

HYDRODYNAMIC INVESTIGATIONS OF POLYELECTROLYTE-SURFACTANT COMPLEXES IN AQUEOUS SOLUTIONS[†]

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(Received 22.4.1999)

Abstract

The effect of cationic surfactant cetylpyridinium chloride, CPC, on hydrodynamic behavior of sodium poly(styrenesulfonate), NaPSS, and sodium poly(acrylate), NaPA, was investigated and compared to the effect of simple salt, NaCl. It was found that the surfactant causes a larger reduction of the viscosity of polyelectrolyte solution than does NaCl. The difference is ascribed to the fact that, in addition to the electrostatic effects in the change of the polymer coil shape, the polymer-induced surfactant micelle causes additional coiling of the polyion chain around itself. The effects are greater in NaPA than in NaPSS solutions. In addition, the mean apparent molar volume change, $\Delta\Phi_v$, is bigger in the presence of NaPA than NaPSS, respectively. Possible reasons for these differences are the more flexible PA^- chain relative to the PSS^- chain, the specific interaction between surfactant micelle and benzenesulfonate ring of NaPSS monomer units, and bigger surfactant micelles in the case NaPA.

INTRODUCTION

The properties of polyelectrolyte solutions are extremely sensitive to environment. This is particularly true for the viscosity. It is well known that the presence of a simple salt reduces the viscosity of the polyelectrolyte considerably [1,2]. The effect is ascribed to the coiling of the initially highly extended macroion chain due to the

[†] Dedicated to Professor Drago Leskovšek on the occasion of his 80th birthday.

shielding of polyelectrolyte charges by the simple electrolyte. Another interesting problem is related to the changes of chain conformation arising from the binding of surfactants. It is well established that in aqueous solutions polyelectrolytes and surfactants with opposite charge form strong complexes already in extremely dilute solutions [3-12]. These are a kind of supramolecular aggregates between micellized surfactant and polyelectrolyte in which the polyelectrolyte chain is wrapped around the surfactant cluster. Consequently, also in this case a sharp decrease in viscosity upon the addition of surfactant to the polyion is expected. This was demonstrated, for example, for the addition of dodecyltrimethylammonium bromide, $C_{12}TAB$, to the sodium poly(styrenesulfonate) solution [6] or for the addition of a nonionic surfactant, poly(ethyleneoxide) to poly(acrylic acid) [13].

This paper is a continuation of our previous work on polyelectrolyte-surfactant interactions [9-12,14] and discusses some results on viscosity and density measurements in aqueous solutions of sodium poly(styrenesulfonate) and sodium poly(acrylate) in the presence of the cationic surfactant, cetylpyridinium chloride, CPC. The effect of the surfactant on the hydrodynamic behavior of a polyelectrolyte will be compared to that of an inorganic electrolyte (NaCl). Simultaneously, changes in shape due to the addition of CPC to polyelectrolyte will be followed by density measurements. We will show that the information obtained by viscometric and volumetric measurements is consistent with our previous findings in solutions of anionic polyelectrolyte and cationic surfactant.

EXPERIMENTAL SECTION

Materials

Sodium poly(styrenesulfonate), 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 [15]. 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 [16]. For all the measurements, a constant concentration of the

polyelectrolyte, NaPSS or NaPA, respectively, equal to $c_p = 5 \times 10^{-4}$ monomol/L was used.

The surfactant, N-cetylpyridinium chloride, CPC (Kemika, Zagreb), was thoroughly purified by repeated recrystallization from acetone and vacuum dried at 50 °C. Surfactant stock solutions, either in pure water or in aqueous polyelectrolyte solutions, were prepared by weight from dried substances using the triple distilled water.

Viscosity Measurements

The viscosity was measured with a capillary viscometer Micro Ubbelohde manual (Schott Geräte, Hofheim) in a thermostated bath at $25 \text{ °C} \pm 0.02 \text{ °C}$. The flow time of water was approximately 89 s. The reduced viscosity in solutions of polyelectrolyte with varying surfactant or simple salt concentration, $[\eta_{\text{red}}]$, was calculated by dividing the specific viscosity ($\eta_{\text{sp}} = \eta/\eta_0 - 1$, where η and η_0 are the viscosity of the solution and solvent, respectively) with the polyelectrolyte concentration expressed in g/dL. No corrections for the dependence of viscosity on shear rate were applied. Control experiments were performed on solutions of pure surfactant without added polyion. In the same concentration range of CPC as studied in polyelectrolyte solutions the viscosity of pure surfactant solutions was essentially that of water. The flow times were all approximately 90 s.

