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ORIGINAL CONTRIBUTION

M.G. Neumann
I.A. Pastre
A.M. Chinelatto
O.A. El Seoud

Effects of the structure of anionic polyelectrolytes on surface potentials of their aggregates in water

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M.G. Neumann · I.A. Pastre
Instituto de Quimica de Sao Carlos
Universidade de Sao Paulo
C.P. 780, 13560-970 Sao Carlos
SP, Brazil

A.M. Chinelatto · Dr. O.A. El Seoud (✉)
Instituto de Quimica
Universidade de Sao Paulo
C.P. 26.077, 05599-970 Sao Paulo
SP, Brazil

Abstract The surface potential, ψ in mV, was determined for the following polyelectrolytes and co-polyelectrolytes in aqueous solution: sodium poly(styrene sulfonate); sodium poly(vinyl sulfonate); poly(vinyl alcohol-co-55% sodium vinyl sulfate); poly(methylmethacrylate-co-40% sodium styrene sulfonate); poly (methylmethacrylate-co-60% sodium styrene sulfonate); poly(styrene-co-56% styrene sulfonate); and poly(styrene-co-80% styrene sulfonate). For comparison, the surface potentials of aqueous sodium dodecyl sulfate and sodium dodecylbenzene sulfonate micelles were also determined. The dyes neutral red and safranine-T were used as indicators. The pKa of the former was calculated from the Henderson– Hasselbach equation, using UV-VIS spectroscopy to determine the concentration of protonated ground state as a function of pH. The surface potential of the aggregates was calculated from the equation:

$$pKa_i = pKa_0 - F\Psi/2.3\ RT$$

where pKa_i and pKa_0 refer to the indicator pKa in the presence of charged and nonionic interfaces, respectively, and the other terms have their usual meaning. The protonation kinetics of the triplet state of safranine-T (measured from the decay of its transient absorption at 830 nm) was used to determine hydronium ion concentrations at aggregate interfaces, and the corresponding surface potentials were calculated from:

$$a_{\mathrm{Hi}} = a_{\mathrm{Haq}} \times \exp(-F\Psi/RT)$$

where a_{Hi} and a_{Haq} refer to the hydronium ion activity at the aggregate interface, and in bulk water, respectively. Surface potentials determined by both techniques were in excellent agreement. Values of ψ were found to depend on the structure of the polyelectrolyte, sodium poly-(styrene sulfonate) versus sodium poly(vinyl sulfonate) and, for the same type of co-polyelectrolyte, on the percentage of charged monomer.

Key words Polyelectrolytes – co-polyelectrolytes – surface potential – acid-base indicators – dyes – neutral red – safranine-T

Introduction

Organized assemblies, e.g., micelles, liquid crystals, microemulsions and polyelectrolytes enhance rates of chemical reactions, shift chemical equilibria and affect photochemical and photophysical processes [1–7]. Most of these interactions are pH-dependent, and quantitative treatment of data thus obtained requires knowledge of "effective" or local pH values at the reaction site, namely the interfacial region [8].

Polyelectrolyte aggregates can be compared to micelles because both have hydrophobic and hydrophilic domains in their structures. In polyelectrolyte solutions, the hydrophilic region is attributed to polar groups which extend along the polymer hydrophobic backbone [9]. However, the physico-chemical properties of polyelectrolyte solutions are much less studied than those of their micellar counterpart. There is, therefore, an increasing interest in understanding the properties of polyelectrolyte solutions at the molecular level, inter alia, the microscopic properties (e.g., polarity) of interfacial water, and local concentrations (e.g., of hydronium ions) at the aggregate interface.

The effect of charged interfaces on acid-base equilibria can be analyzed in terms of two approaches, namely the ion-exchange, and the surface potential. In the first, an "inventory" of local concentrations of all ions at the interface is carried out, based on the ion-exchange formalism. In the second, the surfactant-induced shift of the acid-base equilibrium is analyzed in terms of "medium" and charge effect. In the present paper, the latter approach was used because it allows evaluation of the surface potential, which is not accessible by a direct measurement [8].

