

## The binding ability and solvation properties of cationic spherical polyelectrolyte brushes as studied using acid-base and solvatochromic indicators

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In this work, we examined the spherical cationic polyelectrolyte brushes with (poly)styrene core and grafting density of the polyelectrolyte chains around  $0.033 \text{ nm}^{-2}$  in aqueous media by using a set of common acid-base indicators and some other dyes. The introduction of the cationic polyelectrolyte brushes (0.0014 to 0.0042 mass. %) into the buffered aqueous solutions of the indicator dyes causes substantial decrease in the indices of the so-called apparent ionization constants of the dyes,  $pK_a^{app}$ , from 0.2 to 2 units as compared with the  $pK_a$ s in brushes-free solutions. These effects resemble those repeatedly registered for the same dyes in the presence of cationic surfactant micelles, cationic dendrimers and calixarenes, cationic surfactant-modified silica nanoparticles, etc. However, contrary to the abovementioned colloidal species, the cationic brushes under study do not influence the absorption spectra of the same indicator dyes, including the most sensitive solvatochromic Reichardt's dye. Also, the tautomeric equilibrium shift of Fluorescein and solubilization of a poorly soluble Fluorescein derivative, typical for surfactant micelles and similar colloidal particles, was not registered with the brushes.

Исследованы сферические катионные полиэлектролитные щетки с полистирольным ядром и плотностью прививки полиэлектролитных цепей около  $0.033 \text{ нм}^{-2}$  в водных средах с использованием набора стандартных кислотно-основных индикаторов и некоторых других красителей. Введение катионных полиэлектролитных щеток (от 0.0014 до 0.0042 масс. %) в буферные водные растворы, содержащие индикаторные красители, приводит к существенному снижению показателей так называемых кажущихся констант ионизации красителей,  $pK_a^{app}$ , от 0.2 до 2 единиц, по сравнению со значениями  $pK_a$  в отсутствие щеток. Эти изменения напоминают эффекты, зарегистрированные для тех же красителей в присутствии мицелл катионных ПАВ, катионных дендримеров и каликсаренов, наночастиц кремнезема, модифицированных катионными ПАВ, и т.п. Однако, в отличие от вышеперечисленных коллоидных частиц, исследованные катионные щетки не влияют на спектры поглощения этих индикаторов, включая наиболее чувствительный сольватохромный краситель Райхардта. Кроме того, не зарегистрированы сдвиг таутомерного равновесия Флуоресцеина и солюбилизация его мало-растворимого в воде производного, хотя эти эффекты типичны для мицелл катионных ПАВ и подобных им коллоидных частиц.

## 1. Introduction

Spherical polyelectrolyte brushes (PB) consist of poly(styrene) core with covalently densely grafted polyelectrolyte chains [1–3]. Nowadays, these complicated particles serve as promising functional materials widely used in catalysis [1], as nanoreactors for synthesis of nanosized particles [2, 4–6], for binding of molecules and ions of various nature [7–9], etc. Though the PB do not belong to the self-associated aggregates, their shell resemble to some extent the hydrophilic portion of ionic surfactant micelles. For examining the surfactant micelles, microemulsions, water-soluble polyelectrolytes, etc., the solvatochromic and acid-base indicator dyes are used as useful molecular probes [10]. However, till recently, the ability of the brushes to bind different species was studied mainly by the example of some inorganic ions [5, 6, 9, 11] and enzymes and other proteins [7, 8]. In order to meet this lack, we studied the behavior of several common indicator dyes in solutions of cationic brushes MS4KS, prepared and characterized as described earlier [2].

In organized solutions, such as micellar solutions of colloidal surfactants, microemulsions, solutions of polyelectrolytes, etc., the nature of the experimentally determined ionization constants differs from that in true solutions. Indeed, the key characteristic of a pH-dependent indicator dye  $H_jR^z$ , dissolved in organized media, is the index of the so-called apparent ionization constant as defined by equation (1):

$$pK_a^{app} = p H + \log \frac{[H_jR^z]}{[H_{j-1}R^{z-1}]} \quad (1)$$

The ratio of equilibrium concentrations of  $H_jR^z$  and  $H_{j-1}R^{z-1}$  of a dye is determined vis-spectroscopically; the pH values utilized in calculations characterize only the bulk (aqueous) phase and are as a rule measured with a glass electrode, following the approved procedure.

