

EFFECT OF POLYELECTROLYTE ON THE AGGREGATION OF CATIONIC SURFACTANTS IN AQUEOUS SOLUTIONS¹

Ksenija Kogej and Jože Škerjanc

Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia

Abstract: The effect of the specific nature of the polyelectrolyte on complexation with alkylpyridinium surfactants has been investigated. Two polyelectrolytes with the same linear charge density were studied, i.e. sodium poly(acrylate), NaPA, and sodium poly(styrenesulfonate), NaPSS. It has been found by fluorescence measurements that in the case of a more hydrophobic NaPSS the association of surfactant with the polyion is practically complete whereas for hydrophilic NaPA less than 80% of surfactant is associated with the polymer. Measurements of electrolytic conductivity, Λ , showed that the mobility of surfactant ions is greatly reduced in the presence of oppositely charged polyion. In NaPSS solutions, a pronounced minimum in Λ is seen in the range of cooperative binding. On the contrary, in NaPA solutions only a plateau region is observed. The difference in behavior has been explained by inclusion of the hydrophobic aromatic group on PSS^- into the surfactant micelle leading to formation of a very stable aggregate. This is accompanied by a release of a considerable amount of Na^+ and Cl^- ions into the solution. No such specific interaction is present between PA^- and surfactant aggregate. They are associated more loosely only through electrostatic interactions.

¹ Dedicated to the memory of Professor Anton Šebenik

INTRODUCTION

In the past decades considerable interest has developed in polymer-surfactant solutions because of the importance of these systems in a variety of applications. In the case of oppositely charged polyelectrolytes and surfactants, strong interactions are observed due to a contribution of electrostatic forces and cooperative hydrophobic effects between bound surfactant ions. This results in formation of micelle-like aggregates around the polyion chain, which are detected already much below the ordinary critical micelle concentration. The evidence for the existence of polyelectrolyte-surfactant complexes has come from indirect methods such as surface tension [1] and dye solubilization [2-5], and from direct measurements of binding by the use of surfactant ion-selective electrodes [6-9]. Sometimes, expressions ‘minimicelle’ [2] or polyelectrolyte induced micelle [4,5] are used in this context to stress the similarity with ordinary micelles. The surfactant concentration at which cooperative binding to polyelectrolyte starts depends on the nature of both, the surfactant and the polyelectrolyte. In particular, the surfactant head group and the length of its hydrocarbon tail as well as the polyion charge density play an important role.

In this contribution, we were interested in how the specific nature of the ionic groups on the polymer affects the formation of polyelectrolyte-surfactant complex. We investigated aggregation of dodecyl- (DPC) and cetyl- (CPC) pyridinium chlorides in the presence of two anionic polyelectrolytes, polystyrenesulfonate (PSS^-) and polyacrylate (PA^-).

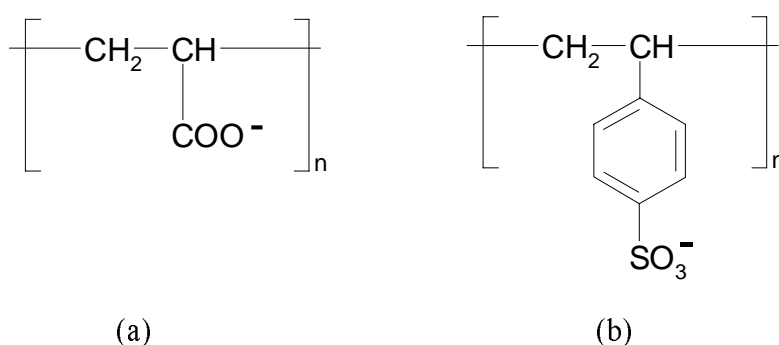


Figure 1: Structure of the monomer unit of the polyelectrolyte: (a) polyacrylate; (b) polystyrenesulfonate.