Two positively charged hydrophobic dyes, neutral red and safranine-T, were used to calculate the surface potential, ψ in mV, of poly(sodium styrene sulfonate), poly(sodium vinyl sulfonate), and their co-polymers with vinyl alcohol, methylmethacrylate, and styrene. The following points are central in the present study: i) comparison of different, and independent experimental techniques to determine the *pKa* of probes in the presence of aggregates; ii) determination of the effects of the structure of the polyelectrolyte and relative composition of the co-polyelectrolyte, on the surface potentials of their aggregates in water.

Experimental

Materials

Neutral red and safranine-T were from Merck, and were crystallized from methanol/*i*-propanol mixture. Sodium dodecylsulfate, SDS and sodium dodecylbenzene sulfonate, SDBS (Aldrich) were crystallized from acetone-ethanol. Triton X-100 (polyoxyethylene (9.5) octylphenyl ether (Rhom & Haas) was purified as given elsewhere [10]. The microscopic polarity probe 2,6-diphenyl (2,4,6-triphenyl-1-pyridinio) phenolate betaine (hereafter referred to as polarity probe) was a gift from Prof. C. Reichardt, University of Heidelberg, Germany, and was used as received.

Polymers

Poly(sodium styrene sulfonate), (NaPStS, Aldrich), poly(sodium vinyl sulfonate), (NaPVS, Aldrich) and poly(vinyl alcohol), (PVA, Merck) were purified by dialysis in distilled water, precipitated with methanol and dried in vacuum.

Poly(vinyl alcohol-co-vinyl sulfate) with 55% of charged monomers (PVA-55% VSa) was prepared by sulfation of PVA with chlorosulfonic acid in pyridine [11]. The product was purified by dialysis in distilled water and precipitated with dioxane/ethanol (2:1). Poly(methyl methacrylate-co-styrene sulfonate) with 40% and 60% of charged monomers (PMMA-40% StS and PMMA-60% StS) were synthesized by co-polymerization of methyl methacrylate and styrene sulfonate in the desired ratio in DMSO at 60 °C, using AIBN as initiator. The products were purified by dialysis in distilled water, then precipitated with methanol. Poly(styrene-co-styrene sulfonate) with 56% and 80% of charged monomers (PSt-56% StS and PSt-80% StS) were prepared by sulfonating polystyrene with acetyl sulfuric acid [12].

All copolymers were characterized by elemental analysis and titration.

Apparatus

UV-VIS spectra were obtained with a Beckman DU-70 spectrophotometer. Transient spectra and decays were obtained with an Applied Photophysics laser spectrophotometric system, provided with a Hamamatsu R928 photomultiplier, a Spectron SL401 Nd-YAG laser source, and interfaced to a Hewlett Packard HP 54504 digitizing oscilloscope. pH Values were measured with Fisher Accumet-50 or Micronal B374 pH-meter.

Methods

All solutions were prepared in Millipore ultra-pure water. The ratio between anionic polymer sites and dye molecules was kept at ca. 1000 and the concentrations of the surfactants were always above their critical micelle concentrations. When required, samples were deareated and homogenized by bubbling oxygen-free nitrogen.

Microscopic polarities, $E_T(30)$ at surfaces of aqueous aggregates (micelles or polyelectrolytes) were determined from the UV-VIS spectra of the polarity probe (5×10^{-6} M) in the aggregate solution, at 30 °C. Values of $E_T(30)$ were calculated from:

$$E_T(30)(\text{kcal/mol}) = 28591/\lambda_{\text{max}}(\text{nm}) \qquad (1)$$

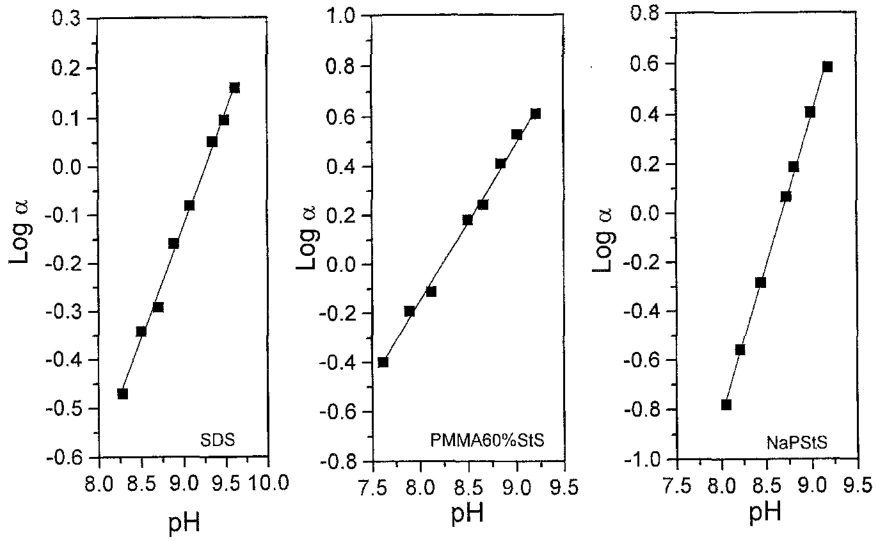


Fig. 1 Representative plots of Eq. (2) for neutral red

where λ_{max} is the longest wavelength of absorption of the polarity probe in the presence of the aggregate. This band corresponds to an intramolecular, polarity-dependent charge-transfer interaction in the probe [13].

The following two techniques were used to determine the surface potential, Ψ in mV, of the interfaces:

i) The *pKa* of neutral red was determined spectrophotometrically. Absorption of the protonated species was used for determination of the analytical concentrations of the two forms of the indicator. The absorption of the indicator obeys Beer's law in the concentration range 2–10 × 10^{-5} M ([polymer or co-polymer] = 0.03 N; [surfactant] = 0.03 M). In *pKa* determinations, the total [indicator] was 5.8 × 10^{-5} M. The following λ_{max} values were used: 530 nm, 537 nm, 537 nm, 541 nm, 534 nm, 530 nm, 536 nm, 541 nm, and 541 nm for water, SDS, SDBS, NaPStS, PVA, NaPVS, PVA-55% VSa, MMA-40% StS and MMA-60% StS, respectively. The *pKa* values were determined from the modified Henderson–Hasselbach equation [14]:

$$\mathrm{pH} = pKa + n \log \alpha \qquad (2)$$

where α is the indicator ratio, given in terms of absorbance by $\alpha = (A_{BH^+} - A)/A)$, where A_{BH^+} and A are the absorbances of the indicator in its completely protonated form, and that at a given pH value, respectively. We used either 0.05 M borate buffer, ionic strength = 0.1 M (NaPStS, MMA-40% StS; MMA-60% StS, SDS, SDBS) or 0.05 M phosphate buffer, ionic strength 0.15 M for the remaining cases. Figure 1 shows representative plots of the application of Eq. (2) to the data of neutral red and the results are given in Table 1.

ii) Transient spectra and decays of safranine-T were obtained by exciting the indicator (3 × 10^{-5} M) at 532 nm, using 80 mJ, 20 ns FWHM pulses of the 2nd harmonic emission of the Nd-YAG laser. The decay kinetics of the monoprotonated triplet state was monitored at 830 nm.

Due to the difference between the *pKa*'s of safranine-T in the ground state (~1.5) and in the triplet state (p^3Ka = 6–8), the monoprotonated form of the latter (^{3}SfH$^+$) will be transformed into the diprotonated state ^{3}SfH$_2^{2+}$, when excited in solutions whose pH is between 2 and 10 [15], see structures below. The lifetime of the initially formed triplet state depends on the hydronium ion activity, or concentration at the site where the probe is located. Pseudo-first order protonation rate constants were obtained in water and in the presence of surfactant or polyelectrolyte aggregate, at different analytical hydronium ion concentrations.