## 2. Experimental

The structure of the studied cationic brushes in solution is given in Fig. 1.

The characterization of the brushes studied is as follows:  $R$  and  $L$  are around 45 and 71 nm, respectively; the grafting density of the polyelectrolyte chains is around  $0.033 \text{ nm}^{-2}$ .

As acid-base indicators, the commercial dyes Methyl Orange ( $HR^\pm \rightleftharpoons R^- + H^+$ ) and

five sulfonephthaleins ( $HR^- \rightleftharpoons R^{2-} + H^+$ ) were used: Bromophenol Blue (3,3',5,5'-tetrabromophenolsulfonephthalein), Bromocresol Green (3,3',5,5'-tetrabromo-2,2'-dimethylphenolsulfonephthalein), Bromocresol Purple (3,3'-dibromo-5,5'-dibromophenolsulfonephthalein), Bromothymol Blue (5,5'-dibromo-3,3-di-*iso*-propyl-6,6'-dimethylphenolsulfonephthalein), and Thymol Blue (3,3'-di-*iso*-propyl-6,6'-dimethylphenolsulfonephthalein). The 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenolate, known as the Reichardt's dye, was utilized as a combined solvatochromic and  $pK_a$ -probe ( $HR^+ \rightleftharpoons R^\pm + H^+$ ). The sample of this dye was a gift of Prof.C.Reichardt (Philipps University of Marburg, Germany). The dye Fluorescein was purified by re-precipitation, and *n*-Decylfluorescein was put to our disposal by Dr.V.I.Alekseeva (Research Institute of Organic Intermediates and Dyes, Moscow, Russia).

For creating different pH values, aqueous hydrochloric, phosphoric, and acetic acids, borax and sodium hydroxide were used. Phosphoric and hydrochloric acids were of analytical grade;  $\text{CH}_3\text{COOH}$  stock solutions were prepared from glacial acetic acid. The sodium tetraborate was re-crystallized twice from water at  $60^\circ\text{C}$  and then dried on air. The stock NaOH solution, prepared from saturated carbonate-free sodium hydroxide solution using  $\text{CO}_2$ -free water, was kept protected from atmosphere and standardized with potassium hydrogen phthalate sample of high purity. Sodium chloride and potassium bromide were used in the preliminary experiments for maintaining the ionic strength; the samples of analytical grade were dried to constant mass.

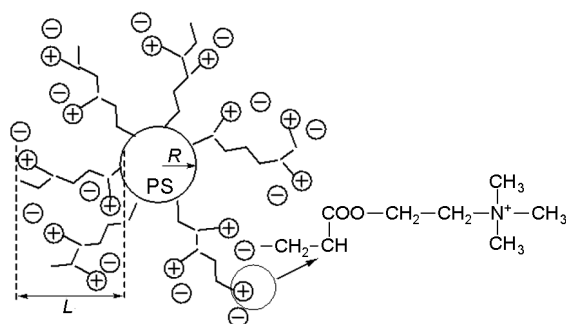


Fig. 1. The schematic structure of the spherical cationic polyelectrolyte brushes: PS is the poly(styrene) core,  $R$  is the radius of the core,  $L$  is the contour length of the polyelectrolyte chain. The counter-ion is  $\text{Cl}^-$ .

