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AQUEOUS SOLUTION OF POLY (HEXAMETHYLENE GUANIDINE HYDROCHLORIDE) AND POLY (DIETHYLENAMINE GUANIDINE HYDROCHLORIDE) AS STUDIED WITH ACID-BASE INDICATORS**A.Yu. Kharchenko^{a,*}, M.A. Romakh^{b,*}, K.V. Yanova,^{c,†}
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In this paper, the properties of cationic polyelectrolytes as tools for governing the protolytic equilibrium of acid-base indicators in water were examined. For this purpose, water-soluble and pH-dependent poly (hexamethylene guanidine hydrochloride), PHMG, and poly (diethylenamine guanidine hydrochloride), PDEG, were studied. As molecular probes, a set of anionic indicator dyes were used; the key parameter is the so-called apparent ionization constant, K_a^{app} . The electrokinetic potential of the above polycationic species in the acidic pH region is substantially positive. As a rule, the polyelectrolytes display marked influence on the absorption spectra and state of the acid-base equilibrium of the anionic dyes at $pH < 7$, especially in the case of PHMG. Both effects resemble those known for the same dyes in aqueous solutions of cationic surfactants but are less expressed. Normally, the acid-base equilibria were studied at polyelectrolyte : dye ratio of 150 : 1, at ionic strength 0.05 M, and 25 °C. The decrease in the pK_a^{app} ($\equiv -\log K_a^{app}$) value on going from water to the PHMG solution is most expressed for bromocresol green ($HB^- \rightleftharpoons B^{2-} + H^+$): $pK_{a,2}^{app} - pK_{a,2}^w = -1.93$. For bromophenol blue, bromocresol purple, and sulfonefluorescein, the shift of the equilibrium is less expressed. Some kinds of specific interactions with the polyelectrolytes were revealed for methyl orange and bromophenol blue. Also, the dependence of pK_a^{app} on logarithm of ionic strength allows estimating the degree of counterion binding by the polycation: $\beta = 0.4 \pm 0.1$.

Keywords: polycation, indicator dye, apparent ionization constant, poly (hexamethylene guanidine hydrochloride), poly (diethylenamine guanidine hydrochloride), sulfonefluorescein, methyl orange, sulfonephthal-eins.

Introduction

This paper is aimed to study the influence of cationic polyelectrolytes on the protolytic equilibrium of acid-base indicators in water. Solutions of cationic polyelectrolytes, particularly poly (hexamethylene guanidine hydrochloride) (PHMG), possess antibacterial properties, so the investigation of surface characteristics of colloidal particles (e.g., the ζ -potential) is necessary for studying interactions poly-ion–bacterium [1]. Cationic polyelectrolytes are used for synthesis of polymer subunit vaccines, for example, polyoxidonium medicine [2]. Also, the cationic polyelectrolytes are applied as flocculants for dyeing wastewater treatment [3-5]. For instance, recently, Jia et al. reported the synthesis of a series of new hydrophobic cationic poly(dimethyldiallylammonium chloride)s and showed the efficiency of the removal of water-soluble dyes in dyeing wastewater using two anionic dyes Reactive Scarlet 3BS and Reactive Black M [3]. It was shown that the composition of a complex of a cationic unit of poly(dimethyldiallylammonium chloride)s with a dye depends on the structure of polyelectrolyte and the polyelectrolyte : dye (P : D) ratio varies from 1 to 4.

On the other hand, indicator dyes were used for the determination of polyelectrolytes concentration [6]. The application of association processes between organic reagents (dyes, e.g., xanthenes) and cationic polyelectrolytes for determination of the later were scrutinized by Chmilenko et al. [7,8]. These investigations were aimed to detect as low as possible polyelectrolyte concentrations, so the P : D ratio was about 1 in these studies. Under such conditions, the influence of polyions on the acid-base equilibria of dyes in solution may somewhat differ from that at high concentrations of the poly-

lectrolytes. Higher P : D ratio, normally 100 : 1, was used by us earlier when studying interactions between indicator dyes and an anionic polyelectrolyte poly (sodium 4-styrenesulfonate) [9].

Therefore, it is important to study the changes of protolytic properties of dyes when their concentration is much lower than that of a cationic polyelectrolyte. This allows ruling out the interaction between dye molecules fixed at the polyion, known as metachromasy.

So, our aim was to determine the acidic strength of common anionic indicator dyes in aqueous solutions of cationic electrolytes, with high P : D values. As a key parameter, the so-called apparent ionization constant, K_a^{app} , was chosen. The present study was devoted to aqueous solutions of poly (hexamethylene guanidine hydrochloride), PHMG, and poly (diethylenamine guanidine hydrochloride), PDEG. The structures of PHMG and PDEG are shown in Figure 1. Owing to the presence of secondary amino groups such polyelectrolytes are pH-dependent [8].

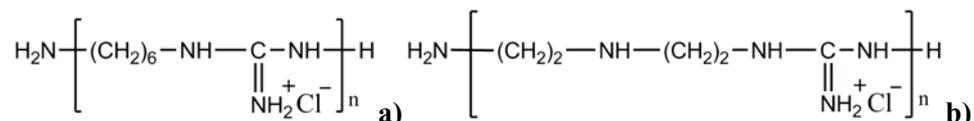
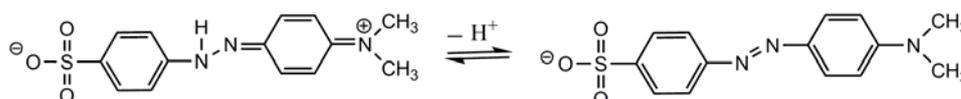


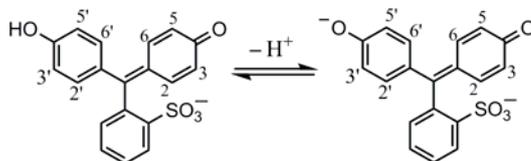
Figure 1. Structural formulae of poly (hexamethylene guanidine hydrochloride) (PHMG) (a) and poly (diethylenamine guanidine hydrochloride) (PDEG) (b).