Polymer structures are shown in Figure 1. These two polyanions are characterized by the same linear charge-density parameter λ , defined as

$$\lambda = \frac{e_0^2}{4\pi\epsilon_0\epsilon kTb} \quad (1)$$

where e_0 is the protonic charge, ϵ_0 and ϵ are the permittivity of vacuum and the dielectric constant of solvent, k is the Boltzmann constant, and b is the average distance between two adjacent charges on the polymer chain. The structural parameter b is the same for all vinylic polymer chains (2.52 nm) and gives the value 2.83 for λ in aqueous solutions at 25 °C. Therefore, the difference between the two polyanions lies in the functional groups of the monomer unit. Due to the aromatic group attached to the chain, PSS⁻ is more hydrophobic than PA⁻. Some specific interactions between the surfactant and the polymer backbone can be expected in the polystyrenesulfonate case. We have chosen conductivity in combination with fluorescence measurements to probe the systems.

EXPERIMENTAL SECTION

Materials

Sodium poly(styrene sulfonate), NaPSS, with a molecular weight of about 70 000 g/mol and degree of sulfonation 1.0, supplied by Polysciences, Inc. (Warrington, PA) was prepared and purified by the procedure described in the literature [10]. Sodium poly(acrylate), NaPA, with a molecular weight around 10 000 g/mol, was prepared from polyacrylic acid, HPA (K & K Laboratories, Inc., Plainview, N. Y.) as reported previously [11]. N-dodecylpyridinium chloride, DPC, a gift from Merck-Schuchardt, and N-cetylpyridinium chloride, CPC (Kemika, Zagreb) were thoroughly purified by repeated recrystallization from acetone and vacuum dried at 50 °C. The fluorescence probe, 8-anilino-1-naphthalenesulfonic acid, ammonium salt (ANS), supplied by Fluka was used as received.

A constant concentration of NaPSS or NaPA, equal to 5×10^{-4} monomol/kg, was used in all experiments. Surfactant stock solutions, either in pure water or in aqueous polyelectrolyte solutions, were prepared by weight from dried substances. The specific conductivity of water used for the preparation of solutions was below $1.2 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$.

Fluorescence

ANS fluorescence spectra were recorded on a Perkin-Elmer Model LS-50 Luminescence Spectrometer with a water thermostated cell holder at 25°C. A 1 cm path quartz cuvette was used. A freshly prepared ANS stock solution was added to systems prior to measurements. The ANS fluorescence intensity at 483 nm was followed to obtain the total degree of coverage of the polyion with surfactant ions. The excitation wave length was 365 nm. Excitation and emission slit widths for recording the spectra were set to 5.0 nm, scan rate was 240 nm min^{-1} , and two scans were accumulated for each run.

Conductivity

The specific conductivity of solutions was measured at 25°C with a Metrohm 712 Conductometer using a Metrohm cell with a cell constant 0.095 cm^{-1} . The measurements were performed in aqueous solutions of pure surfactants and in polyelectrolyte-surfactant solutions at constant NaPSS or NaPA concentration. The concentration of surfactant was changed by a titration technique.

RESULTS AND DISCUSSION

Fluorescence

The fluorescence emission spectrum of ANS exhibits a marked dependence on the polarity of the solvating medium [12]. In nonpolar environment, its fluorescence maximum shifts to shorter wave-lengths ($\sim 483 \text{ nm}$) with concomitant increase in quantum yield. We have followed fluorescence intensity of ANS at 483 nm as a function