Table 1. The  $pK_a^{app}$  values of sulfophthalein dyes in solutions of cationic PB at  $I \sim 0.01$  M, 25°C

Dye (in parenthesis the $pK_a^w$ values at $I \rightarrow 0$ are given)	$pK_a^{app}$ in the presence of PB		$\Delta pK_a^{app}$	
	0.0014 mass. % PB	0.0042 mass. % PB	PB solution, $I \sim 0.01$ M	CPC micellar solution, $I = 0.05$ M [10, 12, 13]
Bromophenol Blue (4.20)	2.78 → 3.20	2.14 → 2.58	-(1.62–2.06)	-2.16
Bromocresol Green (4.90)	3.94±0.03	3.35±0.06	-1.55	-1.68
Bromocresol Purple (6.40)	6.61 → 5.23	5.42±0.02	-0.98	-1.32
Bromothymol Blue (7.30)	7.28±0.05	–	-0.02	-0.94
Thymol Blue (9.20)	8.78±0.05	9.00±0.08	-0.20	-0.37
Reichardt's dye (8.64)	8.15±0.07	–	-0.49	-1.55
Methyl Orange (3.46)	2.99±0.04	3.22±0.10	-(0.24–0.47)	-2.46 <sup>a</sup>

<sup>a</sup>In CTAB solution,  $I = 0.1$  M

Absorption spectra were measured using SF-46 spectrophotometer (Russia) with resolution of 1 nm, in a 1 cm cuvette. The spectra were referenced against the solvent blanks containing all the components except the dyes. The pH measurements were performed at  $25.0 \pm 0.1^\circ\text{C}$  on a P37-1 potentiometer and pH-121 pH-meter (Russia) equipped with a ESL-63-07 glass electrode reversible to  $\text{H}^+$  ions and an Ag/AgCl reference electrode in a cell with liquid junction (aqueous 1 M KCl solution). Standard buffer solutions (pH 1.68, 4.01, 6.86, and 9.18) were used for cell calibration. The experimental uncertainty in the measured pH value in the presence of the brushes did not exceed 0.05 pH units. The stock solutions of sulfonephthaleins, Methyl Orange, and Fluorescein were prepared in water, while in the case of *n*-Decylfluorescein and Reichardt's dye the 96 mass. % aqueous ethanol was used as solvent. The concentrations of the dyes in working solutions were as a rule  $(1-5) \cdot 10^{-5}$  M. The mass fraction of the cationic MS4KS PB in the stock aqueous suspension was 3.4 %. The working solutions were obtained by successive dilution of the initial one; the measurements were made with freshly prepared dilute suspensions. The initial aqueous suspensions of the PB were diluted in order to ensure the absorbance of the blank, i.e., dye-free solution to be  $\leq 0.3$  units.

### 3. Results and discussion

In the preliminary experiments, it was stated that the dyes virtually did not interact with the PB if the ionic strength substantially exceeds 0.01 M. For example, the

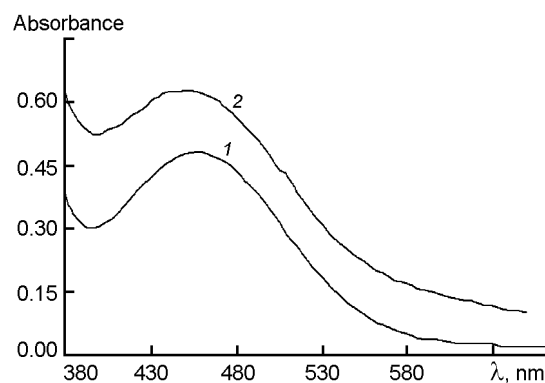


Fig. 2. Absorption spectra of the  $\text{R}^\pm$  zwitterion of the Reichardt's dye in water (1) and in 0.0014 mass. % aqueous solution of cationic PB; pH = 11.

$pK_a^{app}$  value of Bromophenol Blue at ionic strength 0.05 M (buffer + NaCl) is practically the same as in the absence of the PB. The possible reason can be the screening of the net charge of the ethyltrimethylammonium groups by the supporting electrolyte and the folding of the polyelectrolyte chains. Besides, in the presence of elevated concentrations of NaCl or KBr, the PB were salted out. Therefore, the main body of data was obtained at bulk ionic strength 0.01 M, caused exclusively by the buffer solutions. The  $pK_a^{app}$  values are compiled in Table 1. The analysis and interpretation of acid-base equilibria in different media allows to rationalize medium effects, i.e., the  $\Delta pK_a^{app} = pK_a^{app} - pK_a^w$  (in water) quantities. According to the electrostatic model, the apparent value,  $pK_a^{app}$ , under conditions of complete binding of the indicator couple by pseudo-phase depends on the electrostatic surface

potential (electrical potential of the Stern layer),  $\Psi$ , of the micelle or microdroplet [10]:

$$\Delta pK_a^{app} = \log(w\gamma_{H^+}^m / w\gamma_{HR^-}^m) - \Psi F / (RT \ln 10). \quad (2)$$