As indicator dyes, methyl orange, sulfonefluorescein, and three sulfonephthalein dyes were used. The protolytic properties of these anionic dyes in micellar solution are well documented. In our previous work, we obtained the $\text{p}K_a^{\text{app}}$ ($\equiv -\log K_a^{\text{app}}$) values of dyes in 5×10^{-4} M solution of di-tetradecyldimethylammonium bromide and 0.01 M solution of cetyltrimethylammonium bromide [10,11]. The medium effects, i.e., the differences between the so-called apparent $\text{p}K_a^{\text{app}}$ values and the thermodynamic values in water, $\text{p}K_a^{\text{w}}$, vary from -1.1 to -1.8 $\text{p}K_a$ units in the above systems [10,11]. Similar medium effect were observed earlier for bromothymol blue in aqueous solutions of poly [(vinylbenzyl)trimethylammonium chloride] by Baumgartner et al. [12].

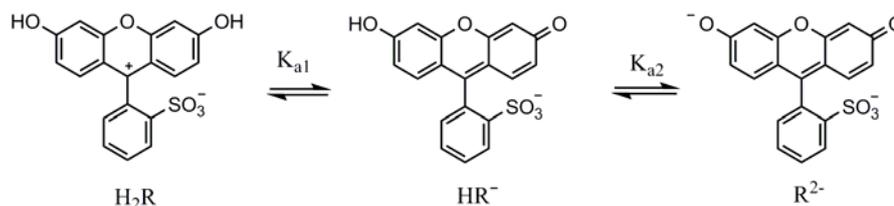
The ionization of the zwitter-ion of methyl orange, HB^{\pm} , corresponds to the charge type $\pm/-$. The second step of sulfonephthaleins ionization occurs according to the charge type $-/=$ (bromophenol blue, bromocresol green, bromocresol purple). Also, sulfonefluorescein was used as a dye which ionizes by two steps ($\pm/-$ and $-/=$). The equilibria of the dyes are shown in Schemes 1–3. Analogously to the systems “cationic dye – polyanion”, these anionic dyes are bound to polycations primarily due to electrostatic interactions [4,9,13–15].



Scheme 1. The ionization of methyl orange.



Scheme 2. The ionization of sulfonephthalein dyes: 3,3',5,5'- tetrabromo- (bromophenol blue); 2,2'-dimethyl-3,3',5,5'-tetrabromo- (bromocresol green); 3,3'-dimethyl-5,5'-dibromosulfonephthalein (bromocresol purple).



Scheme 3. The ionization of sulfonefluorescein.

Experimental section

Materials. The cationic polyelectrolytes poly (hexamethylene guanidine hydrochloride) (PHMG) and poly (diethylenamine guanidine hydrochloride) (PDEG) were synthesized in Ukrainian State University of Chemical Technology, Dnipro; the synthesis is described in publications [16] and [17], respectively. These substances were prepared initially as 25 wt % aqueous solution. The molecular mass of PGMG is $10 \times 10^3 \text{ g mol}^{-1}$ while PDEG is characterized by some less molecular mass of $8 \times 10^3 \text{ g mol}^{-1}$. The stock solutions of PHMG and PDEG with the concentrations, which as a rule didn't exceed 0.10 M, were prepared by weighting. They appeared to be slightly alkaline. The weighted sample of the stock polyelectrolyte solution was diluted with pure water, stirred, and used as a stock solution. The working solutions were prepared by further dilution. Hereafter, the concentrations of polyelectrolytes are expressed in monomer mol dm^{-3} (monomol dm^{-3} or M). The pH values of the diluted polyelectrolyte solutions in water without buffer additives were somewhat enhanced as compared with the air-saturated water. For example, in 0.00132 M PHMG $\text{pH} = 7.23$ and in 0.0145 M PDEG $\text{pH} = 8.33$. Poly (sodium 4-styrenesulfonate), molecular mass of $70 \times 10^3 \text{ g mol}^{-1}$, was purchased from Sigma-Aldrich as a powder. The polyelectrolyte was used as received; its solutions were prepared as described previously [9]. The anionic surfactant sodium *n*-dodecylsulfate was used as received from Vekton (Russia). Hydrochloric, acetic, and phosphoric acids, and borax used for preparation of working solutions were of analytical grade. The aqueous solution of NaOH was prepared using the saturated stock solution of alkali using CO_2 -free water and kept protected from the atmosphere. The ionic strength, *I*, of the acetate buffer mixtures used for determination of the ionization constants did not exceed 0.01 M. The total *I* value of the bulk (aqueous) phase was maintained by appropriate NaCl addition. The samples of the dyes neutral red, bromophenol blue, bromocresol green, bromocresol purple, methyl orange, and sulfonefluorescein were already used in our previous studies [9-11,18,19].

Methods. The apparent ionization constants of indicator dyes were determined via a standard procedure [9–12, 18, 19]. Absorption spectra were measured with Hitachi U-2000 spectrophotometer against pure water as blanks, at 25°C. The pH values were created 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 cell was calibrated with standard buffer solutions: pH 9.18, 6.86, 4.01, and 1.68 at 25°C.

The ionization of an indicator acid in solution can be described by the below equation:



Therefore, the apparent ionization constant, K_a^{app} , should be expressed as:

$$\text{p}K_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HB}^z]_t}{[\text{B}^{z-1}]_t} = \text{pH}_w + \log \frac{A_B - A}{A - A_{\text{HB}}} \quad (2)$$

The brackets denote equilibrium concentrations. The acid-base couple $\text{HB}^z/\text{B}^{z-1}$ is (partly) associated with polycations; pH_w is the pH value of the continuous (aqueous) phase; *A* is the absorbance at the current pH_w value, A_B and A_{HB} are absorbances under conditions of complete transformation of the indicator into the corresponding form. The subscript *t* (total) denotes that the concentration is expressed in moles per dm^3 of the whole solution.

