

Nonequilibrium Features of the Association between Poly(vinylamine) and Sodium Dodecyl Sulfate: The Validity of the Colloid Dispersion Concept

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The effect of different mixing protocols on the bulk and surface properties of the aqueous mixtures of linear poly(vinylamine) (PVAm) and sodium dodecyl sulfate (SDS) has been investigated using pH, electrophoretic mobility, dynamic light scattering, coagulation kinetics, and surface tension measurements. For the preparation of the solutions, two kinds of mixing protocols were applied. The so-called “stop flow mixing” enables a very rapid mixing whereas in the case of “gentle mixing” the mixing of the components is less efficient. At high surfactant concentrations a kinetically stable colloid dispersion of the PVAm/SDS particles is formed via the application of the stop flow mixing method. The mixing protocols have a significant effect on the bulk properties of the PVAm/SDS system, in particular, at the low pH range and at large PVAm concentrations. The effect of mixing can be qualitatively understood in terms of the enhanced local rate of coagulation of the PVAm/SDS complexes as well as of the appearance of polyelectrolyte/surfactant aggregates via the application of a less efficient mixing. The study also reveals that the applied methods of solution preparation do not have a major impact on the bound amount of the surfactant as well as on the surface tension isotherms of the system. This latter finding is attributed to the hindered adsorption of the large polyelectrolyte/surfactant aggregates at the air/water interface.

Introduction

The aqueous mixtures of oppositely charged polyelectrolytes and surfactants are widely used in different formulations as well as they are promising candidates in novel biological applications.^{1–4} Because of the combined technological relevance and scientific challenge, the solution and surface properties of polyelectrolyte/surfactant mixtures represents an area of current interest, which have motivated an intensive research in this field.^{5–10}

Due to the association between the oppositely charged macromolecules and amphiphiles at certain compositions phase separation takes place in such systems. The phase properties have been thoroughly investigated experimentally, and the general findings at constant polyelectrolyte concentration can be described as follows.^{11–14} At low surfactant concentrations, the solution is a transparent system. With increasing surfactant concentration, the solution becomes turbid and phase separation (precipitation or coacervation) occurs. At even larger surfactant concentrations a transparent system might be achieved again.

In the majority of the various theoretical and simulation studies the polyelectrolyte/surfactant interaction is usually treated as an interaction between the polyelectrolyte molecules and surfactant micelles. According to these approaches, the frequently observed phase separation at intermediate surfactant-to-polyelectrolyte ratio is interpreted as a result of the aggregation of the electrically neutral polyelectrolyte/surfactant complexes.^{15–19}

On the other hand, the theoretical studies predict the formation of thermodynamically stable one-phase systems both at high and low polyelectrolyte-to-surfactant ratios due to the considerable net charge of the polyelectrolyte/surfactant complexes. At

low surfactant concentrations the net charge is attributed to the excess charge of the macromolecules with respect to the charges of the bound micelles. At large surfactant excess the charge reversal of the complex is usually explained as the consequence of the excess surface charges of the bound micelles, which significantly overcome the polyelectrolyte charges. The reswelling of the polyelectrolyte/surfactant complexes (and the formation of a thermodynamically stable one-phase system) is also predicted at large excess of the oppositely charged surfactant.¹⁸

Some of the experimental observations, however, do not support these theoretical predictions, in particular, at high surfactant-to-polyelectrolyte ratios. For instance, it was observed for various mixtures of cationic polyelectrolytes and anionic surfactants that a transparent one-phase system cannot be achieved (e.g., the precipitates can not be resolubilised) even at extremely large surfactant excess.^{12,20} Furthermore, in the case of several polyelectrolyte gels reswelling was not observed at large excess of the oppositely charged surfactant.^{21,22} Last but not least, the theoretical studies refer to equilibrium systems whereas the mixtures of polyelectrolytes and oppositely charged surfactants are frequently observed to be trapped in nonequilibrium states.

Recently, a new interpretation was given for the observed phase properties of the aqueous mixtures of hyperbranched poly(ethyleneimine) (PEI) and sodium dodecyl sulfate (SDS).²⁰ According to this approach, at low surfactant concentrations the system is a thermodynamically stable, transparent solution of the complex molecules. The surfactant bounds in the form of monomers to the charged amine groups, which results in increasing ionization degree of the PEI molecules as well as in decreasing charge density and average size of the PEI/SDS complexes with increasing SDS concentration. Due to the increased dispersion forces, acting between the collapsed complex molecules, the system coagulates above a critical

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surfactant concentration (unstable colloid dispersion). At large excess of SDS the adsorption of the anionic surfactant could take place on the surface of the neutral PEI/SDS particles. This process results in a significant negative surface charge density and therefore in a kinetically stable colloid dispersion of the PEI/SDS particles.²⁰

In recent work, it was also shown that the addition of dodecyl maltoside ($C_{12}G_2$, a nonionic sugar surfactant) to the mixtures of PEI and SDS leads to the formation of a colloid dispersion of the composite PEI/SDS/ $C_{12}G_2$ nanoparticles.²³ In comparison with the PEI/SDS system the SDS concentration range of the kinetically stable dispersion was found to increase considerably in the presence of dodecyl maltoside.²³