Here  $w\gamma_i^m$  is the transfer activity coefficient of the corresponding species from water to the pseudophase,  $F$  is the Faraday constant,  $R$  is the gas constant, and  $T$  is absolute temperature. From Table 1 it is clearly seen that in the presence of cationic PB, a substantial decrease in the indices of the apparent ionization constants takes place ( $\Delta pK_a^{app} < 0$ ). In general features this influence resembles that in micellar solutions of cationic surfactants, such as cetylpyridinium chloride (CPC) or cetyltrimethylammonium bromide (CTAB), studied previously [10, 12, 13]. Hence, the electrostatic contribution, expressed by the last item of equation (2), is a decisive factor in formation of the medium effects. The first item, reflecting the non-electrostatic contribution, governed by the  $w\gamma_i^m$  quantities, also should not be underestimated. Indeed, the sequence of  $\Delta pK_a^{app}$  values of sulfonephthaleins is analogous to those registered in CPC micelles (with except of Bromothymol Blue; for this indicator, as for the Reichardt's dye, the experiments with 0.0042 mass. % PB were hindered). In turn, such differentiating influence of the medium upon the acid strength of the indicators resembles those in mixtures of water with non-hydrogen bond donor solvents and was previously ascribed to the specificity of the hydrated Stern layer of cationic micelles [10, 12].

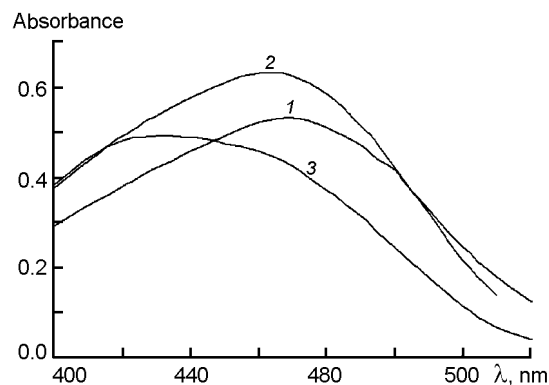


Fig. 3. Absorption spectra of  $R^-$  species of Methyl Orange in water (1) and in the cationic PB aqueous solutions of 0.0014 mass. % (2) and 0.0042 mass. % (3); pH = 5.8.

At the same time, the dyes spectra in the visible region are but slightly altered as compared with those in water. On going from water to non-aqueous microenvironments, including the surfactant micelles, the visible absorption bands of the yellow  $HR^-$  species of sulfonephthaleins display a distinct hypsochromic shift, while in the case of deeply colored  $R^{2-}$  species the bathochromic displacement is registered [12]. The inspection of Table 2 allows concluding that in the PB suspension no expressed alteration of the  $HR^-$  spectra takes place. The  $\Delta\lambda_{max}$  mean value for  $R^{2-}$  is 3 nm, while for the same five dyes in CPC micelles,  $\Delta\lambda_{max}$  is 11 nm on average. The position of the absorption band maximum of the Reichardt's dye stays unaffected in the presence of 0.0014 mass. % of PB (Fig. 2), while in micelles of cationic surfactants a bathochromic shift around 85 nm is registered

Table 2. The  $\lambda_{max}$  ( $\pm 1$  nm) of absorbance spectra of sulfophthalein dyes in solutions of cationic PB at  $I \sim 0.01$  M, 25°C

