

Complex Formation between Sodium Dodecyl Sulfate and Poly(4-vinylpyridine *N*-oxide)

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The interaction of poly(4-vinylpyridine *N*-oxide) (PVPNO) with sodium dodecyl sulfate in aqueous solutions was examined using surface tension, turbidimetry, and light scattering (quasielastic, electrophoretic, and total intensity light scattering). Surface tension measurements show that the polymer begins to interact with SDS at a concentration below the critical micelle concentration (cmc), in a manner similar to the behavior of other nonionic polymer–surfactant systems (e.g., PEO–SDS). Turbidimetric and quasielastic light scattering (QELS) studies at SDS concentrations much above the cmc clearly reveal the formation of a soluble polymer–micelle complex. On the other hand, phase separation, similar to that observed for polyelectrolyte–oppositely charged micellar systems, occurs at low pH, presumably as a consequence of protonation of the polymer to form a polycation. Total intensity data show saturation of the polymer with bound micelles at high SDS concentration, while QELS measurements clearly reveal two peaks: one corresponding to free micelles and the other to the complex. Quasielastic and electrophoretic light scattering measurements were carried out on mixtures of SDS and PVPNO, SDS and PEO, or SDS and both polymers. These indicate that the binding of SDS micelles to PVPNO in 0.10 M NaCl is not as strong as the binding to PEO.

Introduction

The interaction between polymers and surfactants in aqueous solutions has attracted much interest in recent years due to the application of mixed polymer–surfactant systems in various fields.¹ The most extensively studied systems have been those comprised of uncharged polymers and ionic surfactants, and those consisting of polyelectrolytes and oppositely charged surfactants. In the first category, interactions have been observed between uncharged polymers like poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(vinylpyrrolidone) (PVP), poly(vinyl methyl ether) (PVME), and poly(vinyl alcohol) (PVA) and ionic surfactants like sodium dodecyl sulfate (SDS) and alkyltrimethylammonium salts. Specifically, the systems PEO–SDS,^{2–8} PPO–SDS,^{9,10} PVP–SDS,^{11–14} and PVA–SDS^{15–17} have been investigated by various

physicochemical and spectral methods, and it has been found that SDS forms polymer-bound aggregates (smaller than the normal micelles) at concentrations less than the critical micelle concentration (cmc). However, a variety of explanations have been proposed for the force or forces responsible for these interactions (see, for example, ref 8).

In polyelectrolyte–oppositely charged surfactant systems, complexation clearly results from strong Coulombic forces. In contrast to nonionic polymer systems, the interaction leads to phase separation, limiting the studies to surfactant concentrations (C_s), below or near the cmc. The interaction begins at surfactant concentrations far below the cmc and both the monomeric surfactant as well as its aggregates can bind to the polyelectrolyte. In these systems too, the surfactant aggregates are generally reported to be smaller than the polymer-free micelles,^{18,19} but in some cases no change²⁰ or even an increase²¹ in aggregation number has been noticed. In polyelectrolyte–oppositely charged micellar systems, complexes at $C_s > \text{cmc}$ are unstable with respect to phase separation unless the surface charge density of the ionic micelles is reduced, e.g., by addition of a nonionic cosurfactant.²² The most extensively studied system in this regard is poly(dimethylallyl ammonium chloride)–SDS/Triton X-100.^{22–27}

This paper reports studies on the interaction of poly(4-vinylpyridine *N*-oxide) (PVPNO) with SDS. This polymer has a high dipole and behaves as a hydrophilic nonionic macromolecule in water but can also be proto-

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nated to form a cationic polyelectrolyte at highly acidic pH. Thus, the present system provides a way to observe a transition from a micelle–nonionic polymer interaction to a micelle–polyelectrolyte interaction in the same solution. It was also of interest to determine whether the very strong dipole of PVPNO would give rise to a stronger interaction with SDS, so we qualitatively compared the binding of micelles to that found for the more commonly examined PEO–SDS system. The current study utilizes a number of techniques to examine the PVPNO–SDS interaction: surface tension, turbidity, or total intensity measurements, quasi-elastic light scattering, and electrophoretic light scattering. Since these methods differ in regard to the solute concentration range in which they are most useful, there is some variation among the different experimental conditions (i.e., from 0.1% to 0.4% polymer concentration). However, our purpose here is an exploratory investigation of a polymer–surfactant complex not previously studied, which we felt would benefit from the application of a variety of methods.

Experimental Section

Materials. The PVPNO used in this study was a commercial sample from Reilly Industries, Indianapolis, with a nominal molecular weight about 10K. As will be shown, the relatively low MW of PVPNO facilitated the use of QELS for assessing the binding of SDS relative to PEO. PEO samples (MW 900K, 4000K) with narrow MW distribution were purchased from Toya Soda (Tokyo). SDS from Fluka (99.5%) was used. The surfactant showed no minimum in surface tension–concentration plot, confirming its purity. Reagent grade NaCl (Sigma) and standard N/2 HCl solutions (Fisher) were used.

Solutions of PVPNO (concentration 0.4%) and SDS (60 mM) in 0.1M NaCl, made using MilliQ water, were used unless stated otherwise. Solutions for light scattering were filtered using 0.22- μ m filters. All measurements were performed at $24 \pm 1^\circ\text{C}$.