The precise dye concentrations were ascertained by spectrophotometric method using the previously known molar absorptivity values. The dye concentrations in working solutions were about 1×10^{-5} M. Similarly to anionic polyelectrolyte solutions, cationic polyelectrolyte solutions results in metachromasy of some dyes [20]. So, it is necessary to control the polyelectrolyte : dye concentration ratio, P : D, for all chosen dyes.

The polyelectrolyte 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 ns, and 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, the "solvent builder", was used. This program, which is introduced in the Zetasizer soft, allows calculating the viscosity of the dispersant at NaCl additions.

Results and discussion

DLS characterization of polyelectrolyte solutions. The dependence of ζ -potential of PHMG on pH values was already reported by Wojciechowski and Klodzinska [1]. We measured this parameter of PHMG at pH 2. A mean value of $+21 \pm 9$ mV was evaluated. However, the ζ value changed from 8.7 to 39.8 mV, and some precipitation was observed during the measurements. Probably, electrocoagulation is the main reason of this disturbing phenomenon, but in any case a substantial positive charge of the macromolecular species is firmly proved. The same is true for PDEG. A particles' size of 1–2 nanometers was roughly estimated, which is in agreement with the above mentioned molecular mass.

Methyl orange. First of all, methyl orange as indicator dye was used because of its relatively simple structure and well-known solvatochromic properties [21]. As it was shown in our previous paper devoted to aqueous solutions of an anionic polyelectrolyte [9], the appropriate conditions for the determination of apparent ionization constants of dyes are reached in semi-diluted polyelectrolyte solutions. Hereafter, we define the polyelectrolyte : dye concentration ratio as P : D. In general, at P : D = 100 – 1000, one can reach condition similar to those in surfactant micelles, when a dye molecule interacts only with cationic sites of polyelectrolyte and is not influenced by another dye molecule. These conclusions should be correct for methyl orange too. For example, Vleugels et al. [20] carried out a detailed investigation of the interaction between methyl orange and polycations. They have investigated the influence of molecular structure of the cations, composition (i.e., P : D ratio), pH, and ionic strength on association between methyl orange and polycations. It was shown that in solutions of poly (diallyldimethylamine hydrochloride), a pH-independent quaternary ammonium salt with molecular mass of 107×10^3 g mol⁻¹, the metachromatic band of dye aggregates appeared in acetate buffer (pH = 4.0, $I = 0.01$ M) at P : D \approx 0.2–1.0.

In our study in unbuffered systems with pH \approx 7.0 and $I \rightarrow 0$, the methyl orange aggregate band about 350 nm appeared in PDEG solutions even at P : D = 100. This type of aggregates is well documented in the literature [20, 21]. However, under these conditions no distinct bands were observed in the case of PHMG (Figure 2).

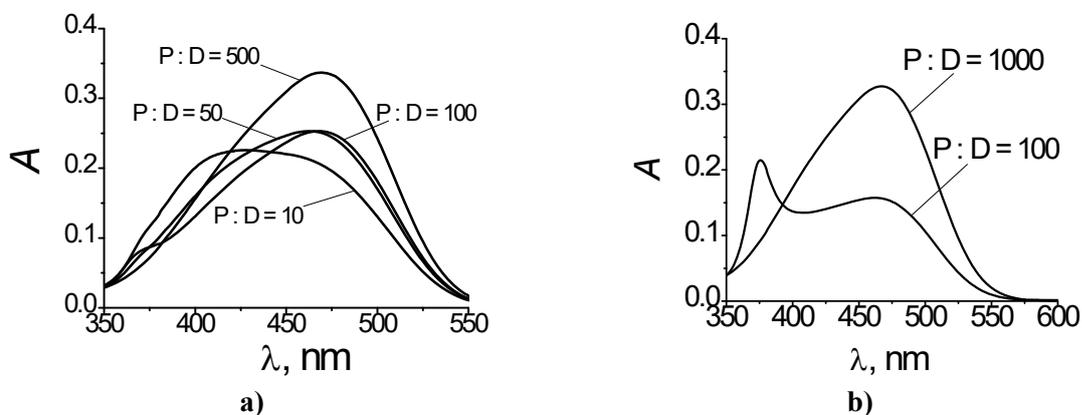


Figure 2. Absorption spectra of methyl orange in PHMG (a) and PDEG (b) solutions at different P : D values, c (dye) = 1.45×10^{-5} M.

The pK_a^{app} values of methyl orange were determined under conditions that allowed to avoid dye aggregation. Therefore, the experiments for PHMG and PDEG were made at the P : D ratio of 500 and 1000, respectively. The pH-dependence of absorption spectra is depicted in Figure 3.

The pK_a^{app} values in colloidal solution of PHMG and PDEG are 2.91 ± 0.03 and 3.19 ± 0.05 , respectively. They are lower as compared with the thermodynamic value in water: $pK_a^{\text{w}} = 3.42 \pm 0.02$ [22]; 3.45 [23], but the decrease in micellar solutions of cationic surfactants and in corresponding microemulsions is much more expressed: the pK_a^{app} values in such systems are below unity [22, 24]. Though methyl orange is a solvatochromic indicator, no significant shifts of absorption maximum was observed. While in a cationic surfactant-based microemulsion, λ_{max} moved from 462–463 nm to 420 nm [24], in PHMG and PDEG solutions $\lambda_{\text{max}} = 469$ nm and 466.5 nm, respectively at pH \approx 7.0,

$I \rightarrow 0$. Hence, these small shifts are bathochromic, which is not typical for the anionic form of methyl orange on going from water to organic microenvironments.