Since the colloid dispersions are nonequilibrium systems, the colloid dispersion concept describes well the tendency toward the formation of nonequilibrium structures in these systems. For instance, in a recent study it was shown that the kinetically stable composition range of the colloid dispersion of PEI/SDS particles considerably depends on the order of addition of the solution components as well as on the mixing methods used for the preparation of the solutions.^{20,23,24} Naderi et al. also observed a considerable effect of the applied mixing protocols on the phase properties of several mixtures of cationic polyelectrolytes and SDS.^{25,26}

One of the main intentions of the present work is to explore whether the formation of a colloid dispersion is the consequence of the hyperbranched architecture of the PEI or this phenomenon can be extended for the linear polyelectrolyte/surfactant systems as well. The focus is on the aqueous mixtures of linear poly(vinylamine) (PVAm) and SDS. The PVAm is a weak polyelectrolyte therefore its ionization degree might be shifted during the complexation with SDS similarly to the PEI/SDS system. Because of the nonequilibrium nature of oppositely charged polyelectrolyte/surfactant systems the preparation of the PVAm/SDS mixtures is controlled via the application of two well-defined mixing protocols.²⁴

In the present paper at first the results of electrophoretic mobility and dynamic light scattering measurements are analyzed to highlight the effect of mixing on the charged nature and size of the PVAm/SDS complexes at different experimental conditions (i.e., pH, compositions, etc.). Furthermore, pH and coagulation kinetics measurements are presented to monitor the bound amount of the surfactant and the colloid dispersion character of the system. Finally, we discuss the effect of solution preparation methods on the surface tension isotherms of PVAm/SDS systems.

Experimental Section

Materials. The PVAm with a mean molecular weight of 340 000 g/mol was a gift from BASF and used as received. The sodium dodecyl sulfate was purchased from Sigma-Aldrich and was recrystallized twice from a 1:1 benzene-ethanol mixture. Throughout this study the initial pH of the PVAm solutions (pH^{in}) was adjusted to $pH^{\text{in}} = 4$ and 7 by HCl and to $pH^{\text{in}} = 10$ by NaOH. The applied supporting electrolyte was NaCl in each experiment. All these chemicals were provided by Sigma-Aldrich. During the experiments double distilled water was used for the preparation of the solutions and all the measurements were performed at 25 ± 0.1 °C.

Mixing Protocols. For the preparation of the mixtures, the same mixing protocols were used as in ref 24.

Gentle Mixing. Equal volumes of pH preadjusted polyelectrolyte and surfactant solutions were added into the same dish simultaneously, and mixed by turning the test tubes upside down a few times.

Stop Flow Mixing. Equal volumes of pH preadjusted polyelectrolyte and surfactant solutions were mixed by means of the stop flow mixing apparatus of Applied Photophysics (Model RX.1000). This mixing method is very efficient since the two solutions are completely mixed within 10 ms.

It should be noted that all the measurements were performed 24 h after the preparation of the PVAm/SDS mixtures.

pH Measurements. The pH was measured by means of a combined pH-glass electrode and a research pH-meter (Radelkis).

Electrophoretic Mobility Measurements. The electrophoretic mobility of the PVAm/SDS complexes was measured using a Malvern Zetasizer NanoZ apparatus. The instrument uses a combination of laser Doppler velocimetry and phase analysis light scattering in a technique called M3-PALS. The details of this method might be found elsewhere.²⁷ Prior to the measurements the instrument was always tested with Malvern Zeta Potential Transfer Standard. The standard error of the electrophoretic mobility was found to be around 5%.

Dynamic Light Scattering Measurements (DLS). The light scattering measurements were performed at scattering angles from 40 to 140° by means of a Brookhaven equipment consisting of a BI-200SM goniometer system and a BI-9000AT digital correlator. An argon-ion laser (Omnichrome, model 543AP) operating at 488 nm wavelength and emitting vertically polarized light was used as the light source. Prior to the measurements the solutions were cleaned of dust particles by filtering through 0.8 μm pore size membrane filters.

The intensity–intensity time–correlation functions were measured, and converted to the normalized electric field autocorrelation functions by means of the Siegert relation. These autocorrelation functions were analyzed by both the cumulant expansion and CONTIN methods. The investigated PVAm and PVAm/SDS solutions were found to be polydisperse, having a broad unimodal distribution. The apparent diffusion coefficient D_{app} was derived from the mean relaxation rate $\bar{\Gamma}(q)$ (first cumulant):

$$D_{\text{app}}(q) = \frac{\bar{\Gamma}(q)}{q^2} \quad (1)$$

where q is the scattering vector ($q = (4\pi n/\lambda_0) \sin(\theta/2)$, n is the refractive index of the solution, λ_0 is the wavelength of the incident light, and θ is the scattering angle). In order to obtain the translational collective diffusion coefficient D_{coll} the apparent diffusion coefficient was extrapolated to zero scattering vector: $D_{\text{coll}} = D_{\text{app}}(q \rightarrow 0)$.²⁸ In principle, the pure translational diffusion coefficient D_0 can be determined only at infinite dilution of the polyelectrolyte solutions when the interaction between the particles becomes negligible:²⁸