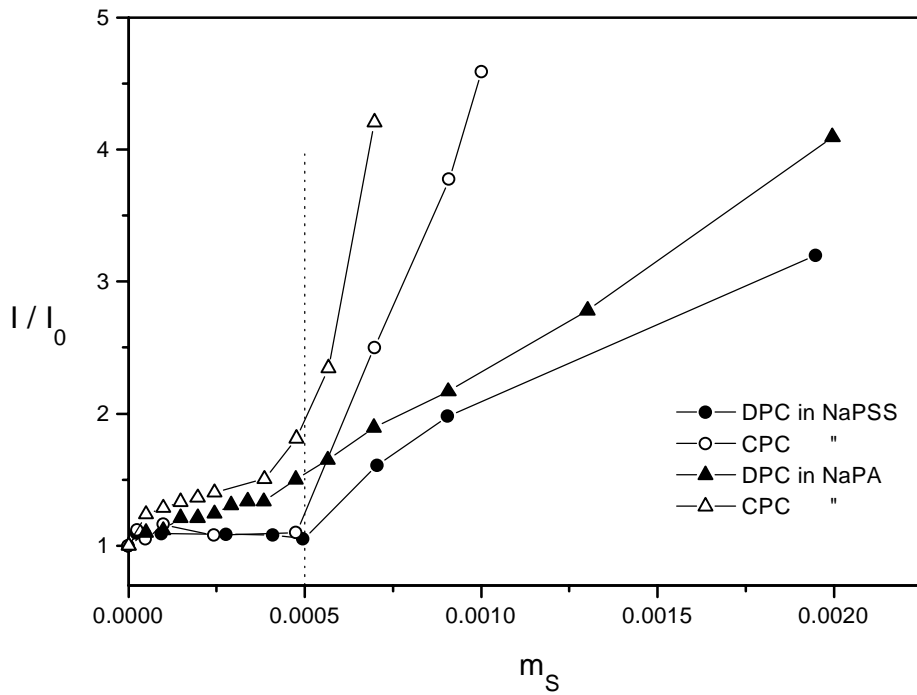


Figure 2: The dependence of fluorescence intensity of ANS on DPC (CPC) concentration (m) in solutions of NaPSS and NaPA.

Polyelectrolyte concentration: $m_p = 5 \times 10^{-4} m$ (dotted line).

of surfactant concentration. The results are shown in Figure 2 as plots of I / I_0 vs. surfactant concentration; I and I_0 are the fluorescence intensities of the probe in polyelectrolyte solutions with various surfactant concentrations and in pure polyelectrolyte solution, respectively. The I / I_0 ratio in NaPSS solutions is at first constant (around 1), indicating that the polarity of the surrounding medium is unchanged and equal to that of pure water. All the surfactant added binds to PSS chain. After the binding is finished, the I / I_0 increases sharply due to the presence of free surfactant in solution and consequently to the decreased polarity of the environment. From the concentration of surfactant at this threshold concentration, m_s , the total degree of coverage, β , of the polyelectrolyte chain with surfactant ions [2] was obtained from expression

$$\beta = \frac{m_s}{m_p} \quad (2)$$

Here, m_p is the constant polyelectrolyte concentration. In this calculation, the concentration of free surfactant was not taken into account. For both surfactants in NaPSS solutions, this threshold surfactant concentration is approximately 5×10^{-4} mol/kg which gives β around 1. This is in agreement with the degree of binding determined by surfactant ion-selective electrode measurements [9] and implies that DPC and CPC are completely associated with polystyrenesulfonate anion.

The measurements in NaPA solutions show a somewhat different picture. Before commenting on this, we have to mention the following. Since ANS is negatively charged it can also interact strongly with cationic surfactants. It may form small aggregates with surfactant cations and even promote the release of DP^+ (CP^+) from polyelectrolyte-surfactant complex by simply displacing the association equilibrium [2]. The concentration of ANS used to probe NaPSS solutions was about 10% lower than the NaPSS concentration ($\sim 4.5 \times 10^{-4}$ mol/kg). The same concentration of ANS in NaPA solutions caused the equilibrium to shift in favor of the probe. The surfactant cations associated more readily with ANS than with polyacrylate anion and consequently no binding of DP^+ (CP^+) to PA^- could be detected. By decreasing the concentration of ANS to about one half of NaPA concentration ($\sim 2.5 \times 10^{-4}$ mol/kg) the usual plots were obtained (see Figure 2). This shows that the association of alkylpyridinium cations with PSS^- anion is much stronger than with PA^- anion.

