Cheng, J. L. Hedrick, Y. Y. Yang, pH and redox dual-responsive biodegradable polymeric micelles with high drug loading for effective anti-cancer drug delivery, Nanomedicine: NBM 13 431-442, doi:10.1016/j.nano.2016.09.016
2. J. H. Hamman, Chitosan Based Polyelectrolyte Complexes as Potential Carrier Materials in Drug Delivery Systems, Marine Drugs 8 (2010) 1305.
3. B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Research 41 (2007) 2301-2324, doi:10.1016/j.watres.2007.03.012
4. A. Y. Kharchenko, N. N. Kamneva, N. O. Mchedlov-Petrossyan, The properties and composition of the SDS – 1-butanol mixed micelles as determined via acid-base indicators, Colloids Surf., A 507 (2016) 243-254, doi:10.1016/j.colsurfa.2016.08.004
5. H. Høiland, E. Ljosland, S. Backlund, Solubilization of alcohols and alkanes in aqueous solution of sodium dodecyl sulfate, J. Colloid Interface Sci. 101 (1984) 467-471, doi:10.1016/0021-9797(84)90058-4
6. N. Mchedlov-Petrossyan, A. Pulyaeva, The sodium/alkyl-ammonium ion exchange at the micellar surface of dodecyl sulfate micelles as studied with the help of pK_a-probes, Funct. Mater. 2 (1995) 530-531.
7. K. Gunaseelan, K. Ismail, Estimation of micellization parameters of sodium dodecyl sulfate in water+1-butanol using the mixed electrolyte model for molar conductance, J. Colloid Interface Sci. 258 (2003) 110-115, doi:10.1016/S0021-9797(02)00065-6
8. G. V. Hartland, F. Grieser, L. R. White, Surface potential measurements in pentanol-sodium dodecyl sulphate micelles, J. Chem. Soc. Faraday Trans. 1 83 (1987) 591-613, doi:10.1039/F19878300591
9. C. J. Drummond, F. Grieser, T. W. Healy, Acid-base equilibria in aqueous micellar solutions. Part 3.-Azine derivatives, J. Chem. Soc. Faraday Trans. 1 85 (1989) 551-560, doi:10.1039/F19898500551
10. N. O. Mchedlov-Petrossyan, Protolytic equilibrium in lyophilic nanosized dispersions: Differentiating influence of the pseudophase and salt effects, Pure Appl. Chem. 80 (2008) 1459, doi:10.1351/pac200880071459
11. D. Wang, X. Gong, P. S. Heeger, F. Rininsland, G. C. Bazan, A. J. Heeger, Biosensors from conjugated polyelectrolyte complexes, Proc. Natl. Acad. Sci. USA 99 (2002) 49-53, doi:10.1073/pnas.012581399
12. L. I. Kazakova, L. I. Shabarchina, S. Anastasova, A. M. Pavlov, P. Vadgama, A. G. Skirtach, G. B. Sukhorukov, Chemosensors and biosensors based on polyelectrolyte microcapsules containing fluorescent dyes and enzymes, Anal. Bioanal. Chem. 405 (2013) 1559-1568, doi:10.1007/s00216-012-6381-0
13. D. Horn, C.-C. Heuck, Charge determination of proteins with polyelectrolyte titration, J. Bio. Chem. 258 (1983) 1665-1670.
14. E. Baumgartner, R. Fernandez-Prini, D. Turyn, Change of apparent acidity constant of indicators in polyelectrolyte solutions, J. Chem. Soc. Faraday Trans. 1 70 (1974) 1518-1526, doi:10.1039/F19747001518
15. K. Tamaki, A. Tsuchiya, The solubilization of Orange OT in aqueous solutions of alkyl-substituted ammonium salts of polystyrenesulfonic acid, Kolloid-Zeitschrift und Zeitschrift für Polymere 200 (1964) 34-37, doi:10.1007/bf01499432
16. C. Bravo, J. R. Leis, M. E. Pena, Effect of alcohols on catalysis by dodecyl sulfate micelles, J. Phys. Chem. 96 (1992) 1957-1961, doi:10.1021/j100183a077
17. D. A. R. Rubio, D. Zanette, F. Nome, C. A. Bunton, Effect of 1-Butanol on Micellization of Sodium Dodecyl Sulfate and on Fluorescence Quenching by Bromide Ion, Langmuir 10 (1994) 1151-1154, doi:10.1021/la00016a030
18. L. P. Loginova, E. Y. Yakovleva, M. N. Galat, A. P. Boichenko, Effect of aliphatic alcohols and aliphatic carboxylic acids on the critical micelle concentration and counter-ion binding degree of sodium dodecylsulfate, Jour. Moll. Liq. 145 (2009) 177-181, doi:10.1016/j.molliq.2008.05.009
19. J. F. Rathman, J. F. Scamehorn, Counterion binding on mixed micelles: effect of surfactant structure, Langmuir 3 (1987) 372-377, doi:10.1021/la00075a017
20. P. Mukerjee, K. Banerjee, A Study of the Surface pH of Micelles Using Solubilized Indicator Dyes, J. Phys. Chem. 68 (1964) 3567-3574, doi:10.1021/j100794a022