$$D_{\text{coll}} = D_0(1 + k_D c) \quad (2)$$

where k_D is a constant and c is the concentration of the polyelectrolyte. In the majority of the scattering experiments only dilute PVAm solutions were used (0.02 to 0.05 wt %). Assuming that at these PVAm concentrations the second term can be neglected in eq 2 and that the polyelectrolyte/surfactant complexes are spherical, the apparent hydrodynamic diameter d_H was calculated from D_{coll} by means of the Einstein–Stokes relation. On the basis of repeated measurements the standard error in d_H can be estimated as 10–15% in the low (prepre-

cipitation) and 3–4% in the high (postprecipitation) SDS concentration range.

Coagulation Kinetics Measurements. The rate of coagulation was measured by a Perkin-Elmer (Lambda 2) spectrophotometer coupled with a stop flow mixing unit (Model RX.1000, Applied Photophysics Ltd.). First the PVAm/SDS mixtures were prepared via the stop flow mixing protocol and left to stand for 24 h. (The systems prepared by gentle mixing were too turbid for the absorbance measurements). Then the PVAm/SDS solutions were mixed by NaCl solutions in equal volumes and the absorbance vs time curves were monitored at 480 nm.

In the case of monodisperse particles the initial rate of coagulation can be approximated by second order kinetics:²⁹

$$-\frac{dn}{dt} = kn^2 \quad (3)$$

where k is the coagulation rate constant and n is the number of particles per unit volume.

The experimental coagulation rate constant k_x can be determined from the initial slope of the absorbance versus time curves ($Ab-t$), provided that the size of the particles is negligible compared to the wavelength of the light beam:²⁹

$$\left(\frac{dAb}{dt}\right)_{t \rightarrow 0} = Ck = k_x \quad (4)$$

where C is a constant (depending on the volume and concentration of the particles as well as on the characteristics of the spectrophotometer cell). It should be emphasized that the experimentally determined k_x is not the absolute rate constant, but it is proportional to it according to eq 4.

For the characterization of the kinetic stability of a colloid dispersion the so-called stability ratio was introduced:³⁰

$$W = \frac{k_{fast}}{k} \quad (5)$$

where k_{fast} is the coagulation rate constant in the fast coagulation regime.

Surface Tension Measurements. The surface tension measurements were carried out by the pendant drop method. The details of the setup can be found in ref 31. The surface tension of pure water was found to be 72.0 ± 0.1 mN/m, being constant for thousands of seconds. For the polyelectrolyte/surfactant solutions the “equilibrium” surface tension σ is determined from the $\sigma-\log(t)$ curves on the basis of the method in ref 32. According to this approach, the time needed for the equilibration of the surface layer is approximated as the measurement time after which the variation of the surface tension do not exceed the experimental error during an order of magnitude increase in time (one unit in the $\log(t)$ scale).³²

Results and Discussion

Bulk Properties of PVAm/SDS Mixtures. The Effect of Mixing on the Charged Nature and Size of PVAm/SDS Complexes. In Figures 1 and 2 the electrophoretic mobility u_ζ and the apparent hydrodynamic diameter d_H of the PVAm/SDS complexes are plotted against the total analytical surfactant concentration at $pH^{in} = 7$ in the presence of 10 mM NaCl for PVAm concentrations $c_{PVAm} = 0.02$ and 0.05 wt %, respectively. In Figures 3 and 4, the same functions are plotted at $pH^{in} = 4$ and 10, respectively, in 10 mM NaCl for $c_{PVAm} = 0.05$ wt %.

The electrophoretic mobility of the PVAm/SDS complexes changes from positive to negative values with increasing surfactant concentration due to the binding of the dodecyl sulfate ions to the PVAm molecules. The apparent hydrodynamic size

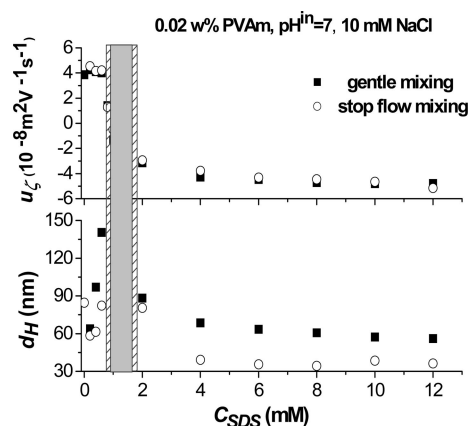


Figure 1. Electrophoretic mobility and apparent hydrodynamic diameter of the PVAm/SDS complexes as a function of the surfactant concentration for the two mixing protocols in the presence of 10 mM NaCl. The precipitated or highly turbid systems are indicated by the gray area and by the gray + sparse areas for the stop flow and gentle mixing protocols, respectively. The measurements were performed 24 h after the preparation of the PVAm/SDS mixtures. The standard error in the values of electrophoretic mobility is commensurable with the size of the symbols. The standard error in d_H can be estimated as 10–15% in the low (preprecipitation) and 3–4% in the high (postprecipitation) SDS concentration range. $pH^{in} = 7$, $c_{PVAm} = 0.02$ wt %.