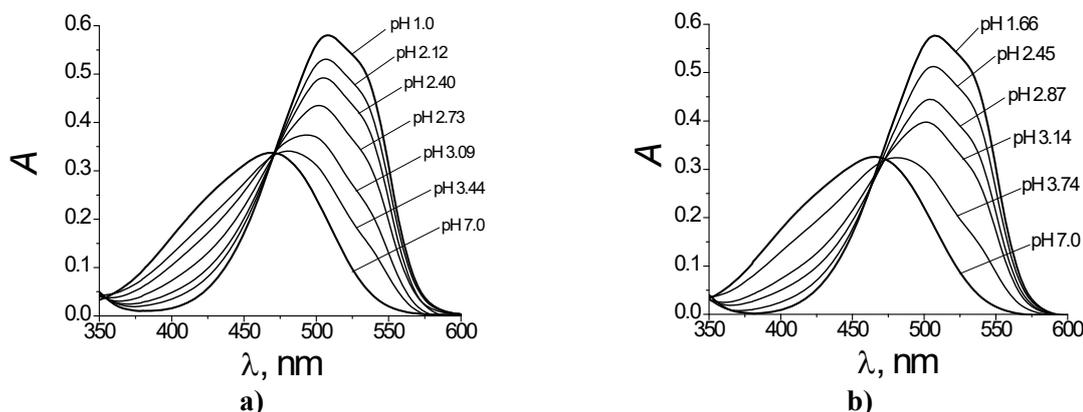


Figure 3. Absorption spectra of methyl orange in PHMG solutions at P : D = 500 (a) and in PDEG solutions at P : D = 1000 (b) at different pH; HCl solutions, $I = 0.05$ M (HCl + NaCl), c (dye) = 1.45×10^{-5} M.

Relatively small medium effects, i.e., the pK_a^{app} shifts, for methyl orange in PHMG and PDEG solutions can result from charge type “zwitter-ion \rightarrow anion”. Also, the incomplete binding of the zwitter-ion by the macromolecule should not be ruled out because the λ_{max} values in the polyelectrolyte solutions are ca. the same as in water.

Sulfonefluorescein. In order to examine the influence of the charge type of an acid-base indicator couple on the medium effects (pK_a^{app} shifts) in cationic polyelectrolyte solutions we used the dye sulfonefluorescein. In this case (Scheme 3), the two-step ionization occurs from the zwitter-ion to the anion and then to the dianion. The absorption spectra of sulfonefluorescein at different pH and $I = 0.05$ M are presented in Figure 4. The ratio P : D = 100 was chosen for the absorption spectra analysis of sulfonefluorescein in PHMG solutions. As sulfonefluorescein is not a metachromatic dye, such P : D ratio is enough for observation of isolated dye molecules in polyelectrolyte microenvironment. Two distinct isosbestic points were observed that opens the possibility to determine the indices of the apparent ionization constants: $pK_{a1}^{\text{app}} = 3.00 \pm 0.08$ and $pK_{a2}^{\text{app}} = 5.77 \pm 0.09$. In water, $pK_a^{\text{w}} = 3.10$ and $pK_a^{\text{w}} = 6.76$ [18]. Thus, the medium effect in the case of the ionization of the anion (-0.99 pK_a units) is much more expressed than in the case of the zwitter-ion \rightarrow anion equilibrium (-0.1 pK_a units). Here, as in the case of methyl orange, the degree of binding of zwitter-ionic form is unclear. By contrast, the association of anionic dye species with the polycation is more probable.

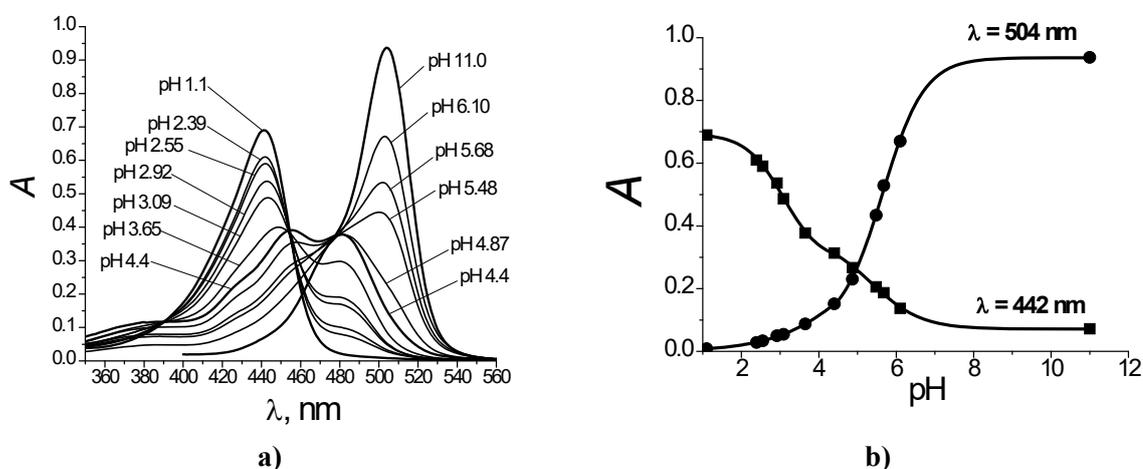


Figure 4. The absorption spectra of sulfonefluorescein in PHMG solution at P : D = 100 at different pH (the HCl solutions, acetate and phosphate buffer were used), $I = 0.05$ M, c (dye) = 1.39×10^{-5} M (a); the dependence of absorption of sulfonefluorescein in PHMG solution on pH, P : D = 100, $I = 0.05$ M (b).

The pK_{a2}^{app} values of the dye in 5×10^{-4} M solution of di-*n*-tetradecyldimethylammonium bromide, $I = 0.01$ M [10] and 0.01 M solution of cetyltrimethylammonium bromide, $I = 0.05$ M [11] are 4.91 and 5.73, respectively. Again, the medium effects in PHMG solutions are less expressed than in micellar solutions of cationic surfactants.

Thus, the influence of PHMG on protolytic equilibria of dyes is much more expressed in the case of the charge type $-/=$. Therefore, sulfonephthalein dyes (Scheme 2) were used for further investigations.