We can see (cf. Figure 2) that the I / I_0 ratio in NaPA increases slightly also below the brake point. The binding to PA^- is completed at approximately 3.9×10^{-4} mol/kg for DPC and 4.0×10^{-4} mol/kg for CPC giving for β the values 0.78 and 0.8, respectively. This is slightly larger than β values reported in the literature [8]. The literature data for β obtained from surfactant ion-selective electrode measurements are 0.7 for tetradecylpyridinium bromide, TPB, and 0.75 for DPC, respectively. Our values are somewhat higher probably owing to the above mentioned simultaneous association of these surfactants with NaPA and ANS.

Comparison of β values in NaPSS and NaPA solutions with the same polyion concentration shows that the degree of binding of DPC and CPC is much lower in NaPA case in spite of the same linear charge density parameter λ for both polyanions. Also, the

aggregate formed between DP^+ (CP^+) and PSS^- seems to be more stable than the aggregate between DP^+ (CP^+) and PA^- .

Conductivity.

The molar conductivity, Λ , for pure surfactant solutions and for surfactant solutions in the presence of polyelectrolyte is presented in Figures 3 and 4. The Λ vs. \sqrt{c} curves (c is the concentration of surfactant in mol/L, M) for pure surfactants show a usual dependence. The distinctive break in the curves observed at higher concentrations corresponds to micelle formation and from this the critical micelle concentration, cmc , was determined for both surfactants. The cmc values are 1.64×10^{-2} M and 8.6×10^{-4} M for DPC and CPC, respectively. They are in a reasonable agreement with the previously determined values [8,9].

The conductivity curves in the presence of polyelectrolyte will be discussed separately for two concentration regions: first, for surfactant concentrations above $\sim 5 \times 10^{-4}$ M (this concentration can be regarded as the 'equivalent' concentration because it is equal to the concentration of charged groups on the polymer), and second, for surfactant concentrations below the 'equivalent point'. At surfactant concentrations above the 'equivalent point', the Λ curves in the presence of the polyion resemble behavior similar to pure surfactant solutions. They show a break at the so called apparent critical micelle concentration, cmc^* . This term is usually used for characterizing formation of free surfactant micelles in the presence of the polymeric component. The cmc^* is higher than the ordinary cmc due to the formation polyelectrolyte-surfactant complex at lower surfactant concentrations. The bound surfactant is not available for micellization, consequently, free micelles appear at somewhat higher total surfactant concentration. From cmc and cmc^* we can also estimate the total degree of binding of surfactant to polyelectrolyte from expression