Table 1 *pKa* values of neutral red and calculated surface potentials of surfactant and polyelectrolytes at 25 °C[a,b,c]

Aggregate system	*pKa*	Surface potential mV
PVA	7.08	
NaPStS	8.69	− 95
NaPVS	7.78	− 41
PVA-55% VSa	7.90	− 49
PMMA-40% StS	8.12	− 61
PMMA-60% StS	8.22	− 67
SDBS	9.26	− 129
SDS	9.27	− 130
Triton X-100	5.75	

[a] Concentrations employed were 0.03 M for SDBS, SDS, and Triton X-100, and 0.03 N for polymers and polyelectrolytes.
[b] *pKa* values were calculated from Eq. (2) and the surface potentials from Eq. (5).
[c] The uncertainty in *pKa* is ± 0.03, resulting in uncertainty of ± 2 mV in ψ.

In general, the observed rate constant for the decay of the monoprotonated triplet state of the dye, k_{obs}, can be expressed by Eq. (3):

$$k_{obs} = k_0 + k_p[H^+] \tag{3}$$

where k_0 and k_p represent rate constant for natural decay of the triplet state monocation, and its quenching by hydronium ions, respectively, k_0 being ca. 2×10^4 $M^{-1}s^{-1}$ [16]. If the protonation reaction is assumed to be diffusional (i.e., $k_p \sim 10^{10}$ $M^{-1}s^{-1}$), then the only decay channel at any pH < 5 will be the protonation reaction. The ratio between hydronium ion activities, or concentrations at the interface, a_{Hi}, and in bulk water, a_{Haq} can be obtained from plots of the observed pseudo first-order rate constants as a function of analytical [hydronium ion]. Therefore, the surface potentials Ψ, are calculated using Eq. (4) [16]:

$$a_{Hi} = a_{Haq} \times \exp(-F\Psi/RT)\,. \tag{4}$$

Results and discussion

A critical analysis of effects of organized assemblies on acid-base equilibria is reported elsewhere [8], only the essential details will be given here. The *pKa* of an indicator in the presence of a charged interface, pKa_i, is given by:

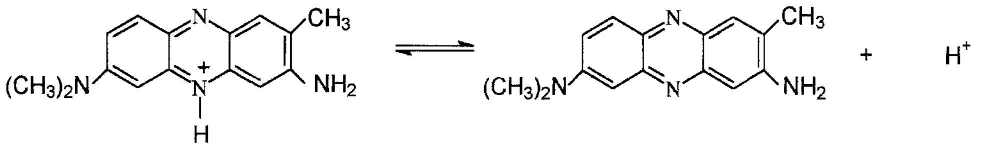
$$pKa_i = pKa_0 - F\Psi/2.3\,RT \tag{5}$$

where F is the Faraday constant, ψ is the mean field potential at the average interfacial site of residence of the prototropic moiety, R is the universal gas constant, and T is the absolute temperature. The term pKa_0 refers to the "medium" effect, i.e., shift of the acid-base equilibrium due to transfer of the indicator from bulk water to a medium (in our case the interface) whose properties (especially polarity and dielectric constant) are different from those of bulk water. The term $F\Psi/2.3RT$ represents electrostatic perturbation of the acid-base equilibrium by the charged interface.

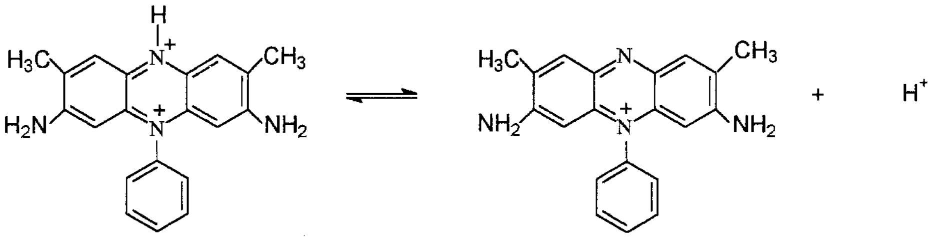
Application of Eq. (5) requires that both forms of indicator bind strongly to the aggregate, so that the (spectroscopic) property measured as a function of the solution pH is that of the aggregate-bound species. Although binding the indicator covalently to the polyelectrolyte via a "tether" is an interesting approach [17], it does not guarantee, a priori, that the probe will be located at the interfacial region. For example, the tether and the attached (hydrophobic) probe may fold back either partially, with the prototropic moiety lying parallel to the interface, or totally, with the probe directed into the core of the aggregate and away from water, by analogy with results in water-in-oil microemulsions [18]. If complete folding back occurs, the probe will be in an environment less hydrophilic than the interface, leading to an overestimation of the pKa_0 term of Eq. (5).