21. U. Böhme, U. Scheler, Counterion condensation and effective charge of poly(styrenesulfonate), Adv. Colloid Interface Sci. 158 (2010) 63-67, doi:10.1016/j.cis.2010.02.010
22. F. Boué, M. Rawiso, J. Combet, C. Rochas, S. Hoffmann, Structure of Polyelectrolytes with Mixed of Monovalent and Divalent Counterions: Poisson-Boltzmann Analysis and SAXS Measurements, Macromolecules 44 (2011) 3039-3052, doi:10.1021/ma102226v
23. B. L. Rivas, I. Moreno-Villoslada, Binding of Cd^{2+} and Na^{+} Ions by Poly(sodium 4-styrenesulfonate) Analyzed by Ultrafiltration and Its Relation with the Counterion Condensation Theory, J. Phys. Chem. B 102 (1998) 6994-6999, doi:10.1021/jp980941m
24. G. S. Manning, Counterion binding in polyelectrolyte theory, Acc. Chem. Res. 12 (1979) 443-449, doi:10.1021/ar50144a004
25. A. V. Dobrynin, M. Rubinstein, Theory of polyelectrolytes in solutions and at surfaces, Prog. Polym. Sci. 30 (2005) 1049-1118, doi:10.1016/j.progpolymsci.2005.07.006
26. S. P. Moulik, B. K. Paul, D. C. Mukherjee, Acid-Base Behavior of Neutral Red in Compartmentalized Liquids (Micelles and Microemulsions), J. Colloid Interface Sci. 161 (1993) 72-82, doi:10.1006/jcis.1993.1443
27. N. N. Kamneva, A. Y. Kharchenko, O. S. Bykova, A. V. Sundenko, N. O. Mchedlov-Petrossyan, The influence of 1-butanol and electrolytic background on the properties of CTAB micelles as examined using a set of indicator dyes, Moll. Liq. 199 (2014) 376-384, doi:10.1016/j.molliq.2014.09.022
28. A. Y. Kharchenko, O. G. Moskaeva, O. R. Klochaniuk, M. O. Marfunin, N. O. Mchedlov-Petrossyan, Effect of poly (sodium 4-styrenesulfonate) on the ionization constants of acid-base indicator dyes in aqueous solutions, Colloids Surf., A 527 (2017) 132-144, doi:10.1016/j.colsurfa.2017.05.030
29. J. J. Tanahatoe, Dynamic Light Scattering of Flexible Highly Charged Polyelectrolytes at Infinite Dilution, J. Phys. Chem. B 101 (1997) 10442-10445, doi:10.1021/jp972428z
30. J. J. Tanahatoe, M. E. Kuil, Dynamic Light Scattering of a Flexible Highly Charged Polyelectrolyte in the Dilute Concentration Regime, Macromolecules 30 (1997) 6102-6106, doi:10.1021/ma9703259