Sulfonephthaleins. A pronounced metachromatic effect was observed for bromophenol blue in solutions of PHMG and PDEG (Figure 5). At low P : D ratio, the dye aggregates manifest themselves in significant changes of absorption spectra. Moreover, in PHMG solution at P : D = 1 a fine-dispersed sediment appears due to association of dye molecules with polyelectrolyte cationic sites.

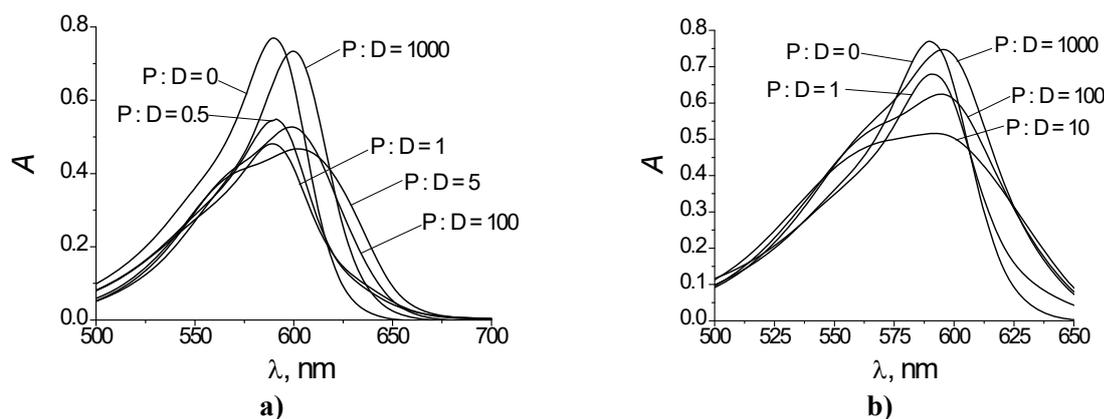


Figure 5. The absorption spectra of bromophenol blue in PHMG (a) and PDEG (b) solution at different P : D values, c (dye) = 1×10^{-5} M, $pH \approx 11.0$, $I \rightarrow 0$.

Correspondingly, the determination of pK_a^{app} values of bromophenol blue was complicated by the abovementioned coagulation processes. In Figure 6, the absorption spectra of bromophenol blue solutions are shown at different pH and P : D = 100 and 1000. In the case of PDEG at higher pH values, pH 12, the dye is displaced from pseudophase due to deprotonation of the polycations and disappearance of its positive charge [8].

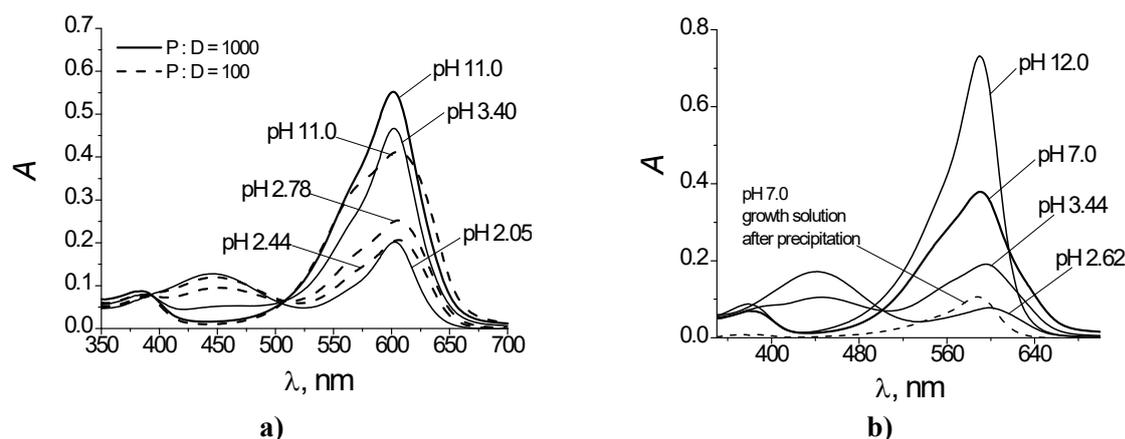


Figure 6. The absorption spectra of bromophenol blue in PHMG solution at P : D = 100 and 1000 at different pH (the HCl solutions were used) (a), and in PDEG solution at P : D = 100 at different pH (the HCl solutions were used) (b), $I = 0.05$ M, c (dye) = 1.0×10^{-5} M.

At low P : D values, bromocresol purple also forms aggregates, but at P : D = 150 it is possible to obtain the pK_a^{app} value in PHMG solutions (Table 1). On the other hand, the polyelectrolyte PDEG cannot bind the dye molecules probably due to deprotonation of the polycation within the pH range

that corresponds to the protolytic equilibrium of bromocresol purple ($pK_a^w = 6.30$). This statement is confirmed by significant dependence of pK_a^{app} values on pH ($pK_a^{app} = 5.98 - 6.33$). The pK_a^{app} value increases along with the pH rise. The highest medium effect is observed for bromocresol green, $pK_a^{app} - pK_a^w = -1.93$. However, in this case the pK_a^{app} value is also influenced by pH: pK_a^{app} changes from 2.74 to 3.18 at pH 2.39 to 3.95. This may be a result of structural changes of the macromolecule. The absorption spectra are represented in Figures 7 and 8.

It may be concluded that the cationic polyelectrolytes under study in this work influence the protolytic equilibria of dyes similarly to micelles of cationic surfactants.

Table 1. The indices of the apparent ionization constants of the dyes in PHMG solutions at P : D = 150 and I = 0.05 M.