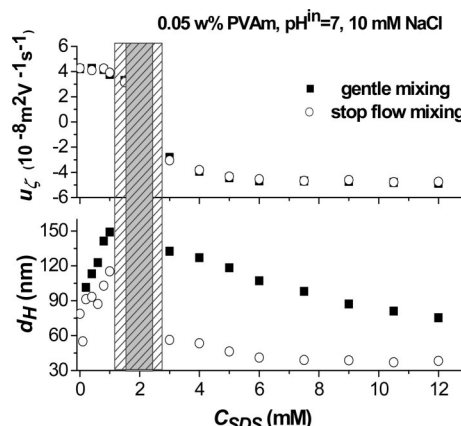


Figure 2. Electrophoretic mobility and apparent hydrodynamic diameter of the PVAm/SDS complexes as a function of the surfactant concentration for the two mixing protocols in the presence of 10 mM NaCl. The precipitated or highly turbid systems are indicated by the gray area and the gray + sparse areas for the stop flow and gentle mixing protocols, respectively. The measurements were performed 24 h after the preparation of the PVAm/SDS mixtures. The standard errors of d_H and u_ζ are the same as in Figure 1. $pH^{in} = 7$, $c_{PVAm} = 0.05$ wt %.

of the complexes decreases at very low surfactant concentrations then starts to increase with c_{SDS} . At a given concentration region precipitation takes place (not suitable for light scattering experiments). A further increase of the surfactant concentration leads to transparent systems again and decreasing d_H values of the complexes.

As it is shown in Figures 1–4, the observed electrophoretic mobility values do not depend on the solution preparation methods within the experimental error. However, the variation of the apparent hydrodynamic diameter of the complexes with the surfactant concentration, as well as the width of the precipitated concentration region is affected by the different mixing procedures. The differences are more pronounced at high surfactant concentrations, where PVAm/SDS complexes of considerably reduced size are formed via the very rapid mixing of the components. By contrast, the application of the less

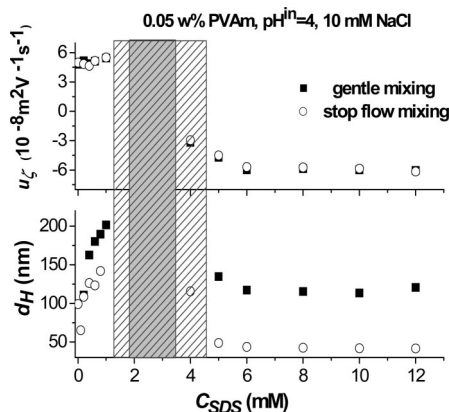


Figure 3. Electrophoretic mobility and apparent hydrodynamic diameter of the PVAm/SDS complexes as a function of the surfactant concentration for the two mixing protocols in the presence of 10 mM NaCl. The precipitated or highly turbid systems are indicated by the gray area and by the gray + sparse areas for the stop flow and gentle mixing protocol, respectively. The measurements were performed 24 h after the preparation of the PVAm/SDS mixtures. The standard errors of d_H and u_{ξ} are the same as in Figure 1. $\text{pH}^{\text{in}} = 4$, $C_{\text{PVAm}} = 0.05$ wt %.

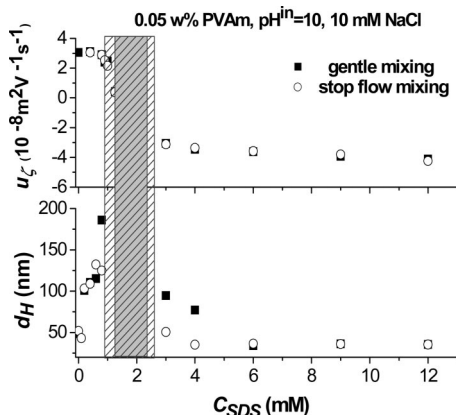


Figure 4. Electrophoretic mobility and apparent hydrodynamic diameter of the PVAm/SDS complexes as a function of the surfactant concentration for the two mixing protocols in the presence of 10 mM NaCl. The precipitated or highly turbid systems are indicated by the gray area and by the gray + sparse areas for the stop flow and gentle mixing protocol, respectively. The measurements were performed 24 h after the preparation of the PVAm/SDS mixtures. The standard errors of d_H and u_{ξ} are the same as in Figure 1. $\text{pH}^{\text{in}} = 10$, $C_{\text{PVAm}} = 0.05$ wt %.

efficient mixing results in larger average size of the complexes as well as in a more extended two phase region compared with the results of stop flow mixing.

Figures 1 and 2 clearly demonstrate that with increasing polymer concentration the effect of mixing becomes more pronounced. At PVAm concentrations larger or equal to 0.1 wt % the application of the gentle mixing protocols leads to precipitated and highly turbid systems in a very wide surfactant concentration range (the solutions are not suitable for the determination of d_H due to multiple scattering effects, see Figure S1 in the Supporting Information). In contrast, PVAm/SDS mixtures with low turbidity can be prepared by the stop flow mixing protocol in the same SDS concentration range.