31. Z. Adamczyk, M. Zembala, P. Warszyński, B. Jachimska, Characterization of Polyelectrolyte Multilayers by the Streaming Potential Method, Langmuir 20 (2004) 10517-10525, doi:10.1021/la040064d
32. G. M. Pavlov, A. S. Gubarev, I. I. Gavrilova, E. F. Panarin, Conformations of sodium poly(styrene-4-sulfonate) macromolecules in solutions with different ionic strengths, Polym. Sci. Ser. A 53 (2011) 1003-1011, doi:10.1134/S0965545X11110095
33. A. Y. Kharchenko, O. G. Moskaeva, The acid-base equilibrium of cationic dyes in the aqueous solutions of poly (sodium 4-styrenesulfonate), Kharkiv University Bull. Chem. Series 26 (2016) 12-25.
34. P. Dell' Antone, R. Colonna, G. F. Azzone, The Membrane Structure Studied with Cationic Dyes, Eur. J. Biochem. 24 (1972) 566-576, doi:10.1111/j.1432-1033.1972.tb19719.x
35. N. O. Mchedlov-Petrossyan, L. P. Loginova, V. N. Klesch'evnikova, The influence of salts on the ionization of indicators in the Stern layer of cationic micelles, Zhur. Fiz. Khim. 67 (1993) 1649-1653 (in Russian).
36. H. Cottet, P. Gareil, O. Theodoly, C. E. Williams, A semi-empirical approach to the modeling of the electrophoretic mobility in free solution: application to polystyrenesulfonates of various sulfonation rates, Electrophoresis 21 (2000) 3529-3540, doi:10.1002/1522-2683(200011)21:17<3529::AID-ELPS3529>3.0.CO;2-2
37. A. Marcilla, F. Ruíz, M. M. Olaya, Liquid-liquid-solid equilibria of the quaternary system water-ethanol-1-butanol-soldium chloride at 25°C, Fluid Phase Equil. 105 (1995) 71-91, doi:10.1016/0378-3812(94)02595-R
38. Z. Li, Y. Tang, Y. Liu, Y. Li, Salting effect in partially miscible systems of n-butanol–water and butanone–water 1. Determination and correlation of liquid-liquid equilibrium data, Fluid Phase Equil. 103 (1995) 143-153, doi:10.1016/0378-3812(94)02615-8
39. R. Stephenson, J. Stuart, Mutual binary solubilities: water-alcohols and water-esters, J. Chem. & Engineering Data 31 (1986) 56-70, doi:10.1021/je00043a019
40. A. Oudshoorn, M. C. F. M. Peters, L. A. M. van der Wielen, A. J. J. Straathof, Exploring the potential of recovering 1-butanol from aqueous solutions by liquid demixing upon addition of carbohydrates or salts, J. Chem. Tech. & Biotech. 86 (2011) 714-718, doi:10.1002/jctb.2577