Indicator dye	pK_a^w	pK_a^{app}	$pK_a^{app} - pK_a^w$
Methyl orange, $pK_{a,1}$	3.44	2.91 ± 0.03^a	-0.53
Sulfonefluorescein, $pK_{a,1}$	3.10	3.00 ± 0.08^b	-0.10
Sulfonefluorescein, $pK_{a,2}$	6.76	5.77 ± 0.09^b	-0.99
Bromocresol purple, $pK_{a,2}$	6.30	4.88 ± 0.08^c	-1.42
Bromophenol blue, $pK_{a,2}$	4.20	$\approx 2.5^d$	≈ -1.7
Bromocresol green, $pK_{a,2}$	4.90	2.97 ± 0.18	-1.93

^a In PDEG solutions, $pK_a^{app} = 3.19 \pm 0.05$; ^b P : D = 100; ^c in PDEG solutions, $pK_a^{app} = 6.19 \pm 0.16$; ^d in PDEG solutions, $pK_a^{app} \approx 3.3$.

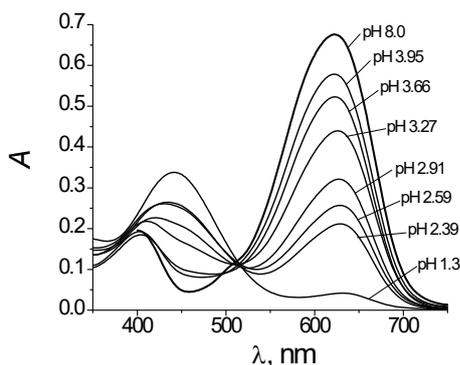


Figure 7. The absorption spectra of bromocresol green in PHMG solutions at different pH values (the HCl solutions were used) at P : D = 150 and I = 0.05 M, $c(\text{dye}) = 1.7 \times 10^{-5}$ M.

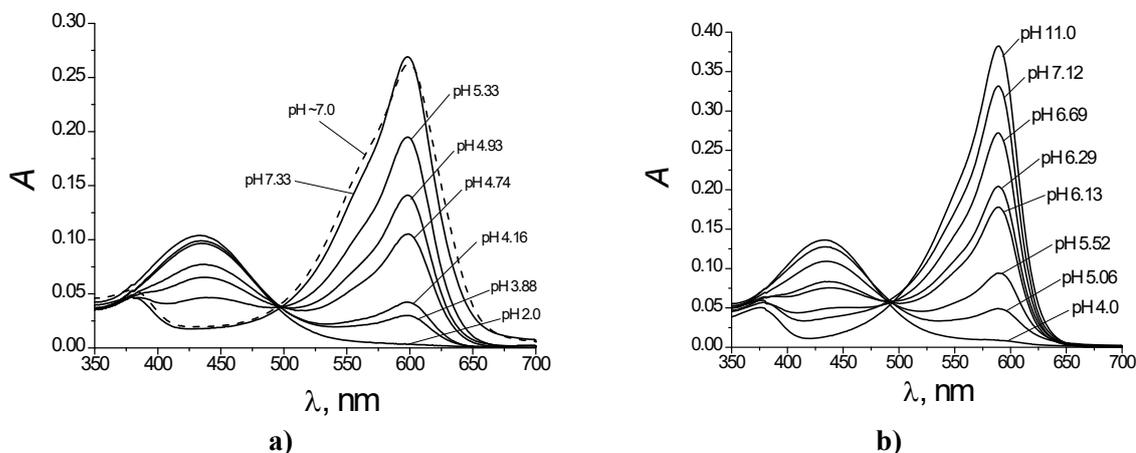


Figure 8. The absorption spectra of bromocresol purple in PHMG solutions at different pH values (acetate and phosphate buffer were used) at P : D = 140 and I = 0.05 M, $c(\text{dye}) = 9 \times 10^{-6}$ M (a); the absorption spectra of bromocresol purple in PDEG solutions at different pH values (acetate and phosphate buffer were used) at P : D = 150 and I = 0.05 M, $c(\text{dye}) = 9 \times 10^{-6}$ M (b).

Dependence of pK_a^{app} on ionic strength of PHMG solution. We have also examined the influence of the ionic strength maintained by NaCl on the acid-base equilibrium in these systems. As an example, the ionization of sulfonefluorescein was chosen because of less expressed tendency to precipitation in the presence of the polyelectrolytes under study. The absorption spectra of the dye at different pHs are exemplified in Figures 9, 10. It should be noted that at higher ionic strength, the isosbestic point that corresponds to the anion to dianion transition is somewhat fuzzy. As a probable reason the structural changes of the macromolecule in the acidic pH region may be assumed.

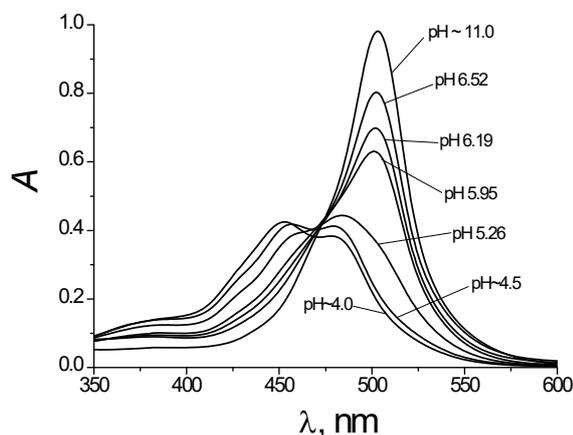


Figure 9. The absorption spectra of sulfonefluorescein in PHMG solution at P : D = 100 at different pH (acetate and phosphate buffer were used), $I = 0.10$ M, c (dye) = 1.35×10^{-5} M.