Density Measurements

The density of solutions was measured with a Paar digital precision density meter DMA 60 with an external measuring cell DMA 602. An ultrathermostat attached to the instrument controlled the temperature at $25.000 \pm 0.002 \text{ °C}$. The accuracy of density measurements was within $\pm 4.5 \times 10^{-6} \text{ g cm}^{-3}$. For the calculation of the apparent molar volume in pure CPC solutions below critical micellization concentration ($\text{cmc} = 6.3 \times 10^{-4} \text{ M}$ [5,9], confirmed also by density measurements in this paper) the experimental densities were corrected by linear regression. For the densities in the presence of polyelectrolyte no corrections were made.

RESULTS AND DISCUSSION

Viscosity

Figure 1 shows the effect of the addition of NaCl and CPC on the reduced viscosity, $[\eta_{\text{red}}]$, of 5×10^{-4} monomol/L NaPSS and NaPA solution, respectively. It should be noted that measurements were performed in a very dilute concentration range below the point where surfactant causes precipitation in solutions with polyelectrolyte component present. Therefore, the results are only of a comparative nature. As we can see, $[\eta_{\text{red}}]$ of polyelectrolyte solution of constant polyion concentration exhibits strong dependence on the concentration of the additive, NaCl or CPC, respectively. The measurements in NaCl are included to show the effects of altered ionic strength. The influence of simple salt on the viscosity of polyelectrolyte solutions is well known. Due to the repulsive electrostatic forces between adjacent charges on the polyion chain, the chain has a highly extended conformation in salt free solutions. The addition of simple

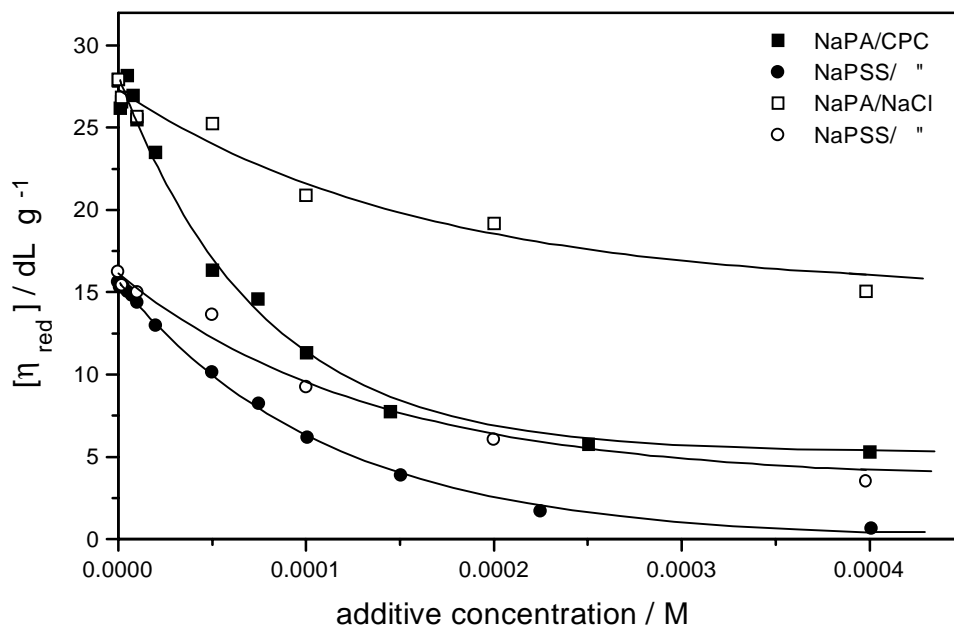


Figure 1. The effect of the addition of NaCl and CPC on the reduced viscosity, $[\eta_{\text{red}}]$, of NaPSS and NaPA solutions, respectively. Polyelectrolyte concentration: $c_P = 5 \times 10^{-4}$ monomol/L.

electrolyte results in shielding of ionic groups on the polyion. Consequently, the coil dimension reduces and leads to a decrease in viscosity with increasing concentration of NaCl or CPC. However, we can see from Figure 1 that the influence of CPC on $[\eta_{\text{red}}]$ is stronger than the influence of NaCl, particularly in the case of NaPA. In the presence of a surfactant, we have to consider two effects. In the first place, the binding of surfactant cations leads to a decreased effective charge of the polymer chain, similarly as the binding of sodium ions. In the case of surfactant cations, the additional effect can be expected since they bind to the polyion chain cooperatively in the form of the so called “polymer-induced” micelles [3]. That is to say, the surfactant ions are not evenly distributed along the chain but they are rather localized in the form of smaller or bigger aggregates [7,8,14]. It is likely that polyelectrolyte chain encircles the surfactant micelles to some extent and this is accompanied by a further decrease in dimensions and viscosity.