The comparison of the data in Figures 2–4 reveals that the charge density of the polyelectrolyte plays an important role in the nonequilibrium features of PVAm/SDS systems. The method of solution preparation has the largest impact on the phase properties at $\text{pH}^{\text{in}} = 4$, where the PVAm molecules are

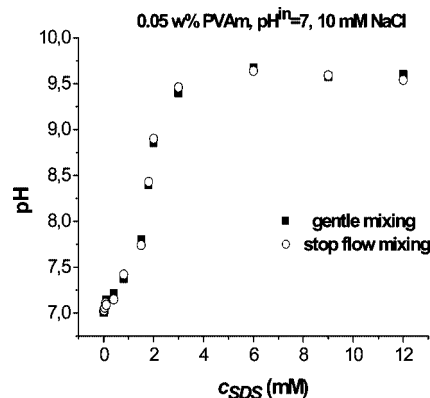


Figure 5. pH of PVAm/SDS mixtures as a function of the surfactant concentration for the two mixing protocols in the presence of 10 mM NaCl. The measurements were performed 24 h after the preparation of the PVAm/SDS mixtures. The standard error of pH measurements is commensurable with the size of the symbols. $\text{pH}^{\text{in}} = 7$, $C_{\text{PVAm}} = 0.05$ wt %.

considerably charged (i.e., $\sim 90\%$ of the amine groups is protonated).³³ On the other hand, at $\text{pH}^{\text{in}} = 10$, where only about 10% of the amine groups of the PVAm molecules is charged,³³ the effect of mixing becomes nearly negligible.

It can be concluded that the larger the concentration and ionization degree of the PVAm molecules the more pronounced the effect of mixing on the PVAm/SDS complex formation becomes. It should be noted, that no changes were observed in the values of d_H and u_{ξ} within the experimental error for a couple of months in the transparent composition ranges of Figures 1–4. This finding will be discussed in the following sections.

The Effect of Mixing on the Bound Amount of the Surfactant. As it has been shown in the previous section, the method of mixing significantly influences the size distribution of the polyelectrolyte/surfactant complexes and the precipitation composition range, but do not affect the electrophoretic mobility of the PVAm/SDS complexes considerably. The electrophoretic mobility of the polyelectrolyte/surfactant complexes is closely related, among other factors, to the bound amount of the surfactant. Therefore, it is important to explore whether the applied mixing protocols affect or not the bound amount of the surfactant in the PVAm/SDS aggregates formed via the application of the different solution preparation methods.

The variation of the pH with the surfactant concentration provides a simple tool to monitor the binding of ionic surfactants to oppositely charged weak polyelectrolytes.^{20,34} In Figure 5, the pH of the PVAm/SDS mixtures is plotted against the surfactant concentration at $\text{pH}^{\text{in}} = 7$ in the presence of 10 mM NaCl. As it is indicated by the data the addition of SDS to the PVAm solution results in a huge increase of the pH. This finding is attributable to the complexation of the anionic surfactant with the charged amine groups inducing additional charging of the PVAm molecules.^{20,34} The variation of pH with SDS concentration was quantitatively described for the hyperbranched PEI/SDS system within the framework of a simple model that combines the surfactant binding equilibrium with the acid/base equilibrium of the amine groups.²⁰ In principle, this model can be applied for any kind of polyamine/surfactant solution, and thus for PVAm/SDS mixtures, as well. One of the most important predictions of this approach is that the pH of a polyamine/SDS solution is a monotonous function of the bound amount of the surfactant.²⁰

Figure 5 shows that the pH of the PVAm/SDS mixtures does not depend on the applied methods of solution preparation within

the experimental error. Similar results were observed at $\text{pH}^{\text{in}} = 4$ and 10. (The data are not shown.) This means that the applied mixing protocols do not affect considerably the bound amount of the surfactant in the formed PVAm/SDS aggregates.

The Thermodynamic State of the PVAm/SDS Mixtures Formed by Stop Flow Mixing at a Large Excess of SDS. According to Figures 1–4, the application of stop flow mixing at high SDS concentrations results in negatively charged polyelectrolyte/surfactant complexes of significantly reduced size. At large excess of the surfactant the d_H values do not depend on the polyelectrolyte concentration, and only slightly depend on the pH ($d_H = 36 \pm 2$ nm and 38 ± 2 nm at $\text{pH}^{\text{in}} = 7$ for $c_{\text{PVAm}} = 0.02$ and 0.05 wt %, respectively; $d_H = 41 \pm 2$ nm and 36 ± 2 nm for $c_{\text{PVAm}} = 0.05$ wt % at $\text{pH}^{\text{in}} = 4$ and 10, respectively, for solutions prepared by the stop flow mixing method).

