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

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Polyions of poly (sodium 4-styrenesulfonate) in aqueous solution may be considered as colloidal pseudo-phase. 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 spectrophotometrical 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 $pK_a^{app} = 7.90 \pm 0.07$ at $I = 0.02$ M whereas $pK_a^{app} = 8.45 \pm 0.04$ with NaCl at the same ionic strength. It can be explained by specific 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-

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 $70 \times 10^3 \text{ g mol}^{-1}$. 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 'Filtracido hydrochlorico extracta' (Specialpapierfabric Niederschlag, Germany). The precise dye concentration was ascertained by spectrophotometric method using molar absorptivity value, $1.72 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at 530 nm [26]. The dye concentrations in work solutions was about $3 \times 10^{-5} \text{ M}$. Hereafter, $1 \text{ M} = 1 \text{ mol dm}^{-3}$.

The pH values of the solutions were adjusted using HCl for $\text{pH} < 4$, or buffer solutions: phosphate ($\text{pH} 5.8 - 8.5$) or borate ($\text{pH} 7.8 - 10.0$). 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:

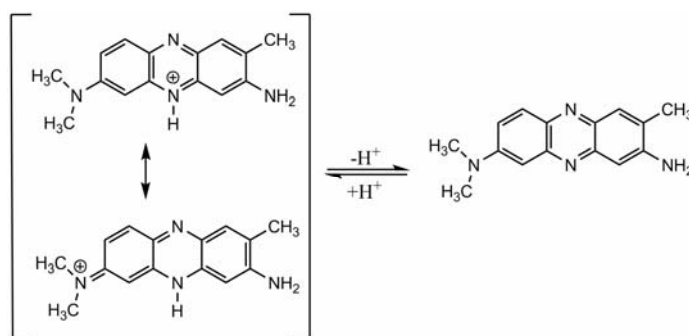


Therefore, the apparent ionization constant should be expressed as:

$$\text{p}K_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HB}^+]_t}{[\text{B}]_t} = \text{pH}_w + \log \frac{A_B - A}{A - A_{\text{HB}}} \quad (2)$$

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 $[\text{HB}^+]_t/[\text{B}]_t$ 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 + But₄NI, NaPSS + Et₄NBr 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.

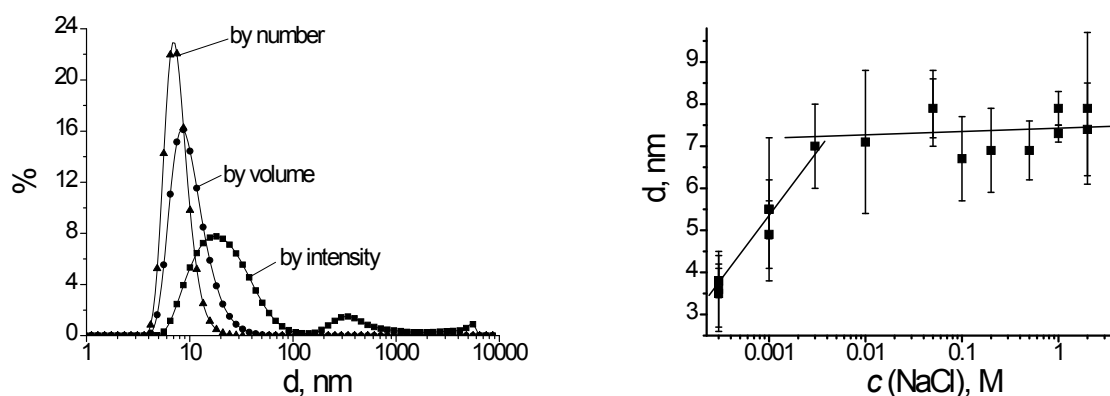


Figure 1. The macromolecules size distribution by intensity, by volume, and by number in 0.001 M NaPSS solution with 0.05 M NaCl, d (by intensity) = 25 ± 5 nm, d (by volume) = 13.3 ± 2.7 nm, d (by number) = 7.9 ± 0.7 nm (a); the dependence of polyions size (by number), d , on NaCl concentration, c (NaPSS) = 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 But₄NI and Et₄NBr 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 But₄NI. 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 polyelectro-

lyte '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.