For an easier survey of the data at lower concentrations and because of a wide range of surfactant concentrations studied, a semi log plot of the reduced viscosity is presented in Figure 2. We can see that up to the concentration of surfactant equal to approximately 1×10^{-5} M the viscosity of polyelectrolyte remains approximately constant (a slight maximum in NaPA is detected) and afterwards it decreases rapidly with increasing surfactant content. This is in complete agreement with our previous findings. We showed by calorimetric [9,10] and potentiometric measurements [9,12] that appreciable cooperative binding of CPC to NaPSS and NaPA, respectively, starts above 1×10^{-5} M CPC. In the literature, this threshold concentration at which an abrupt change in many properties of mixed polyelectrolyte-surfactant solutions is observed, is termed the critical aggregation concentration, c_{ac} . In view of the above discussion, this has to be accompanied by an extensive reduction in the polyelectrolyte-chain dimensions.

On the basis of comparative viscosity measurements in NaCl and CPC, we have pointed above to the differences in binding of CPC to poly(acrylate), PA^- , and to poly(styrenesulfonate), PSS^- , anion. The distinctions in binding of cationic surfactants to these two vinyl polyelectrolytes have already been pointed out [11,12,17,18]. In this case, the reason for a greater influence of the surfactant on the viscosity of PA^- chain relative to the PSS^- chain, lies in different chain flexibility. As pointed out by simulations

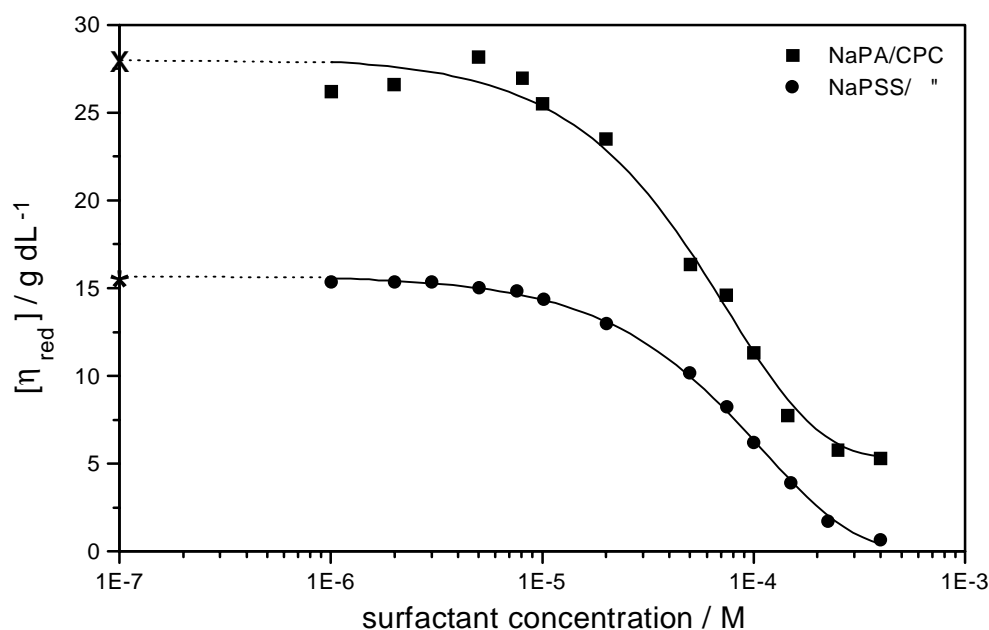


Figure 2. The semi logarithmic plot of the reduced viscosity of NaPSS and NaPA solutions, respectively, in the presence of CPC. Symbols * and × indicate the values for $[\eta_{\text{red}}]$ in NaPSS and NaPA solution, respectively, without any additive.