$$\beta = \frac{cmc^* - cmc}{m_p} \quad (3)$$

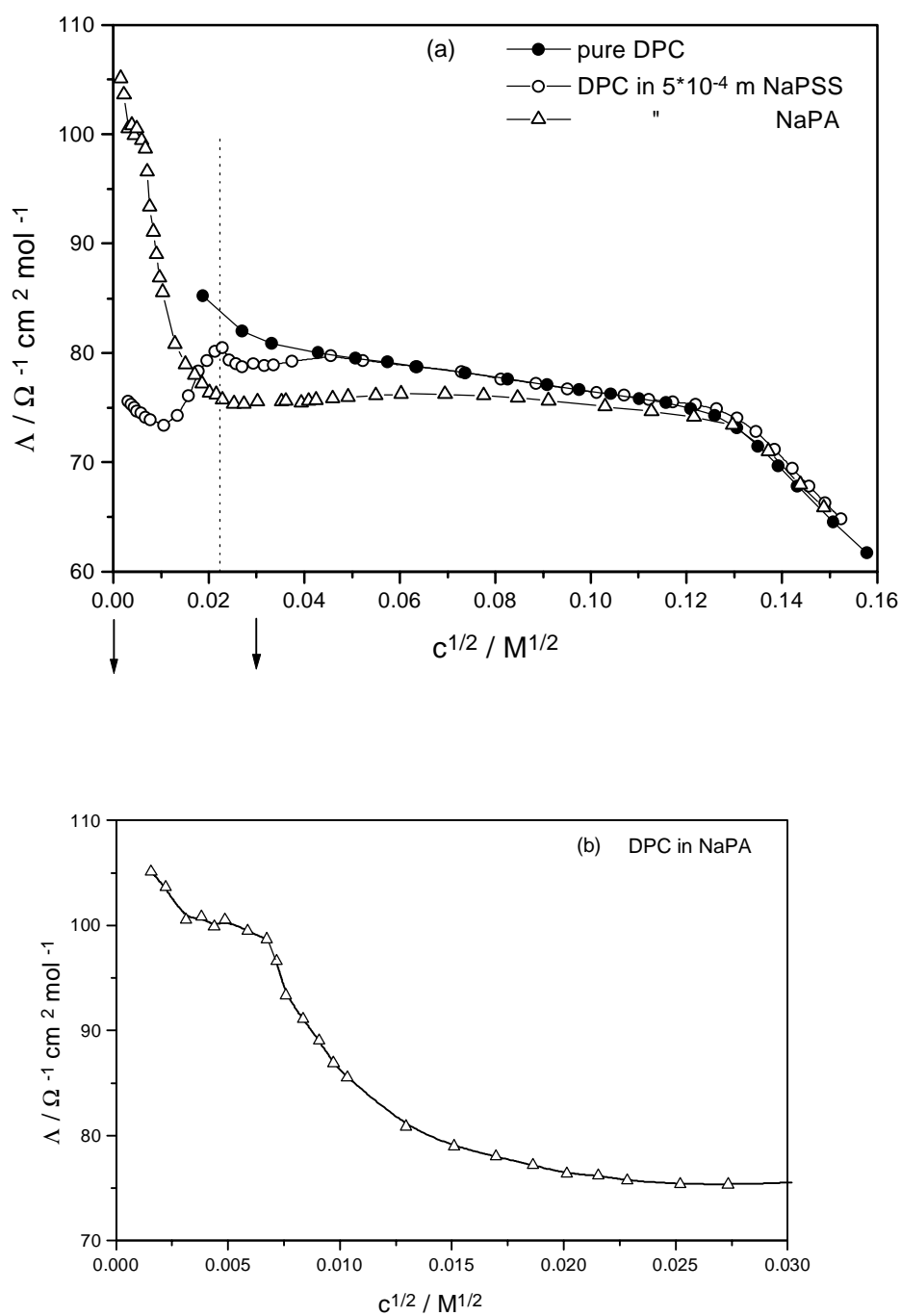


Figure 3. (a) Molar conductivity, Λ , at 25°C in aqueous solutions of DPC in the absence and in the presence of NaPA or NaPSS.

dotted line: polyelectrolyte concentration, $m_P = 5 \times 10^{-4} \text{ m}$.

(b) the enlargement of the plot in NaPA solutions at surfactant concentrations below the 'equivalent point'.