Dye	Water		CPC micelles [10, 12]		Cationic PB suspension			
	$HR^-$	$R^{2-}$	$HR^-$	$R^{2-}$	0.0014 mass. %		0.0042 mass. %	
					$HR^-$	$R^{2-}$	$HR^-$	$R^{2-}$
Bromophenol Blue	438	591	430	606	440	600–602	440	599–602
Bromocresol Green	444	617	434	627	443	614	440	622
Bromocresol Purple	430	588	418	602	430	588	430	588
Bromothymol Blue	436	616	426	626	435	616	–	–
Thymol Blue	438	597	438	611	446	596	446	596
Reichardt's dye <sup>a</sup>	453	–	538	–	452	–	–	–
Methyl Orange <sup>b</sup>	463	510	420	510	460	510	433	506–507

<sup>a</sup> The zwitterionic species,  $R^\pm$ . <sup>b</sup>  $HR^\pm$  and  $R^-$  species, respectively.

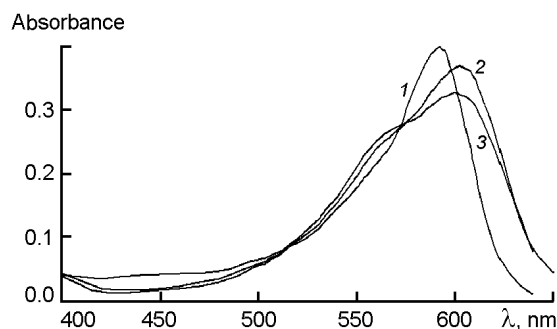


Fig. 4. Absorption spectra of  $R^{2-}$  species of Bromophenol Blue in water (1) and in the cationic PB aqueous solutions of 0.0014 mass % (2) and 0.0042 mass % (3);

(Table 2). The anion  $R^-$  of Methyl Orange also possesses solvatochromic properties: its band in the visible portion shifts from 463 nm in water up to 420 nm in cationic surfactant micellar solutions (Table 2), microemulsions, etc. [13]. In the 0.0014 mass % solution of the cationic PB, the shift is negligible, and in 0.0042 mass % solution  $\lambda_{max}$  was with 433 nm also smaller as compared with that in CTAB micellar solutions.

As it is seen in Figs. 3, 4 and some data in Tables 1 and 2, the threefold increase in the PB concentration strengthens the binding of dye species by the brushes. Hence, the influence of the latter upon the dye equilibria and spectra should be more expressed in concentrated suspensions. Moreover, some of the dyes species can be bound by the polyelectrolyte chains incompletely or can be located exclusively in the bulk water. For instance, it can be the case with the colorless cationic species  $HR^+$  of the Reichardt's dyes and red zwitterionic species  $HR^\pm$  of Methyl Orange. However, further elevation of the PB content in the working solutions was undesirable because of the ascending turbidity. In any case, the spectral data give evidence for strong hydration of dye species in the presence of 0.0014–0.0042 mass % of cationic PB, even

under conditions of marked reduction of the  $pK_a^{app}$  as compared with  $pK_a^w$ . The extreme length of the polyelectrolyte contour and relatively small distance between the chains certainly confine the penetration depth of the dyes.

Three negative tests with fluorescein dyes (Fig. 5) described below also support the idea of strong hydration of the cationic PB and of the absence of available hydrophobic sites. In aqueous solutions of Fluorescein at pH around 3.3, the predominating species are neutral ones [14]. The neutral species exist as a mixture of colored zwitterionic and quinonoidal tautomers (not shown here) and the colorless lactonic molecule (Fig.5) [12, 14–16]. In micellar solutions of surfactants, the binding of neutral species results in a distinct shift of the tautomeric equilibrium toward the lactone, accompanied by the drop of absorptivity [14–16]. Similar effects, more or less expressed, have been observed in solutions of cationic dendrimers [17] and CTAB-covered silica nanoparticles [18]. However, in the solutions of cationic PB the Fluorescein spectra at pH = 3.3 stays unchanged as compared with that in brushes-free aquatic media, with  $\lambda_{max} = 437$  nm and the same intensity.