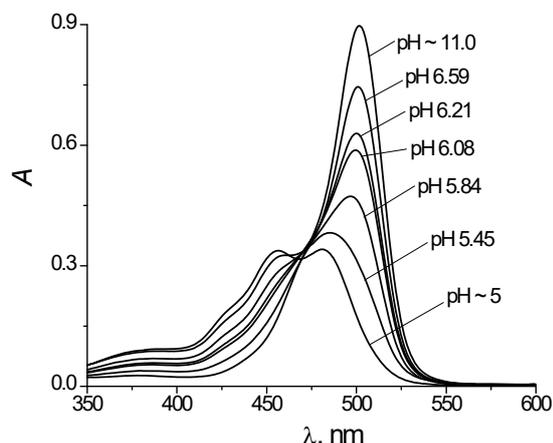


Figure 10. The absorption spectra of sulfonefluorescein in PHMG solution at P : D = 100 at different pH (acetate and phosphate buffer were used), $I = 0.20$ M, c (dye) = 1.35×10^{-5} M.

Assuming that the degree of binding of the dye anions by the PHMG stays unaffected during the I (NaCl + buffer mixture) variation and following the relations derived for ionic surfactants [18, 19], the slope of the pK_a^{app} vs $\log I$ may be considered as the degree of counterions binding, β . Here, Cl^- should be considered as counterion.

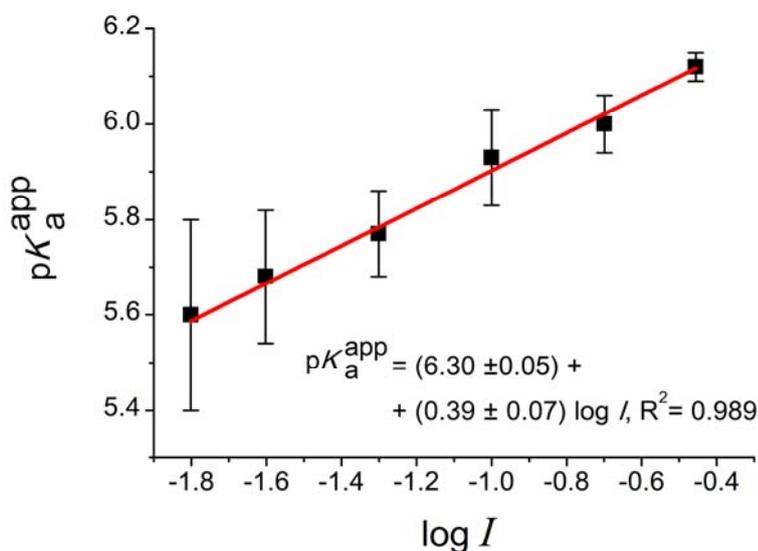


Figure 11. Dependence of pK_a^{app} on logarithm of ionic strength; sulfonefluorescein in the PHMG – NaCl system.

This β value is lower than that estimated with the help of the same dye for the cetyltrimethylammonium bromide – Br⁻ system (0.76 ± 0.02) [11]. The β value for the poly (sodium 4-styrenesulfonate) – Na⁺ system determined using a set of cationic dyes varies within the range of 0.58–0.72 [9]. For cationic polyelectrolytes, ion exchange constants of different counterions are available [25, 26]. They give evidence for relatively low affinity of the Cl⁻ ions to the cationic polyions.

Interaction of PHMG with an anionic polyelectrolyte. In addition to the above results we examined the interaction between a cationic polyelectrolyte and an anionic one. As cationic component, PHMG was chosen, whereas the previously studied poly (sodium 4-styrenesulfonate) [9] was used as a macroscopic counterion. Mixing these compounds predictably resulted in mutual coagulation. Next, the addition of sodium *n*-dodecylsulfate (0.02 M) caused peptization: the colloidal system was restored (Figure 12a).

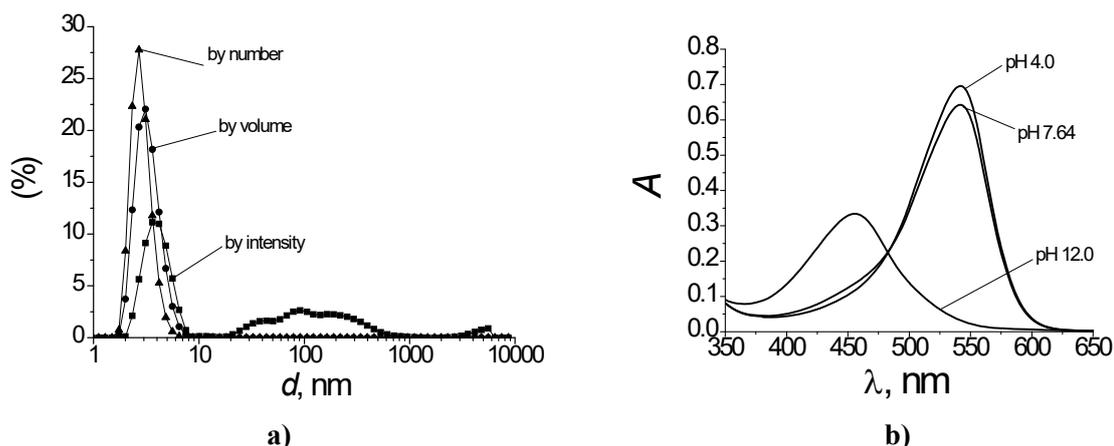


Figure 12. The size distribution of particles in system poly (sodium 4-styrenesulfonate) – PHMG – sodium *n*-dodecylsulfate, the analytical concentration was c (poly (sodium 4-styrenesulfonate)) = 0.0047 M, c (PHMG) = 0.005 M, c (sodium *n*-dodecylsulfate) = 0.02 M (a), the absorption spectra of neutral red in system poly (sodium 4-styrenesulfonate) – PHMG – sodium *n*-dodecylsulfate at $I = 0.05$ M, poly (sodium 4-styrenesulfonate) : D \sim 150, c (poly (sodium 4-styrenesulfonate)) = c (PHMG) = 0.005 M, c (sodium *n*-dodecylsulfate) = 0.02 M (b).

In Figure 12b, the absorption spectra of anionic dye neutral red are shown. The pK_a^{app} value of neutral red in the restored mixed colloid system was found of about 8.70 that semi-quantitatively agrees with that one in micellar solution of sodium *n*-dodecylsulfate, 9.21 [27]. Hence, the charge of thus obtained colloidal species is certainly negative, which explains the driving force of the peptization phenomenon.