The simpler approach of using extrinsic probes which bind strongly to the polymers and co-polymers was employed in this work. Safranine-T and neutral red bind quite strongly to NaPStS, having association constants of 1.46×10^5 M^{-1} and 7.47×10^4 M^{-1}, respectively [19]. Furthermore, λ_{max} for both forms of these indicators was independent of the concentration of the polymer, or co-polymer in the range 0.01 to 0.05 N, as expected for strongly bound indicators [8].

The acid-base equilibria involved are shown below:



NEUTRAL RED



SAFRANINE - T

They are of the type $(+1 \rightarrow 0)$ for neutral red and $(+2 \rightarrow +1)$ for safranine-T. Transfer of these equilibria from bulk water to a less polar medium, e.g., interfacial water should shift them to the right side, resulting in lower *pKa* values [8]. In water, the *pKa* of safranine-T triplet state is 7.0 [20, 21]. The isosbestic point for neutral red in water is ill defined, probably due to a pH-dependent self-aggregation of the dye [22], and there is a relatively large uncertainty in this *pKa* value, e.g., 7.38 and 6.7 ± 0.3 have been reported [23, 24]. The results presented here, as well as those obtained by others researchers [23], show that this experimental problem does not exist in the presence of aggregates of surfactants and polyelectrolytes. Furthermore, any uncertainty in the *pKa* in water has no bearing on the calculation of the surface potential, as seen from Eq. (5). Transfer of these indicators from water to the interface of PVA resulted in lowering the *pKa* to 7.08 and 6.10 for neutral red and safranine-T, respectively, because interfacial water of the polymer is less polar than bulk water.

pKa of ground state of neutral red

To take into account medium effects on *pKa*, given by the term pKa_0 in Eq. (5), nonionic aggregates have been used [8]. The two models employed in the present work were PVA for polyelectrolytes, and the nonionic surfactant Triton X-100 for the micelles.

Table 1 shows the *pKa* values of neutral red in the presence of micellar and polymer solutions, obtained from absorption. The surface potentials, shown in Table 1, were calculated from Eq. (5) by using for pKa_0 the value obtained in PVA solution.

The *pKa* of neutral red in the presence of Triton X-100 micelles is similar to that for the same indicator in Brij-35 micelles (polyoxyethylene(23) lauryl ether) [23]. This *pKa* is much lower than that obtained in PVA, and its use as pKa_0 in Eq. (5) leads to unreasonable values of Ψ, e.g., -208 mV for SDS. In order to explain this lower *pKa* value one needs to address the question of the (average) solubilization site of neutral red in the so-called "palisade" layer of Triton X-100. As the hydrophilic moiety of this surfactant is coiled, water is unevenly distributed along the chain, the outer ethylene oxide units being more hydrated than the inner ones [25]. Neutral red may penetrate into the inner, less polar part of the palisade layer, leading to a lower *pKa* value. This explanation is backed by the microscopic polarities, $E_T(30)$ in kcal/mol, reported in Table 3.

The $E_T(30)$ value of water is 63.1 kcal/mole, whereas $E_T(30)$ values of 58.9 kcal/mole (typical for ionic micelles and polyelectrolytes) and 52 kcal/mole (Triton X-100) correspond to polarities of acetonitrile-water mixtures containing 13%, and 93% (v/v) of the organic solvent, respectively [13]. The much lower polarity of Triton X-100 can only be explained as a result of penetration of the polarity probe into its inner, less hydrated region. A similar solubilization site for neutral red explains why its *pKa* in Triton X-100 is much lower than that in PVA.

In the present work, the surface potential of SDS micelles was calculated and compared with literature data based on other probes e.g., acridine orange, nile blue and 9-heptadecyl acridine [8, 23, 26, 27]. As seen from Tables 1 and 2, the micellar surface potentials determined by both experimental techniques agree quite well with the previously reported range of -130 to -140 mV. This also shows that both indicators bind strongly to the micellar interface. Note that other probes which bind weakly to SDS micelles indicate very different surface potential, e.g., -27 mV for umbelliferone [28].