of polyelectrolyte-surfactant interactions [19], this factor should play a major role in determining the nature of the complex. The greater flexibility of PA^- enables a tighter contact between polyelectrolyte and surfactant micelle (the PA^- chain may even form loops around the micelle) and, therefore, a closer packing within the complex. Hence, the dimensions of the chain are reduced to a greater extent in comparison to the PSS^- chain. This is followed by a greater reduction of the viscosity of the polyion. The complex between PSS^- and CP^+ micelle, on the other hand, is formed by inclusion of the hydrophobic benzenesulfonate ring of the polyion into the interior of the micelle [11,18], thus making the PSS^-/CP^+ complex more stable but at the same time more rigid than the PA^-/CP^+ one. In addition, it seems that surfactant micelles which form in the presence of PSS^- are smaller than those formed in the presence of PA^- . For example, the aggregation numbers of alkyltrimethylammonium bromides, C_nTAB , in the PA^- system do not differ from the ones found for ordinary micelles in pure C_nTAB solutions, whereas in the PSS^- system they are approximately one half of the normal aggregation numbers

[7,8]. Some authors [6] report even very small values, between 7 and 10, for C₁₂TAB in NaPSS solutions. From purely geometric considerations, one can conclude that a greater part of the polyelectrolyte chain is necessary to surround a bigger micelle than a smaller one. Therefore, the overall dimensions of the chain for the same amount of the added surfactant change more in the case of NaPA than in the case of NaPSS.

Apparent Molar Volumes

From measured densities of pure CPC solutions and CPC solutions in the presence of 5×10^{-4} monomol/L NaPSS or NaPA, respectively, the apparent molar volumes were calculated. For a two component aqueous surfactant solution, the apparent molar volume, ϕ_v , was obtained from a known expression [20]

$$\phi_v = \frac{1}{\rho} \left(M + \frac{1}{m_s} \cdot \frac{\rho_0 - \rho}{\rho_0} \right) \quad (1)$$

where ρ is the density of the solution, M is the molar mass of the surfactant, m_s is its molality in mol/kg, and ρ_0 is the density of pure solvent, i.e. water.

For a ternary system composed of water, surfactant, and polyelectrolyte it is convenient to define the mean apparent molar volume, Φ_v , by the relation [20]

$$\Phi_v = \frac{V - n_1 V_1^0}{n_2 + n_3} \quad (2)$$

In eq 2, V is the volume of solution, V_1^0 is the molar volume of pure water, n_1 , n_2 , and n_3 are the amounts of water, polyelectrolyte, and surfactant in a solution with 1 kg of water, respectively, expressed in moles. The mean apparent molar volume, Φ_v , may be easily and directly determined from measured densities, ρ , of mixed polyelectrolyte-surfactant solutions. From eq 2, by putting $V = \frac{1}{\rho}(m_1 + m_2 + m_3)$ ($m_1 = 1$ kg is the mass of water;

m_2 and m_3 are the masses of polyelectrolyte and surfactant, respectively, in 1 kg of water) and rearranging, the following expression is obtained for Φ_V

$$\Phi_V = \frac{1}{\rho} \left(\bar{M} + \frac{1}{m_p + m_s} \cdot \frac{\rho_0 - \rho}{\rho_0} \right) \quad (3)$$

Here, m_p and m_s are the molalities of polyelectrolyte and surfactant, respectively, expressed in mol/kg, and \bar{M} is the average monomolar mass of the polyelectrolyte-surfactant complex.

$$\bar{M} = X_p M_p + X_s M_s \quad (4)$$

In eq 4, M_p and M_s are the molar masses of the polyelectrolyte monomer unit and surfactant, respectively, and X_p and X_s are the corresponding mole fractions in mixed solutions.

The relative mean apparent molar volume of polyelectrolyte-surfactant complex, $\Delta\Phi_V$, and the relative apparent molar volume of pure surfactant, $\Delta\phi_V$, are presented in Figure 3a, where

$$\Delta\Phi_V = \Phi_V - \Phi_V^p \quad (5)$$

$$\Delta\phi_V = \phi_V - \phi_V^0 \quad (6)$$

In eqs 5 and 6, Φ_V^p refers to the polyelectrolyte in solution without added surfactant, ($\Phi_V^p = 96 \text{ cm}^3 \text{ monomol}^{-1}$ for NaPSS and $26 \text{ cm}^3 \text{ monomol}^{-1}$ for NaPA at concentration $5 \times 10^{-4} \text{ monomol/L}$), and ϕ_V^0 is the value for the apparent molar volume of surfactant at infinite dilution in the solution without added polyelectrolyte, obtained by extrapolation of ϕ_V values below cmc to zero concentration ($\phi_V^0 = 342 \text{ cm}^3 \text{ mol}^{-1}$, see Figure 3b). The $\Delta\phi_V$ or $\Delta\Phi_V$ change should reflect any hydrophobic-aggregate formation, like micellization in pure surfactant solutions.