Conclusions

1. The cationic polyelectrolytes examined in this paper exhibit strong interaction with anionic dyes. Besides the well-known metachromatic effect, the macromolecules display an expressed shift of the protolytic equilibria of indicators towards the acidic region.
2. The quantitative processing of the data at appropriate polyelectrolyte : dye ratio allows determining the apparent ionization constants of the indicators. Their values resemble the corresponding effect of micelles of cationic surfactants.
3. The dependence of pK_a^{app} vs. logarithm of ionic strength in the PHMG – NaCl system was treated analogously to the corresponding salt effects in micelles of ionic surfactants. This allowed estimating the degree of counterion Cl⁻ binding by the polycation as $\beta = 0.4 \pm 0.1$.
4. Interaction between PHMG and poly (sodium 4-styrenesulfonate) results in a kind of mutual coagulation. The deposit thus formed is dissolved by adding sodium *n*-dodecylsulfate. This procedure leads to appearance of negatively charged colloidal species.

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А.Ю. Харченко*, М.А. Ромах*, К.В. Янова†, М.Н. Терещук†, Н.О. Мchedlov-Петросян*. Водные растворы поли (гексаметилен гуанидин гидрохлорида) и поли (диэтиленамино-гуанидин гидрохлорида): исследование при помощи кислотно-основных индикаторов.

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В настоящей статье исследованы свойства катионных полиэлектролитов как средства управления протолитическими равновесиями кислотно-основных индикаторов в воде. С этой целью изучены водорастворимые pH-зависимые поли (гексаметилен гуанидин гидрохлорид), ПГМГ, и поли (диэтиламин гуанидин гидрохлорид), ПДЕГ. В качестве молекулярных зондов использован набор анионных индикаторных красителей, при этом ключевым параметром являются так называемые кажущиеся константы ионизации, K_a^{app} . Электрокинетический потенциал обоих катионных макромолекул в кислой области pH существенно положительный. Как правило, исследованные полиэлектролиты оказывают заметное влияние на спектры поглощения и положение кислотно-основных равновесий анионных красителей при pH < 7, особенно выраженное в случае ПГМГ. Оба упомянутых эффекта напоминают таковые для этих же красителей в растворах катионных ПАВ, но менее выражены. Кислотно-основные равновесия исследовались главным образом при соотношении полиэлектролит : краситель = 150 : 1, при ионной силе 0.05 М и 25 °С. Снижение значения pK_a^{app} ($\equiv -\log K_a^{app}$) при переходе от воды к растворам ПГМГ наиболее значителен для бромкрезолового зелёного ($HB^- \rightleftharpoons B^{2-} + H^+$): $pK_{a,2}^{app} - pK_{a,2}^w = -1.93$. Для бромфенолового синего, бромкрезолового пурпурного и сульфифлуоресцеина соответствующий сдвиг менее выражен. Обнаружены также некоторые специфические взаимодействия метилоранжа и бромфенолового синего с полиэлектролитами. Кроме того, зависимость pK_a^{app} от логарифма ионной силы позволяет оценить степень связывания протоионов поликатионом: $\beta = 0.4 \pm 0.1$.

Ключевые слова: поликатион, индикаторный краситель, кажущаяся константа ионизации, поли (гексаметилен гуанидин гидрохлорид), поли (диэтиламин гуанидин гидрохлорид), сульфифлуоресцеин, метилоранж, сульфифталеины.

А.Ю. Харченко*, М.О. Ромах*, К.В. Янова†, М.М. Терещук†, М.О. Мчедлов-Петросян*. Водні розчини полі (гексаметилен гуанідін гідрохлориду) та полі (диетиленаміно-гуанідін гідрохлориду): дослідження за допомогою кислотно-основних індикаторів.

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В цій статті досліджено властивості катіонних поліелектролітів як засобів керування протолітичними рівновагами кислотно-основних індикаторів у воді. З цією метою вивчено водорозчинні рН-залежні полі (гексаметилен гуанідін гідрохлорид), ПГМГ, та полі (діетиламін гуанідін гідрохлорид), ПДЕГ. Як молекулярні зонди використано набір аніонних індикаторних барвників, причому ключовим параметром є так звані уявні константи іонізації, K_a^{app} . Електрокінетичний потенціал обох макромолекул в кислій області рН суттєво позитивний. Як правило, досліджені поліелектроліти помітно впливають на спектри поглинання та стан кислотно-основних рівноваг барвників при рН < 7, особливо в разі ПГМГ. Обидва зазначені ефекти нагадують такі що спостерігалися для цих самих барвників у розчинах катіонних ПАВ, але не настільки виражені. Кисотно-основні рівноваги досліджувалися здебільшого при співвідношенні поліелектроліт : барвник = 150 : 1, при іонній силі 0,05 М і 25 °С. Зниження значення pK_a^{app} ($\equiv -\log K_a^{app}$) при переході від води до розчинів ПГМГ найбільш значне для бромкрезолового зеленого ($HB^- \rightleftharpoons B^{2-} + H^+$): $pK_{a,2}^{app} - pK_{a,2}^w = -1.93$. Для бромфенолового синього, бромкрезолового пурпурного та сульфифлуоресцеїна відповідний зсув менш виражений. Виявлено також деякі специфічні взаємодії метилоранжу та бромфенолового синього з поліелектролітами. Крім того, залежність pK_a^{app} від логарифму іонної сили дозволяє оцінити ступінь зв'язування протиіонів полікатионом: $\beta = 0.4 \pm 0.1$.

Ключові слова: полікатион, індикаторний барвник, уявна константа іонізації, полі (гексаметилен гуанідін гідрохлорид), полі (диетиленаміно-гуанідін гідрохлорид), сульфифлуоресцеїн, метилоранж, сульфифталеїни.

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