The surface potential of SDBS is similar to that of SDS. There is indication, e.g., from dynamic light scattering and ^{1}H NMR data, that the charge densities at the surfaces of aqueous micelles of SDS and SDBS are similar [29, 30]. That is, the presence of benzene rings at the aggregate interface has no detectable effect on the solubilization site of the dye, hence on the calculated surface potential. This justifies the use of the same polymer, PVA, as reference for medium effects for all polyelectrolytes employed, whether they carry, or not phenyl rings.

Table 2 Results for safranine-T in the presence of surfactant micelles and polyelectrolyte aggregates at 25 °C[a, b]

Aggregate system	τ (μs)	slope ($k_i \cdot K' \cdot r_\gamma$) ($10^{10}$ M^{-1} s^{-1})	K'	Surface potential, mV
PVA	28	1.2 ± 0.3	4.0	
NaPStS	52	8.7 ± 0.3	29.1	-86
NaPVS	24	1.7 ± 0.2	5.7	-45
PVA-55% VSa	82	6.2 ± 0.1	20.7	-77
PMMA-40% StS	47	2.5 ± 0.1	8.5	-55
PMMA-60% StS	58	3.1 ± 0.4	10.3	-60
PSt-56% StS	150	3.8 ± 0.3	12.8	-67
PSt-80% StS	51	$4.8 + 0.1$	15.9	-71
SDBS	25	43.0 ± 0.2	141.7	-127
SDS	18	25.6 ± 0.1	85.3	-114

[a]) K' values from ref. 39.
[b]) Surfactant and polyelectrolyte concentrations are the same as in Table 1.

Table 3 Measured $E_T(30)$ values for micellar and polyelectrolyte systems

System	SDBS		NaPStS		Triton X-100
concn.	0.05 M	0.1 M	0.03 N	0.1 N	0.03 M
$E_T(30)$ (kcal/mole)	59.3	58.1	59.3	58.7	51.9

Hydronium ion concentration effects from kinetic measurements

Under the conditions used to obtain the kinetic decays of monoprotonated triplet state of Safranine-T, protonation is the only reaction effectively contributing to the disappearance of this species. Thus, the observed first-order rate constant, k_{obs}, can be expressed as the local bimolecular protonation rate constant, k_i, times the activity, or concentration, of hydronium ions at the interface, $[H^+]_i$, as shown in Eq. (6):

$$k_{obs} = k_i \cdot [H^+]_i \tag{6}$$

The value of $[H^+]_i$ cannot be measured directly, but is related to that in the bulk of the solution $[H^+]_{aq}$ by the equilibrium

$$(H^+)_{aq} + \text{aggr} \Leftrightarrow (H^+)_i \tag{7}$$

where aggr represent the microdomains present in the system. The corresponding equilibrium constant will be

$$K' = \frac{[H^+]_i}{[H^+]_{aq} \times [\text{aggr}]} \cdot r_\gamma \tag{8}$$

where r_γ is the ratio of activity coefficients for the species present in the solution. Introducing the expression for $[H^+]_i$ obtained from Eq. (8) into Eq. (6), the observed rate constant becomes

$$k_{obs} = K_i \cdot K' \cdot r_\gamma \times [H^+]_{aq} = k_R \times [H^+]_{aq} \tag{9}$$

predicting a linear relationship between the observed rate constant k_{obs} and the analytical concentration of protons $[H^+]_{aq}$, as shown in Fig. 2. In this figure all the lines go practically to zero, confirming the assumption that the natural decay of the triplet state is negligible compared with the protonation reaction. The slopes of these lines correspond to the constant k_R $(= k_i \cdot K' \cdot r_\gamma)$. Considering that the protonation rate constant at the interface is diffusional ($k_i \sim 3 \times 10^9$ $M^{-1}s^{-1}$) and neglecting the activity coefficients, values for the proton exchange equilibrium constant K' are obtained and shown in Table 2. The potentials at the interfaces are then calculated from

$$[H^+]_i/[H^+]_{aq} = \exp(-F\Psi/RT)\ . \tag{10}$$

Surface potentials of polyelectrolyte aggregates and micelles

The data of Tables 1 and 2 show two trends for the surface potential: first, its magnitude is larger for NaPStS than for NaPVS, for co-polymers the sruface potential is a function of the percentage of the ionic monomer. According to Manning's theory [31], polyelectrolytes are characterized by the dimensionless charge density parameter, ξ:

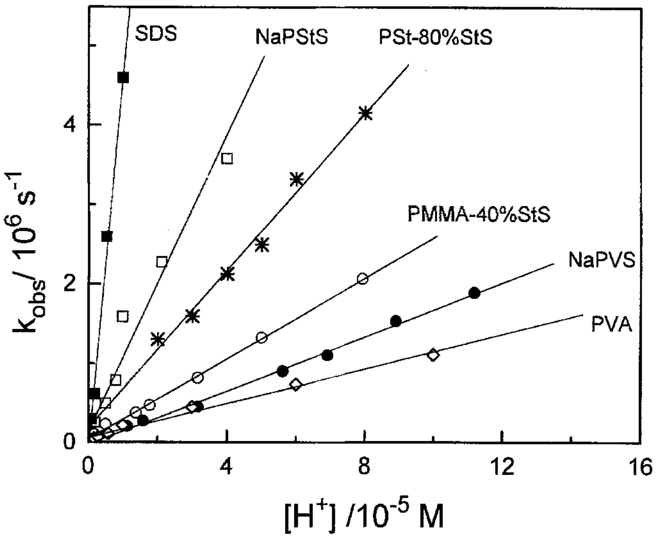


Fig. 2 pH dependence of the observed rate constants for the protonation reaction of the triplet state of Safranine-T in the presence of micelles and polyelectrolytes

$$\xi = e^2/\varepsilon kTb \tag{11}$$

where e, ε, k, T, and b are the protonic charge, the dielectric constant of water, the Boltzmann constant, the absolute temperature, and the average axial distance between stoichiometric charges along the polyelectrolyte chain, respectively [31]. The main difference between NaPStS and NaPVS is due to the term b in Eq. (11), its value being largely determined by the flexibility and diameter of the polyelectrolyte chain. Flexible polyelectrolytes, with small diameters are associated with large b values, and therefore with small charge densities [32–34]. The pendant phenyl ring in NaPStS increases the diameter of the polyelectrolyte chain when compared to NaPVS, making it less flexible due to steric hindrance of rotation and hydrophobic interactions [32]. This rigidity is also responsible for the high glass transition temperature (≥ 400 °C) calculated for poly(styrene sulfonic acid) [35]. Our result, $|\psi(\text{NaPStS})| > |\psi(\text{NaPVS})|$, agrees with those of potentiometric measurements [33], sodium ion tracer diffusion measurements [36], and Raman spectroscopy [37], which showed that the degree of dissociation of NaPStS is larger than that of NaPVS. The fact that $|\psi(\text{NaPStS})| < |\psi(\text{SDBS})|$ can be ascribed to the fact that packing of sulfonate groups is closer at the surface of the micelle. This interpretation agrees with observed low surface activity of NaPStS in solution [38].

Similar arguments explain the increase in $|\psi|$ as a function of increasing the percentage of charged monomer, which probably leads to formation of "pseudo-micellar" structures, with a concomitant increase in charge cooperativity of the polyelectrolyte groups.

Conclusions

Surface potentials of anionic micelles and polyelectrolytes, determined with two cationic indicators using two experimental techniques are in good agreement. To our knowledge, this is the first time that surface potentials of micelles and polyelectrolytes have been determined by independent procedures. This lends credence to the use of dyes to probe interfacial regions of polyelectrolytes and organized assemblies in general.

$|\psi(\mathrm{NaPStS})| > |\psi(\mathrm{NaPVS})|$ as expected from Manning's theory. Values of $|\psi|$ of co-polyelectrolytes containing nonionic and anionic monomers increase as a function of increasing the concentration of the latter.

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