In this concentration range a considerable amount of bound dodecyl sulfate ions is incorporated within the small volume of the PVAm/SDS complexes. Therefore, it is straightforward to assume that polyelectrolyte/surfactant particles rather than solvated complexes are formed via the rapid mixing of the components. Since no reswelling of the polyelectrolyte/surfactant complexes can be observed at high SDS concentrations, the significant charge reversal of the complexes can be explained by the adsorption of the anionic surfactant on the outer layer of the neutral PVAm/SDS nanoparticles. Similar observations were also reported for mixtures of SDS with PEI as well as with 2-((propionyloxy)ethyl)trimethylammonium chloride.^{20,24,35} This finding suggests that the transparent PVAm/SDS mixtures formed at high surfactant concentrations can be considered as electrostatically stabilized colloid dispersions of the polyelectrolyte/surfactant particles.

In order to give further evidence for the formation of a colloid dispersion, coagulation kinetics measurements were carried out at large excess of SDS (at $c_{\text{PVAm}} = 0.05$ wt % final PVAm concentration). It should be noted that the PVAm/SDS mixtures shown in Figures 1–4 were prepared in the presence of 10 mM NaCl. In the coagulation kinetics experiments, however, PVAm/SDS mixtures without added salt were mixed with equal volume of NaCl solutions of different concentrations. In a separate series of experiments the u_ζ vs c_{SDS} as well as the d_H vs c_{SDS} curves were measured without added salt. The nature of these curves is similar to those measured in 10 mM NaCl medium. This is demonstrated in Figure S2 of the Supporting Information for $\text{pH}^{\text{in}} = 7$ and $c_{\text{PVAm}} = 0.05$ wt % (compare with Figure 2).

Figure 6 shows the dependence of the stability ratio on the NaCl concentration for PVAm/SDS mixtures at $\text{pH}^{\text{in}} = 7$ ($c_{\text{SDS}} = 3$ mM, $c_{\text{PVAm}} = 0.05$ wt %), and $\text{pH}^{\text{in}} = 10$ ($c_{\text{SDS}} = 2$ mM, $c_{\text{PVAm}} = 0.05$ wt %). $\log W$ decreases linearly with $\log c_{\text{NaCl}}$ until a certain concentration value, i.e. the critical coagulation concentration (ccc) is reached where $\log W$ becomes zero. This latter part of the curve corresponds to the region of rapid coagulation.

The shape of the $\log W$ vs $\log c_{\text{NaCl}}$ functions in Figure 6 strongly resembles experimental stability plots of electrostatically stabilized colloid sols, which are in qualitative agreement with the predictions of the DLVO theory.³⁰ The same behavior was observed in a wide surfactant concentration range (in the postprecipitation regime) at $\text{pH}^{\text{in}} = 4$, 7, and 10 as well. Therefore, it can be concluded that the PVAm/SDS system at high surfactant concentrations is not a thermodynamically stable solution of the solvated polyelectrolyte/surfactant complexes but a colloid dispersion of the PVAm/SDS nanoparticles.

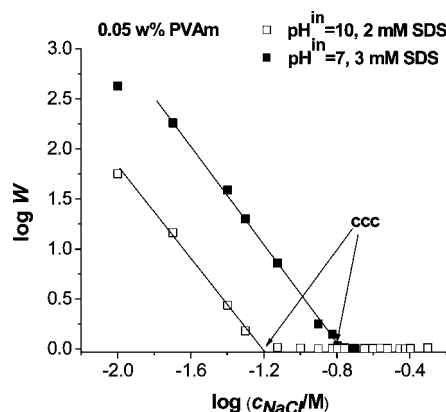


Figure 6. Logarithm of the stability ratio as a function of the logarithm of the NaCl concentration for $\text{pH}^{\text{in}} = 7$, $c_{\text{PVAm}} = 0.05$ wt % and $c_{\text{SDS}} = 3$ mM (■) as well as for $\text{pH}^{\text{in}} = 10$, $c_{\text{PVAm}} = 0.05$ wt % and $c_{\text{SDS}} = 2$ mM (□). At first, the PVAm/SDS mixtures without added salt were prepared using the stop flow mixing equipment and left to stand for 24 h. These mixtures were then mixed with NaCl solutions of different concentration via the stop flow mixing method. The standard error of $\log W$ is commensurable with the size of the symbols.

Our results clearly reveals that the formation of a colloid dispersion is not limited to the hyperbranched PEI/SDS system but it is a more general phenomenon of oppositely charged polyelectrolyte/surfactant mixtures. The idea that these mixtures should form an equilibrium one phase system at large excess of the surfactant is supported by theoretical approaches which are based on the concept of cooperative surfactant binding. However, in the case of PEI a noncooperative surfactant binding was detected at low SDS concentrations, which was followed by the adsorption of the anionic surfactant on the surface of the PEI/SDS nanoparticles in a second binding process at high SDS concentrations.²⁰ It is possible that the binding mechanism of SDS on the PVAm molecules is similar to the ones mentioned above. Nevertheless, further investigations are necessary to explore the detailed mechanism of surfactant binding on oppositely charged polyelectrolytes and the relationship between the surfactant binding and the thermodynamic state of the system.