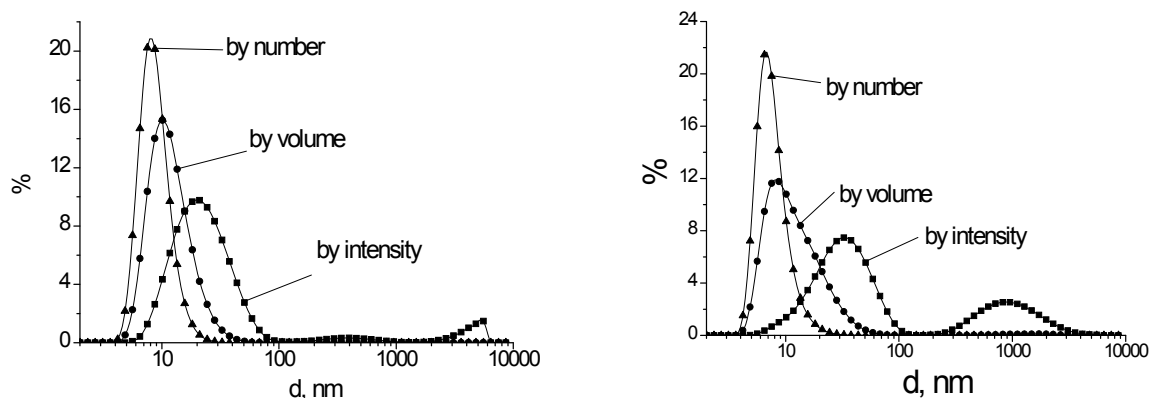


Figure 2. The macromolecules size distribution by intensity, by volume, and by number in 0.001 M NaPSS solution with 0.02 M But_4NI addition (a) and with 0.02 M Et_4NBr addition (b).