Поступила до редакції 12 квітня 2017 р.

А.Ю. Харченко, Е.Г. Москаева. Влияние ионных и неионных добавок на кислотную силу нейтрального красного в водных растворах поли (4-стиролсульфоната натрия).

Полиионы поли (4-стиролсульфоната натрия) в водном растворе можно считать коллоидной псевдофазой. Аналогично мицеллам, некоторые соединения могут связываться также с заряженными полиэлектролитными клубками. В данной работе окрашенные кислотно-основные индикаторные красители были использованы для изучения проникновения ионных и неионных компонентов раствора в полиэлектролитные клубки. Такой анализ основывается на изменениях кислотной силы красителей. Целью данной работы было определение зависимостей кажущихся констант ионизации нейтрального красного, $K_\mathrm{a}^\mathrm{app}$, от ионной силы раствора, I, в разных смешанных системах, которые содержат поли (4-стиролсульфонат натрия) (NaPSS) и тетраэтиламмоний бромид, тетра-*н*-бутиламмоний иодид, или бутанол-1 с добавкой NaCl. Нейтральный красный фиксируется на полиэлектролитных клубках благодаря электростатическим и гидрофобным взаимодействиям. Отношение концентраций полиэлектролит : краситель, P : D, которое является важным параметром для спектрофотометрических измерений, равно 100. Обнаружено, что тетра-*н*-алкиламмониевые соли сильнее влияют на кислотную силу нейтрального красного по сравнению с NaCl. Например, в случае тетраэтиламмония бромида $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ = 7.90 ± 0.07 при I = 0.02 M, тогда как в присутствии NaCl при такой же ионной силе $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ = 8.45 ± 0.04. Это может быть объяснено специфической адсорбцией тетра-*н*-алкиламмониевых катионов на «поверхности» полиионов. Введение бутанола-1 значительно повышает кислотную силу нейтрального красного также, однако его влияние не является монотонным с изменением ионной силы. Обсуждены зависимости $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ от log I, исходя из закономерностей, которые хорошо известны для мицеллярных систем ПАВ. Все вышеупомянутые системы были изучены методом динамического рассеяния света с помощью прибора Zetasizer Nano ZS Malvern Instruments. Было обнаружено, что при ионной силе 3×10^{-3} M и выше, размер (по числу частиц) полиионов в присутствии NaCl составляет около 7 нм. Введение добавок приводит к некоторому увеличению размеров: при добавках бутанола-1 размер частиц NaPSS составляет 10 нм.

Ключевые слова: полиэлектролит, поли (4-стиролсульфонат натрия), нейтральный красный, кажущаяся константа ионизации, бутанол-1, тетра-*н*-алкиламмониевый катион.

А.Ю. Харченко, О.Г. Москаєва. Вплив іонних і неіонних добавок на кислотну силу нейтрального червоного в водних розчинах полі (4-стиренсульфонату натрію).

Полііони полі (4-стиренсульфонату натрію) в водному розчині можна вважати колоїдною псевдофазою. Аналогічно з міцелами, деякі сполуки можуть зв’язуватися також з зарядженими полієлектролітними клубками. В даній роботі забарвлені кислотно-основні індикаторні барвники були використані для вивчення проникнення іонних та неіонних компонентів розчину в полієлектролітні клубки. Такий аналіз ґрунтується на змінах кислотної сили барвників. Метою роботи було визначення залежностей уявних констант іонізації нейтрального червоного, $K_\mathrm{a}^\mathrm{app}$, від іонної сили розчину, I, в різних змішаних системах, що містять полі (4-стиренсульфонату натрію) (NaPSS) і тетраетиламоній бромід, тетра-*н*-бутиламоній іодид, або бутанол-1 з добавкою NaCl. Нейтральний червоний є зафіксованим на полієлектролітних клубках завдяки електростатичним та гідрофобним взаємодіям. Відношення концентрацій полієлектроліт : барвник, P : D, що є важливим параметром для спектрофотометричних вимірювань, дорівнює 100. Виявлено, що тетра-*н*-алкіламонієві солі сильніше впливають на кислотну силу нейтрального червоного порівняно з NaCl. Наприклад, у випадку тетраетиламонію броміду $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ = 7.90 ± 0.07 при I = 0.02 M, тоді як в присутності NaCl при такій же іонній силі $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ = 8.45 ± 0.04. Це може бути пояснено специфічною адсорбцією тетра-*н*-алкіламонієвих катіонів на «поверхні» полііонів. Введення бутанолу-1 значно підвищує кислотну силу нейтрального червоного також, однак його вплив не є монотонним зі зміною іонної сили. Обговорено залежності $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ від log I, виходячи з закономірностей, які є добре відомими для міцелярних систем ПАР. Всі вищезгадані системи були вивчені методом динамічного розсіювання світла за допомогою приладу Zetasizer Nano ZS Malvern Instruments. Було виявлено, при іонній силі 3×10^{-3} M і більше, розмір (за числом частинок) полііонів в присутності NaCl становить близько 7 нм. Введення добавок приводить до деякого збільшення розміру: при добавках бутанолу-1 розмір частинок NaPSS складає 10 нм.

Ключові слова: полієлектроліт, полі (4-стиренсульфонат натрію), нейтральний червоний, уявна константа іонізації, бутанол-1, тетра-*н*-алкіламонієвий катіон.