The Effect of Mixing Protocols on the Phase Properties of PVAm/SDS Mixtures. According to Figures 1–5, the application of the stop flow mixing protocol results in lower apparent hydrodynamic diameter of the complexes and smaller two phase area as compared with the gentle mixing. On the other hand, the way of the solution preparation does not affect the bound amount of the surfactant in the polyelectrolyte/surfactant aggregates. This latter finding suggests that the aggregates, formed via gentle or stop flow mixing, are built of similar primary PVAm/SDS complexes which contain the same amount of bound surfactant. One of the possible interpretations of these results is summarized below.

During the mixing procedure the system—regardless of its final state—goes through different unstable states due to the local inhomogeneities developed upon the application of a specific blending procedure. The sequences of the subsequent events crucially depend on the time the mixture is in unstable states. The final state of the system will be considerably affected by the local rate of aggregation of the polyelectrolyte/surfactant complexes, which depends on a number of factors including the local rate of surfactant binding, the conformational changes of the macromolecules etc. The large concentration gradients developed upon the application of a less efficient mixing method may significantly enhance the local rate of coagulation and

therefore the precipitation range, compared to those polyelectrolyte/surfactant mixtures in which the components are mixed extremely rapidly.

An important consequence of the initial local inhomogeneities is the appearance of aggregates of the primary PVAm/SDS complexes in addition to the individual polyelectrolyte/surfactant complexes. It is likely that during a less efficient mixing procedure the formation of large polyelectrolyte/surfactant aggregates becomes much more pronounced than in the case of a very rapid mixing of the components. If the net charge of the primary polyelectrolyte/surfactant complexes is large enough, the system might reveal a considerable kinetic stability even in the presence of polyelectrolyte/surfactant aggregates. This reasoning could explain the time independent features of the observed d_H vs c_{SDS} and u_ζ vs c_{SDS} curves of Figures 1–4 in the transparent composition range.

It should be noted that the same amount of bound surfactant at a given composition does not explain the observed same electrophoretic mobility values of the PVAm/SDS aggregates which have different average size in the case of the different mixing methods. One of the possible interpretations of this latter observation could be that in the case of the less efficient mixing method only a small fraction of large aggregates appears in addition to the dispersion of the primary PVAm/SDS particles. (Due to the high polydispersity of the PVAm sample, the exact size and fraction of the PVAm/SDS aggregates cannot be determined.) This could increase significantly the average size of the complexes derived on the basis of dynamic light scattering measurements compared with the results of the stop flow mixing method. In contrast, the presence of a small percent of large aggregates may not affect considerably the average electrophoretic mobility values of the PVAm/SDS complexes.

It is straightforward to assume that the mentioned consequences of the mixing procedure (e.g., the decreased kinetic stability or the formation of polyelectrolyte/surfactant aggregates) are more pronounced at high concentration of the primary complexes as well as in the case of a large amount of bound surfactant, i.e., at high concentration and charge density of the polyelectrolyte. It must be emphasized, however, that further investigations, focusing on mixtures with monodisperse polyelectrolytes and oppositely charged surfactants, are needed to explore further details of the effect of mixing on the size distribution of the polyelectrolyte/surfactant complexes.

Surface Properties of PVAm/SDS Mixtures. In order to test the effect of mixing protocols on the surface properties of PVAm/SDS mixtures the surface tension isotherms were measured at different ionization degrees of the PVAm molecules (at $pH^{in} = 4, 7$, and 10).

The electrophoretic mobility and the surface tension σ is plotted as a function of the total surfactant concentration in Figure 7 at $pH^{in} = 7$ and for $c_{PVAm} = 0.05$ wt % in 10 mM NaCl. At small surfactant concentrations the surface tension of the PVAm/SDS mixtures decreases with increasing c_{SDS} and the observed surface tension values are significantly below the ones, which can be measured for the solutions of SDS or PVAm only at the same concentration range. (See Figure S3 in the Supporting Information.) Similar synergistic lowering of the surface tension was also observed for a number of oppositely charged polyelectrolyte/surfactant mixtures at low surfactant concentrations.³⁶ The phenomenon is attributed to the strong surface complexation between the polyelectrolytes and the surfactants at the air/water interface. Further increase of the surfactant concentration results in increasing surface tension as well as a sharp upturn of the σ vs c_{SDS} curves to surface tension

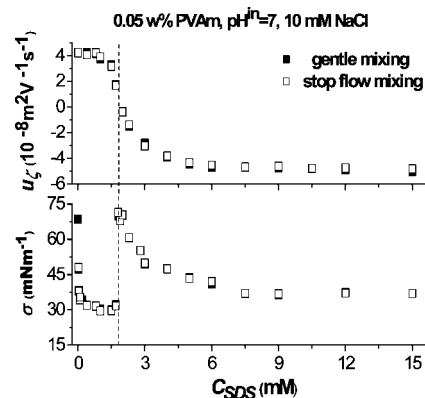


Figure 7. Electrophoretic mobility and surface tension of the PVAm/SDS mixtures as a function of the surfactant concentration for the two mixing protocols. The measurements were performed 24 h after the preparation of the PVAm/SDS mixtures. $pH^{in} = 7$, $c_{PVAm} = 0.05$ wt %, $c_{NaCl} = 10$ mM.