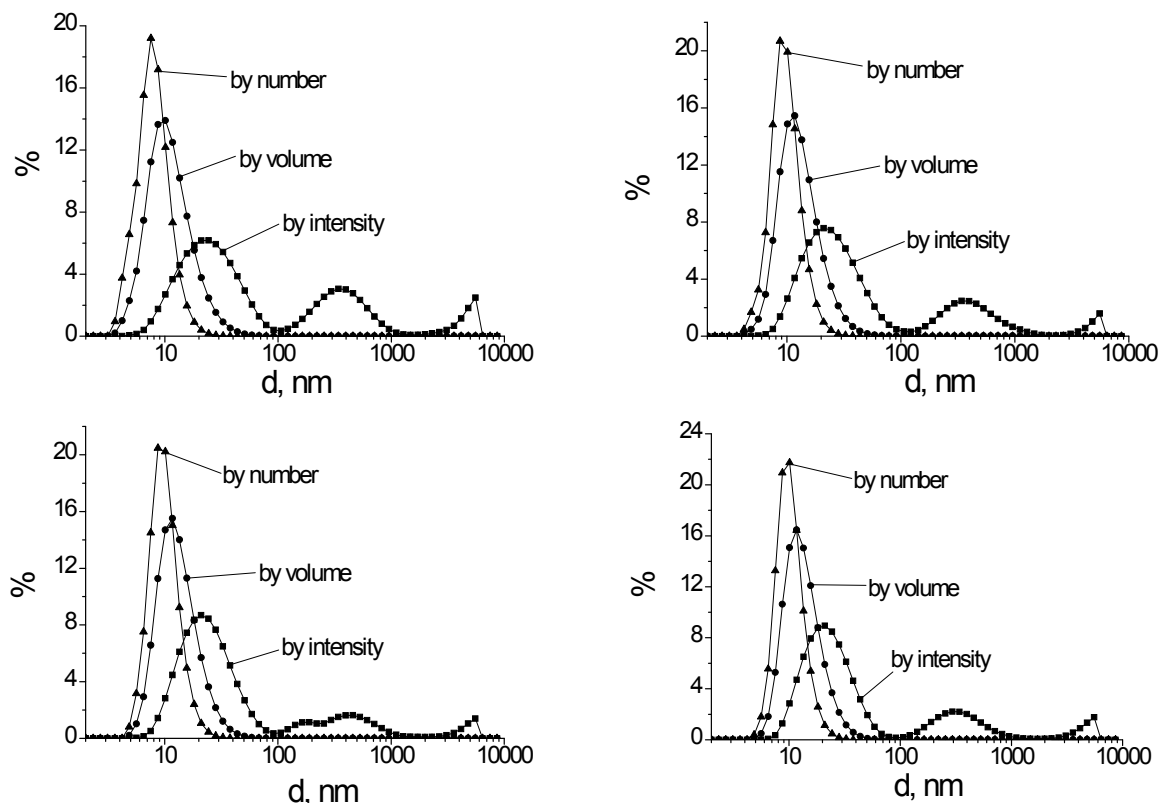


Figure 3. The macromolecules size distribution by intensity, by volume, and by number in 0.003 M NaPSS solution with 0.8 M 1-butanol: (a) 0.01 M NaCl; (b) 0.045 M NaCl; (c) 0.05 M NaCl; (d) 0.20 M NaCl.

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

$c(\text{NaPSS}), \text{M}$	$c(\text{NaCl}), \text{M}$	$d_{\text{Intensity}}$	d_{Volume}	d_{Number}	d_{hd}	$D \times 10^7, \text{cm}^2/\text{s}$
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 $\text{p}K_a^{\text{app}}$ values reported in this paper were obtained at polyelectrolyte : dye concentration ratio, $P : D$, equals 100. It allows avoiding polyelectrolyte-induced metachromatic 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 $\text{p}K_a^{\text{app}}$ values of NR. As reported earlier [20,35], in micellar solution the dependences of $\text{p}K_a^{\text{app}}$ on $\log I$ (or more precisely $\log c_{\text{counterion}}$) 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:

$$\text{p}K_a^{\text{app}} = B - b \times \log [Na_w^+] \quad (3)$$

$$\beta = - \frac{\partial \text{p}K_a^{\text{app}}}{\partial \log [Na_w^+]} \quad (4)$$

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 $I = 0.02 \text{ M}$ 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 $\text{p}K_a^{\text{app}}$ 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 $\text{p}K_a^{\text{app}}$ 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, $\text{p}K_a^{\text{app}}$ 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 $\text{p}K_a^{\text{app}}$ 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 pK_a^{app} values. These values are mentioned in Table 2, but they aren't used in further discussion because of their non-systematic character.

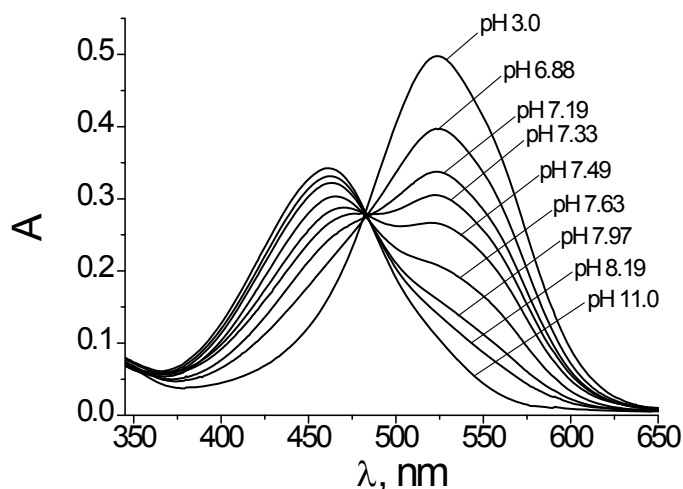


Figure 4. The spectra of NR in ternary system water – NaPSS – Et₄NBr at $I = 0.10$ M, $c(\text{Et}_4\text{NBr}) = 0.08 - 0.09$ M; $c_{\text{dye}} = 3.48 \times 10^{-5}$ M; phosphate buffer solutions except pH 3.0 (HCl solution), pH 11.0 (NaOH solution), and pH 7.6 – 8.2 (borate buffer).