The absorption band of the intensively fluorescing  $R^{2-}$  dianion of Fluorescein undergoes a distinct bathochromic shift of ca. 9–13 nm if bound to the cationic surfactant micelles [12, 16] and similar positively charged colloidal particles [17, 18]. By contrast, no spectral changes were registered at pH = 10–12, where the  $R^{2-}$  species predominate, after adding the PB under study. Finally, the dye *n*-Decylfluorescein, sparingly soluble in water due to its long hydrocarbon chain, can be solubilized by surfactant micelles and also is able to associate with cationic dendrimers [17] and CTAB-modified  $SiO_2$  particles [18]. Such stabilization in the presence of PB appeared to be impossible: when the initial *n*-Decylfluorescein solution in 96 % ethanol was injected into the aqueous solution of

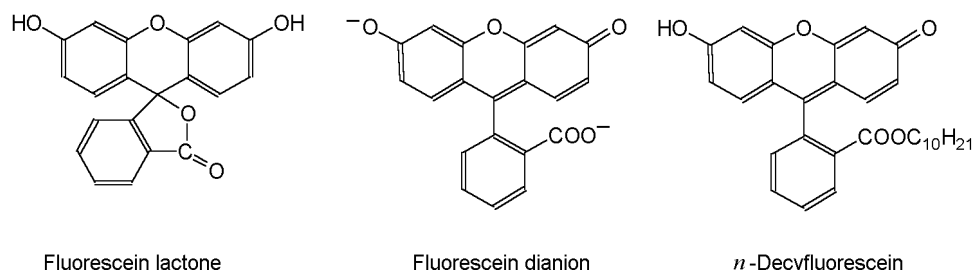


Fig. 5. The structures of fluorescein dyes.

brushes, the dye readily deposited despite intensive mixing. This indicates the lack of hydrophobic regions, available for indicator dyes, in the polyelectrolyte mantle surrounding the polystyrene core.

#### 4. Conclusions

The influence of the highly hydrated polyelectrolyte chains on the dye equilibrium is governed mostly by the expressed electrostatic interactions and modification of water properties inside the polyelectrolyte region. The  $pK_a^{app}$  shifts caused by the sign of  $\Psi$ , accompanied by the differentiating of acid strength of molecular probes, and in general insignificant alterations of the absorption bands are typical for ionic dyes located near strongly hydrated charged interfaces, for example, in the trapped water within the droplets of Aerosol OT-based reversed microemulsions [19].

From the results obtained with fluoresceins, a preliminary conclusion should be made about the absence of hydrophobic sites available for the indicator dyes within the large hydrophilic mantle of the brushes. The influence of the polyelectrolyte chains on the dye equilibrium is governed mostly by the expressed electrostatic interactions and modification of water properties inside the polyelectrolytic portion.

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**Здатність до зв'язування та сольватаційні властивості катіонних поліелектролітних щіток, досліджені з використанням кислотно-основних та сольватохромних індикаторів**

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Досліджено сферичні катіонні поліелектролітні щітки з полістирольним ядром та щільністю прищеплення поліелектролітних ланцюгів близько  $0.033 \text{ нм}^{-2}$  у водних середовищах з використанням набору стандартних кислотно-основних індикаторів і деяких інших барвників. Введення катіонних поліелектролітних щіток (від 0.0014 до 0.0042 мас. %) у буферні водні розчини, що містять індикаторні барвники, приводить до суттєвого зниження показників так званих уявних констант іонізації барвників,  $pK_a^{app}$ , від 0.2 до 2 одиниць, у порівнянні зі значеннями  $pK_a$  у відсутності щіток. Ці зміни нагадують ефекти, зареєстровані для цих же барвників у присутності міцел катіонних ПАР, катіонних дендримерів і каліксаренів, наночастинок кремнезему, модифікованих катіонними ПАР, тощо. Але, на відміну від вище перелічених колоїдних частинок, досліджені катіонні щітки не впливають на спектри поглинання цих індикаторів, включаючи найчутливіший сольватохромний барвник Райхардта. Крім того, не зареєстровано ані зсув таутомерної рівноваги Флуоресцеїну, ані сольбілізацію його малорозчинного у воді похідного, хоча ці ефекти є типовими для міцел катіонних ПАР та подібних їм колоїдних частинок.