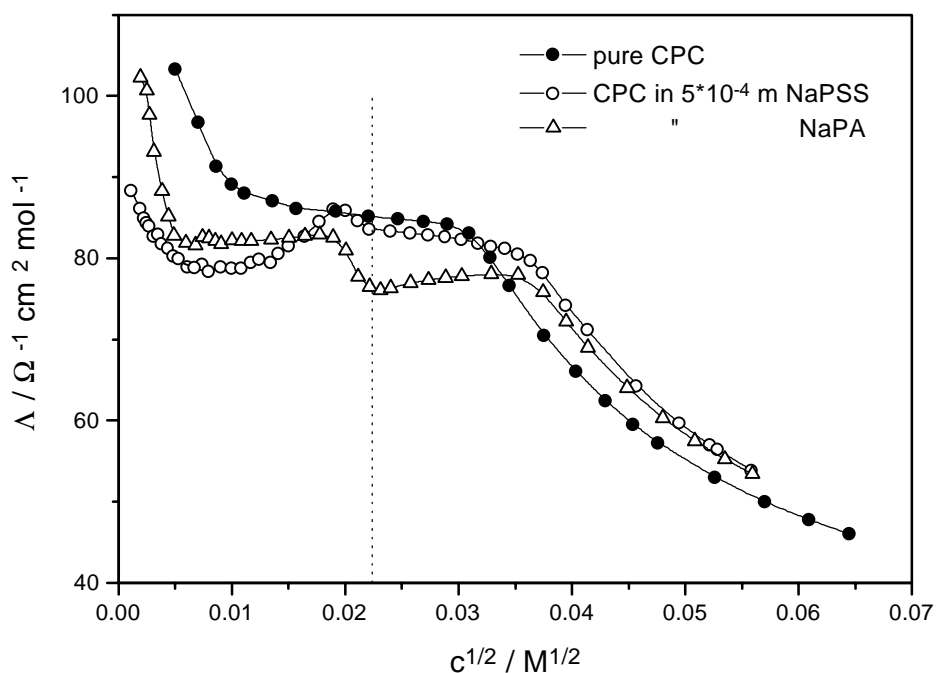


Figure 4. Molar conductivity, Λ , at 25°C in aqueous solutions of CPC in the absence and in the presence of NaPA or NaPSS.

dotted line: polyelectrolyte concentration, $m_p = 5 \times 10^{-4} m$.

In NaPSS, cmc^* values are 1.69×10^{-2} and $1.36 \times 10^{-3} M$ and the corresponding β values are around 1 for DPC and CPC, respectively, again indicating quantitative 1:1 complexation between PSS^- and DP^+ (CP^+). In NaPA, we find cmc^* 1.68×10^{-2} and $1.25 \times 10^{-3} M$, giving for β 0.80 and 0.78 for DPC and CPC, respectively. These values are in agreement with results obtained by fluorescence.

Below the 'equivalent point', conductivity curves in polyelectrolyte exhibit a very different behavior in comparison to pure surfactant solutions. In NaPSS, Λ first decreases with increasing concentration. In this range, the mobility of surfactant cations is strongly reduced due to the electrostatic field of the polyanion. After the minimum the conductivity starts to increase up to approximately the 'equivalent point'. The appearance of a minimum cannot be explained solely by electrostatic interactions

between surfactant minimicelle and polyelectrolyte chain, especially because the curves in NaPA solutions show no minima. In this case, Λ first also decreases sharply with increasing \sqrt{c} but reaches a plateau region of rather constant value in the concentration range where minimum in NaPSS solutions has been observed (this concentration range is enlarged in Figure 3b for solutions of DPC in NaPA). The region of nearly constant Λ is afterwards followed by another steep decrease up to approximately the 'equivalent point'.

This remarkable difference in conductivity curves for alkylpyridinium cations in NaPSS and NaPA solutions leads to a conclusion that other effects besides the charge density of the polyion have to be taken into account. Since cooperative binding occurs in both systems [8,9] the observed difference must be due to the presence of the hydrophobic benzenesulfonate group in NaPSS which avoids contact with water. In fact, it has been shown [13] that a very stable and compact aggregate is formed in the case of NaPSS by inclusion of aromatic rings of PSS^- chain into the hydrophobic interior of the micelle (similar to ion pairing). In this way, the polyion chain wraps very tightly around surfactant minimicelles. This causes a release of small counterions originating from both, the polyion and the surfactant, into the solution and consequently, the conductivity starts to increase above a certain critical degree of complexation.

The minimum in DPC/NaPSS solutions is found at about 1×10^{-4} M (cf. Figure 3). For CPC/NaPSS it seems to be at somewhat lower concentrations, around 8×10^{-5} M (cf. Figure 4). However, because in this case the minimum is rather broad, it is difficult to position it precisely. In our former investigations of similar systems, i.e. solutions of NaPSS and alkyltrimethylammonium bromides [14], the minimum was ascribed to the point where the polyelectrolyte chain becomes saturated with surfactant minimicelles. Thereafter, it has been shown [14] that surfactant binds to the polymer in the monomer form only.