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

I, M	NaCl ^a	Et ₄ NBr, borate buffer	Et ₄ NBr, phosphate buffer
0.01	8.62 ± 0.06 (borate buffer)	8.24 ± 0.12 $7.93 \pm 0.04^{\text{b}}$	—
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 $7.50 \pm 0.04^{\text{b}}$
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 pK_a^{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 But₄NI $pK_a^{\text{app}} = 7.69 \pm 0.04$ when borate buffer were used or 7.89 ± 0.07 in the case of phosphate buffer at $I = 0.02$ M and $c(\text{But}_4\text{NI}) = 0.01$ M. The decrease in pK_a^{app} value as compared with pK_a^{app} in water – NaPSS – NaCl system is considerable even at low salt concentration. Due to low solubility of But₄NI 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 – Na₂B₄O₇ system the dependences of pK_a^{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 – Et₄NBr – 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 adsorption 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.

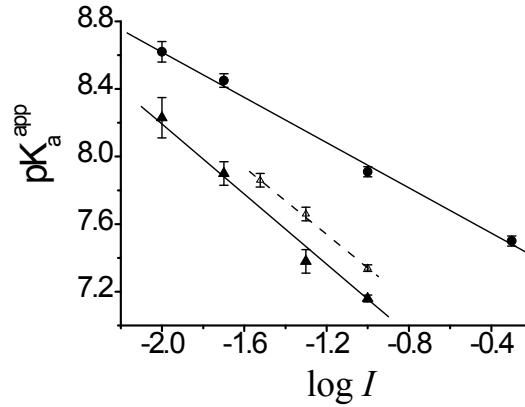


Figure 5. The dependence of pK_a^{app} s on logarithm of ionic strength (Et₄NBr or NaCl) in NaPSS-based systems. The characteristics of dependences are:

circles (NaCl): $pK_a^{\text{app}} = (7.28 \pm 0.03) - (0.67 \pm 0.03) \times \log I$, $n=4$, $R^2=0.9973$;

full triangles (Et₄NBr, borate buffer): $pK_a^{\text{app}} = (6.12 \pm 0.09) - (1.04 \pm 0.08) \times \log I$, $n=4$, $R^2=0.9949$;

empty triangles (Et₄NBr, phosphate buffer): $pK_a^{\text{app}} = (6.33 \pm 0.09) - (1.01 \pm 0.08) \times \log I$, $n=3$.

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 $\log \gamma_B / \gamma_{\text{HB}}$ becomes more negative [Eq. (5)] due to decrease in ε :

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

Here e is the elemental charge, N_A is Avogadro number, $\varepsilon_0 = 8.854 \times 10^{-12}$ 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 $\Delta G_{\text{tr}}^{\text{sol}}$ 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 °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°C it is 8.03 % (wt) or at 30.8°C it is 7.07 % (wt). The solubility of 1-butanol decreases with temperature rise up to 60°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 pK_a^{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 pK_a^{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 pK_a^{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 pK_a^{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	pK_a^{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 pK_a^{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, $\lambda_{\text{max}} = 530$ 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, $\lambda_{\text{max}} = 525 \pm 1$ 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.

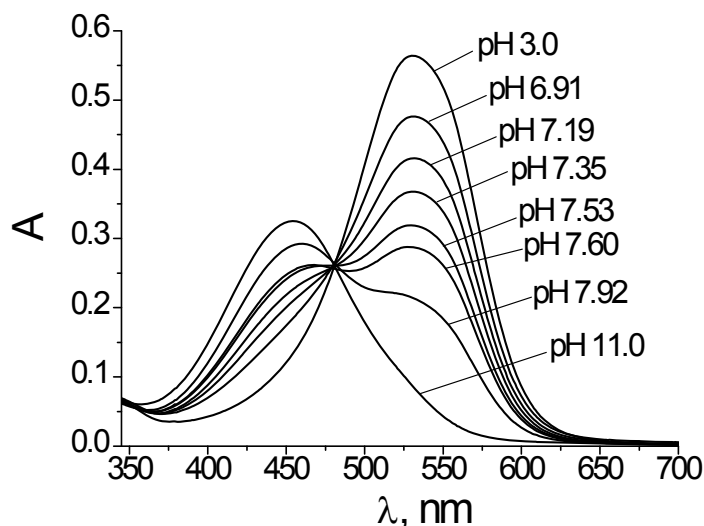


Figure 6. The spectra of NR in quaternary system water – NaPSS – 1-butanol – NaCl at $I = 0.04$ M; $c_{\text{dye}} = 3.44 \times 10^{-5}$ M; phosphate buffer solutions except pH 3.0 (HCl solution) and pH 11.0 (NaOH solution).