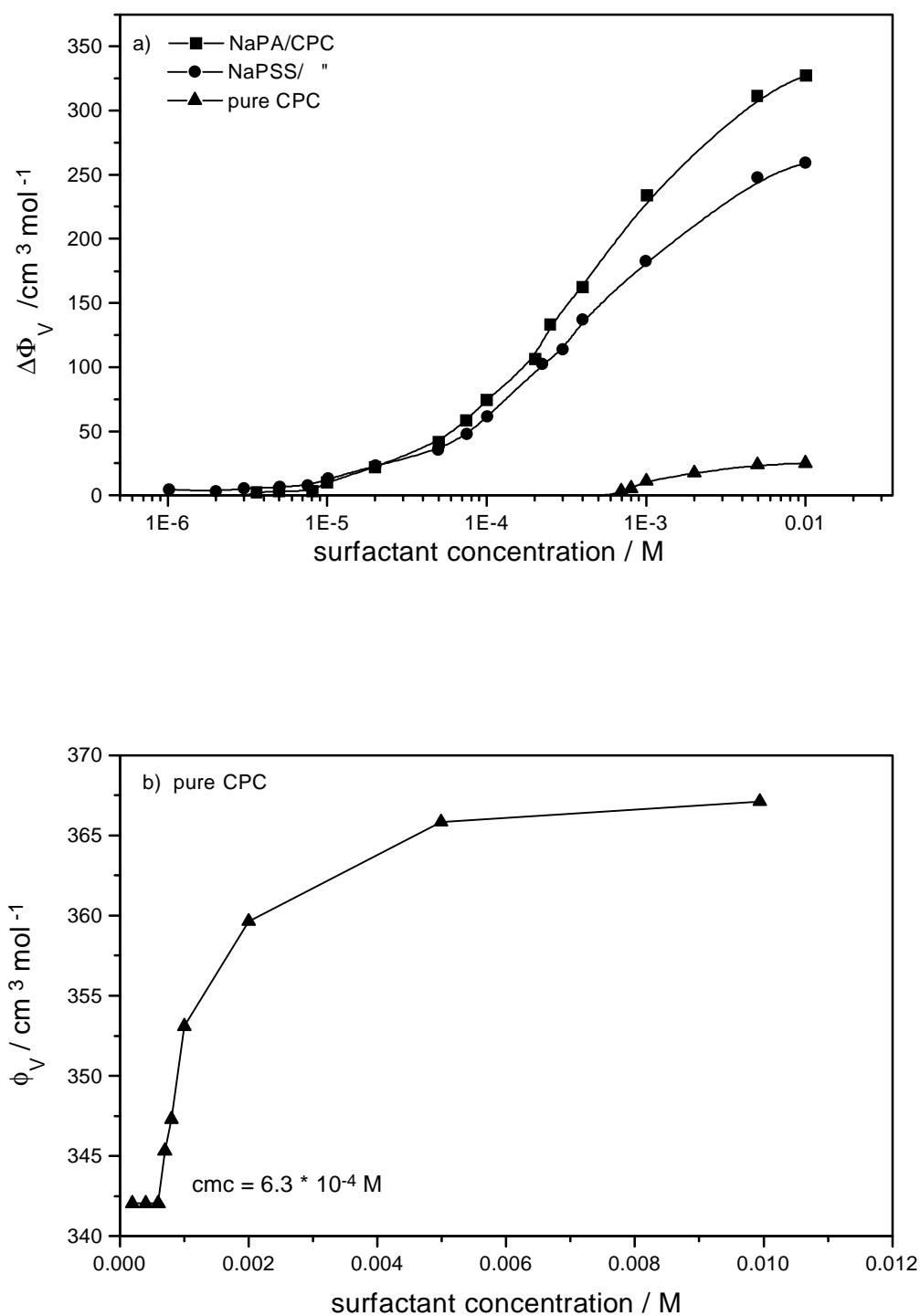


Figure 3 a. $\Delta\phi_V$ (eq 6) in aqueous solutions of CPC at 25 °C and $\Delta\Phi_V$ (eq 5) in the presence of polyelectrolyte, NaPSS and NaPA, respectively. Polyelectrolyte concentration: $c_P = 5 \times 10^{-4}$ monomol/L. **b.** Apparent molar volume, ϕ_V (eq 1), in pure CPC solutions.