In the case of polyacrylate anion, the COO^- functional group has no tendency to avoid contact with water and to incorporate itself into the micellar aggregate. Therefore, the association between DPC (CPC) minimicelles and PA^- is purely electrostatic. We can conclude, that polyelectrolyte induced micelles of DPC (CPC) bind to PA^- as a

multivalent counterion without specific effects which would additionally stabilize the aggregate. The PA^-/DP^+ (PA^-/CP^+) complex is thus much more flexible and sensitive to the environment, the fact that was discussed previously in the light of strong effect of ANS on the association equilibrium. Also, lower values for parameter β in the case of NaPA reflect a weaker interaction between the polyanion and surfactant.

REFERENCES

- [1] B. Cabane, *J. Phys. Chem.* **1977**, *81*, 1639.
- [2] E. B. Abuin, J. C. Scaiano, *J. Am. Chem. Soc.* **1984**, *106*, 6274.
- [3] D. Chu, J. K. Thomas, *J. Am. Chem. Soc.* **1986**, *108*, 6270.
- [4] M. Almgren, P. Hansson, E. Mukhtar, J. van Stam, *Langmuir* **1992**, *8*, 2405.
- [5] P. Hansson, M. Almgren, *Langmuir* **1994**, *10*, 2115.
- [6] I. Satake, J. T. Yang, *Biopolymers* **1976**, *15*, 2263.
- [7] K. Hayakawa, P. J. Santerre, J. C. T. Kwak, *Macromolecules* **1983**, *16*, 1642.
- [8] A. Malovikova, K. Hayakawa, J. C. T. Kwak, *J. Phys. Chem.* **1984**, *88*, 1930.
- [9] J. Škerjanc, K. Kogej, G. Vesnaver, *J. Phys. Chem.* **1988**, *92*, 6382.
- [10] J. Škerjanc, M. Pavlin, *J. Phys. Chem.* **1977**, *81*, 1166.
- [11] J. Škerjanc, *Biophys. Chem.* **1974**, *1*, 376.
- [12] K. S. Birdi, H. N. Singh, S. U. Dalsager, *J. Phys. Chem.* **1979**, *83*, 2733.
- [13] Z. Gao, J. C. T. Kwak, R. E. Wasylishen, *J. Colloid Interface Sci.* **1988**, *126*, 1, 371.
- [14] K. Kogej, J. Škerjanc, *Langmuir*, submitted.

POVZETEK

Proučevali smo vpliv specifične narave polielektrolita na kompleksacijo z alkilpiridinijevimi surfaktanti. Izbrali smo dva polielektrolita z enako linearno gostoto naboja, natrijev poliakrilat, NaPA, in natrijev polistirensulfonat, NaPSS. Z merjenjem fluorescence smo ugotovili, da je v primeru bolj hidrofobnega NaPSS asociacija surfaktanta s poliiomom skoraj popolna, medtem ko se na bolj hidrofilen polielektrolit NaPA veže manj kot 80% surfaktanta. Elektrolitska prevodnost raztopin Λ je pokazala, da se gibljivost ionov surfaktanta v prisotnosti nasprotno nabitega poliiiona močno zmanjša. V raztopinah NaPSS smo v območju kooperativnega vezanja opazili izrazit minimum v krivulji $\Lambda(\sqrt{c})$. V raztopinah NaPA pa je, nasprotno, prevodnost v tem območju precej konstantna. Razliko v obnašanju smo razložili z dejstvom, da se hidrofobna aromatska skupina na PSS^- vključi v notranjost surfaktantne minimicele, pri čemer nastane zelo stabilen agregat. Pri tem se v raztopino sprosti precejšnja množina Na^+ and Cl^- ionov. Taka specifična interakcija med PA^- in agregatom surfaktanta ni možna. Do asociacije slednjih dveh pride le zaradi elektrostatskih interakcij.