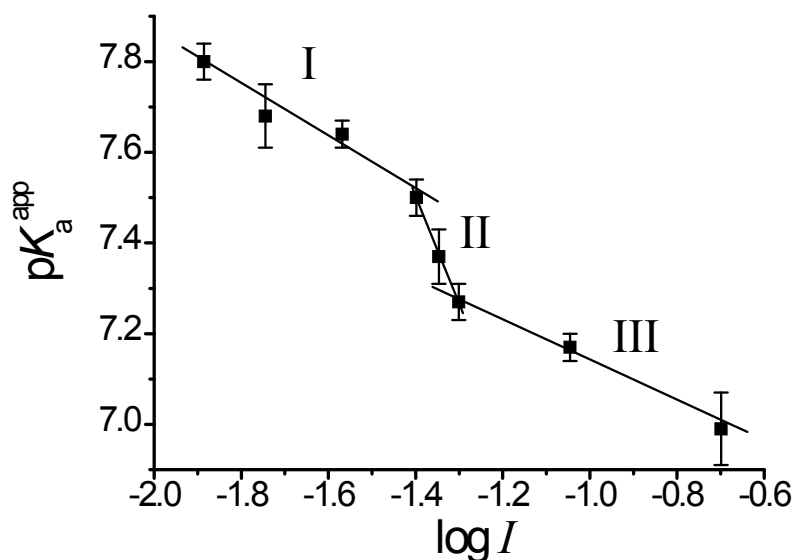


Figure 7. The dependence of pK_a^{app} s on logarithm of ionic strength (NaCl) in NaPSS-based systems contained 0.80 M 1-butanol. The characteristics of different sections of dependence are:

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

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

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

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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_a^{app} , от ионной силы раствора, I , в разных смешанных системах, которые содержат поли (4-стиролсульфонат натрия) (NaPSS) и тетраэтиламмоний бромид, тетра-*n*-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-*n*-алкиламмониевые соли сильнее влияют на кислотную силу нейтрального красного по сравнению с NaCl. Например, в случае тетраэтиламмония бромида $pK_a^{\text{app}} = 7.90 \pm 0.07$ при $I = 0.02$ М, тогда как в присутствии NaCl при такой же ионной силе $pK_a^{\text{app}} = 8.45 \pm 0.04$. Это может быть объяснено специфической адсорбцией тетра-*n*-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 pK_a^{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} М 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-*n*-алкиламмониевый катион.

А.Ю. Харченко, О.Г. Москаева. 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 поліелектролітними клубками. В даній роботі забарвлені кислотно-основні індикаторні барвники були використані для вивчення проникнення іонних та неіонних компонентів розчину в поліелектролітні клубки. Такий аналіз ґрунтується на змінах кислотної сили барвників. Метою роботи було визначення залежностей уявних констант іонізації нейтрального червоного, K_a^{app} , від іонної сили розчину, I , в різних змішаних системах, що містять полі (4-стиренсульфонату натрію) (NaPSS) і тетраетиламоній бромід, тетра-*n*-бутиламоній іодид, або бутанол-1 з добавкою NaCl. Нейтральний червоний є зафіксованим на поліелектролітних клубках завдяки електростатичним та гідрофобним взаємодіям. Відношення концентрацій поліелектроліт : барвник, $P : D$, що є важливим параметром для спектрофотометричних вимірювань, дорівнює 100. Виявлено, що тетра-*n*-алкіламонієві солі сильніше впливають на кислотну силу нейтрального червоного порівняно з NaCl. Наприклад, у випадку тетраетиламонію броміду $pK_a^{\text{app}} = 7.90 \pm 0.07$ при $I = 0.02$ М, тоді як в присутності NaCl при такій же іонній силі $pK_a^{\text{app}} = 8.45 \pm 0.04$. Це може бути пояснено специфічною адсорбцією тетра-*n*-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 pK_a^{app} від $\log I$, виходячи з закономірностей, які є добре відомими для міцеллярних систем ПАВ. 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} М 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: поліелектроліт, полі (4-стиренсульфонат натрію), нейтральний червоний, уявна константа іонізації, бутанол-1, тетра-*n*-алкіламонієвий катіон.