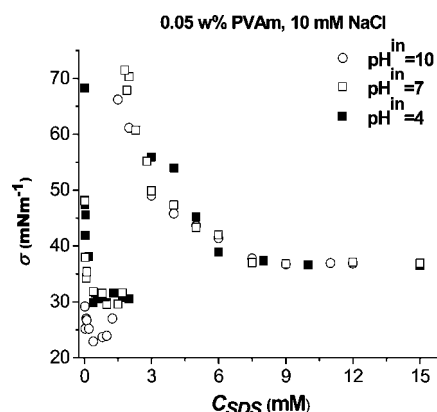


Figure 8. Surface tension of the PVAm/SDS mixtures as a function of the surfactant concentration in the presence of 10 mM NaCl at different pH. The measurements were performed 24 h after the preparation of the PVAm/SDS mixtures. ($pH^{in} = 4$ (■), $pH^{in} = 7$ (□) and $pH^{in} = 10$ (○) in the case of stop flow mixing).

values close to that of the pure water. This upward jump can be observed in a narrow SDS concentration range belonging to the formation of PVAm/SDS complexes of nearly zero electrophoretic mobility and to the appearance of precipitation. At even higher SDS concentrations the surface tension decreases again with c_{SDS} until, similarly to the values of u_ζ , it becomes roughly constant because of the appearance of free micelles in the mixtures (at the cmc of SDS in the presence of PVAm).

As is shown in Figure 8, the σ vs c_{SDS} curves have very similar shape at $pH^{in} = 4, 7$ and 10 . According to the classification of Taylor et al.,³⁶ this kind of surface behavior corresponds to the so-called type 2 surface tension isotherm, which has been observed for various oppositely charged polyelectrolyte/surfactant mixtures.^{36,37} The peculiar shape of the σ vs $c_{surfactant}$ curves has been interpreted as a consequence of the competition between the bulk and surface complexation of the polyelectrolyte with the surfactant.³⁸

An interesting feature of Figure 8 is that at low surfactant concentrations the most surface active PVAm/SDS complexes are formed at $pH^{in} = 10$, i.e. when the PVAm molecules are only slightly charged. Similar results were reported for the hyperbranched PEI/SDS mixtures by Penfold et al.³⁹ The very large surface activity of the PEI/SDS system at the high pH range was explained by the pronounced role of hydrophobic interactions in the binding of anionic surfactants to polyamines of low charge density.³⁹ Alternatively, one might argue that the

formation of the most surface active complexes correlates with the lowest extent of repulsion between the PVAm segments at the air/water interface.

The data of Figure 7 reveals that the surface tension values do not depend on the solution preparation methods within the experimental error. Similar results were observed at $\text{pH}^{\text{in}} = 4$ and 10 (see Figures S4 and S5 in the Supporting Information). One of the possible interpretations of this finding is that the adsorption of the larger aggregates formed via the application of the gentle mixing is hindered due to their large size and/or the electrostatic repulsion they experience approaching the similarly charged surface layer.

Conclusions

We have shown that at high surfactant concentrations negatively charged PVAm/SDS nanoparticles with significantly reduced size are formed via the very rapid mixing of the components. Coagulation kinetics measurements support the idea that these systems, similarly to the mixtures of hyperbranched PEI and SDS, are kinetically stable colloid dispersions of the PVAm/SDS nanoparticles rather than thermodynamically stable solutions. Therefore, the formation of a colloid dispersion at large excess of the surfactant is not the consequence of the hyperbranched structure of PEI but it is a more general phenomenon of oppositely charged polyelectrolyte/surfactant mixtures. This also means that the widely accepted view, according to which at high surfactant concentrations these mixtures are always true solutions of the solvated complexes of oppositely charged macromolecules and amphiphiles, needs to be reconsidered. Since this classical view is supported by theoretical approaches based on the concept of cooperative surfactant binding, further studies are necessary to explore the interrelation between the mechanism of surfactant binding and that of the thermodynamic state of the system. These kinds of investigations are in progress in our laboratory.

The present paper also reveals that the method of mixing could considerably affect the bulk properties of PVAm/SDS system, in particular, at the low pH range and at large PVAm concentrations. The effect of mixing can be qualitatively understood in terms of the enhanced local rate of coagulation of the PVAm/SDS complexes as well as of the appearance of large polyelectrolyte/surfactant aggregates, in addition to the primary complexes, via the application of a less efficient mixing method. The formation of aggregates as well as the decrease in the observed kinetically stable composition range is more pronounced at large concentration and ionization degree of the PVAm molecules.

The applied solution preparation methods have a significant impact neither on the electrophoretic mobility of the PVAm/SDS complexes, nor on the bound amount of the surfactant, nor on the surface tension isotherms of the PVAm/SDS systems. This latter finding indicates that the adsorption of the large polyelectrolyte/surfactant aggregates, formed via the application of the gentle mixing method, might be considerably hindered at the free aqueous surface.

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Supporting Information Available: Figures showing additional experimental information as discussed in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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