From Figure 3a we can see that below the cac ($cac = 1 \times 10^{-5}$ M for CPC, see above) $\Delta\Phi_v$ is very small (approximately zero). We can say that below this concentration surfactant contributes negligibly little to the total volume of the solution. Above cac, $\Delta\Phi_v$ starts to increase. This increase is similar to the corresponding increase in pure surfactant solutions above the cmc and is therefore ascribed to the formation of micelle-like aggregates with a hydrophobic interior in the vicinity of the polyion. The $\Delta\Phi_v$ volume changes are much greater than the volume changes for ordinary micellization, $\Delta\phi_v$. This is inherent in the calculation procedure. In $\Delta\Phi_v$ change, Φ_v^P is subtracted from the mean apparent molar volume of the aggregate (eq 5), whereas in $\Delta\phi_v$ the molar volume of the monomer surfactant at infinite dilution, ϕ_v^0 , is subtracted (eq 6), which is more than 3 times larger than Φ_v^P . In the presence of the polyelectrolyte also ordinary CPC micelles appear somewhat above cmc. This is seen from the $\Delta\Phi_v$ values which are here close to the absolute values for the apparent molar volume in pure CPC solutions above cmc. For comparison, Figure 3b shows ϕ_v in pure CPC solutions. Below cmc, it is approximately constant (around $342 \text{ cm}^3 \text{ mol}^{-1}$). Above cmc, at surfactant concentration equal to 0.01 M, it reaches $367 \text{ cm}^3 \text{ mol}^{-1}$, whereas in polyelectrolyte solutions at the same surfactant concentration the maximum Φ_v values are $353 \text{ cm}^3 \text{ mol}^{-1}$ and $355 \text{ cm}^3 \text{ mol}^{-1}$ in NaPA and NaPSS, respectively. We can conclude, that ordinary surfactant micelles prevail in the solution over the polymer-bound ones.

Finally, Figure 3a also demonstrates differences in binding of CPC to NaPA and NaPSS. The volume changes in NaPA/CPC system exceed the ones in NaPSS/CPC system. Therefore, the greater overall contraction of the PA^- chain is accompanied both by a larger reduction in the reduced viscosity and by a larger volume change.

At the end, it is interesting to point out how different accessions/views supplement the picture of the complexation phenomena between polyelectrolytes and surface active agents. One can start from a “polymer-centered” point of view and inspect how the properties of the polyion chain change by the addition of surfactant. The viscosity measurements certainly belong to this group. On the other hand, one can look at the problem from the “surfactant-centered” side and explain the observations by the strong tendency of surfactant to self-aggregate. According to this, polymer-surfactant

complexation is essentially surfactant micellization in the presence of the polyion. Various experimental observations like dye solubilization, cooperative character of binding isotherms, surface tension behavior, and, among numerous others, also volume changes presented here, can be explained by the phenomenon of surfactant self-association.

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Povzetek

Proučevali smo vpliv kationskega surfaktanta, cetil piridinijevega klorida, CPC, na hidrodinamsko obnašanje natrijevega polistirensulfonata (NaPSS) in natrijevega poliakrilata (NaPA) ter ga primerjali z vplivom enostavne soli (NaCl). Ugotovili smo, da surfaktant po vzro čvečje zmanjšanje viskoznosti raztopine polielektrolita kot NaCl. Razliko smo pripisali dejstvu, da poleg elektrostatskih efektov pri spremembi oblike polimerne verige, surfaktantna micela, ki jo inducira polimer, povzroči še dodatno zvijanje verige poliiiona okoli nje same. Efekti so večji v raztopinah NaPA kot v raztopinah NaPSS.

Poleg tega je v NaPA večja tudi sprememba povprečnega molskega volumna, $\Delta\Phi_v$. Možni razlogi za te razlike so večja fleksibilnost PA^- verige, specifična interakcija med surfaktantno micelo in benzensulfonskim obročem monomerne enote PSS^- verige ter večje micelle, ki se tvorijo v raztopinah NaPA kot pa v raztopinah NaPSS.