Methods. Tensiometry. The surface tension of solutions, γ , was measured using a Kruss Tensiometer (Hamburg). These measurements were made at 25°C , in water and in 0.1 M NaCl at neutral pH, for SDS in the absence and presence of PVPNO (0.1%). The SDS concentration range was 0.004–10 mM.

Turbidimetry. Turbidity, recorded as $100 - \%T$, was measured with a Brinkmann PC 800 probe colorimeter equipped with a 2-cm path length fiber optics probe at 420 nm. The pH values of PVPNO–SDS solutions were adjusted by titrating with N/2 HCl with a Gilmont 2-mL microburet. The measured values were corrected by subtracting the turbidity of a polymer-free blank.

Light Scattering. The scattering intensity, I_s (counts per second), was measured via the photon counting rate using a Brookhaven BIC instrument (Holtville, NY) at scattering angle 90° with a 400- μ m pinhole aperture for the EMI photomultiplier tube. Each measurement was carried out for 5 min and the average of 10 such measurements was taken as I_s . These measurements were carried out in the surfactant concentration range $5 < C_s < 70$ mM, in the absence and presence of 0.2% PVPNO, in 0.1 M NaCl. Quasielastic light scattering measurements were carried out at 90° scattering angle on solutions of polymers, surfactant, and mixtures thereof at varying pH, using a Brookhaven system equipped with a 72-channel digital correlator (BI-2030 AT) and using an Omnicrome Ar-ion laser at a wavelength in vacuum $\lambda_0 = 488$ nm. The distribution of diffusivities and hence the size distribution function was obtained by inverse Laplace transformation using the program CONTIN.²⁸ The interpretation of the autocorrelation function in terms of a size distribution involves a number of assumptions, primarily that interparticle interactions do not make a significant contribution to the mutual diffusion coefficient. Ample evidence exists in support of the assumption that the relaxation time of the polymer–micelle complex is related to the translational diffusion coefficient, based on the angular dependence of the

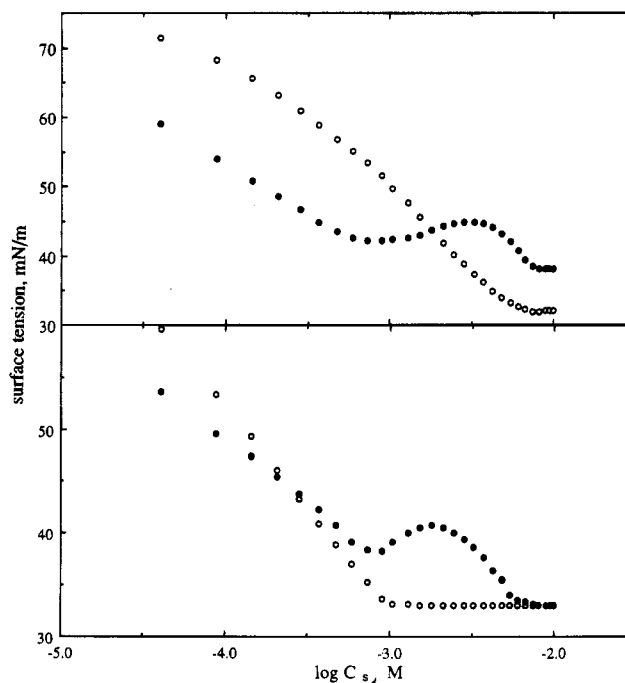


Figure 1. Surface tension vs SDS concentration at 25°C in water (upper) and 0.1 M NaCl (lower). Open circles represent data in absence of PVPNO. Solid circles represent data in the presence of 0.1% PVPNO.

decay constant for the closely related PEO–SDS complex⁸ and on comparison of the QELS-hydrodynamic radius with the viscosity-hydrodynamic radius for polyelectrolyte–micelle complexes.²⁷

Electrophoretic Light Scattering. Measurements were made with a Coulter (Hialeah, FL) DELSA 440 apparatus at four angles ($8.6, 17.1, 25.6, 34.2^\circ$) at 25°C . The electric field was applied at a constant current of 8–14 mA in an electrophoretic cell with a rectangular cross section connecting the hemispherical cavities in each electrode. The measured electrophoretic mobility was the average value at the stationary level and at the four angles. The details of the method are described elsewhere.⁸

Results and Discussion

Figure 1 shows the results of surface tension measurements of aqueous SDS solutions in water and 0.1 M NaCl, respectively, both in the absence and presence of 0.1% PVPNO. The polymer itself has no surface activity, and any difference in surface tension between the polymer-free and polymer-added systems can only be ascribed to polymer–surfactant interactions. In the absence of polymer, the surface tension (γ) behavior of SDS is typical, showing a break-point at the cmc. These cmc values (7–8 mM in water and 1 mM in 0.1 M NaCl) agree well with the literature values.²⁹ In the presence of PVPNO, the surface tension– $\log C_s$ concentration plots show three distinct regions. The first exhibits a linear decrease in γ up to about 0.7 mM SDS and may be considered the region where the surfactant does not bind to the polymer. Above this concentration (often identified as the critical aggregation concentration, or cac), a leveling off and then a decrease in surface activity of SDS (i.e., a maximum in γ) was observed with increasing surfactant concentration. This region extends up to about 10 mM SDS and corresponds to the progressive binding of SDS aggregates onto PVPNO. With further increase in C_s above 10 mM (region 3), the surface tension does not change. This region, where γ attains a constant value, shows the

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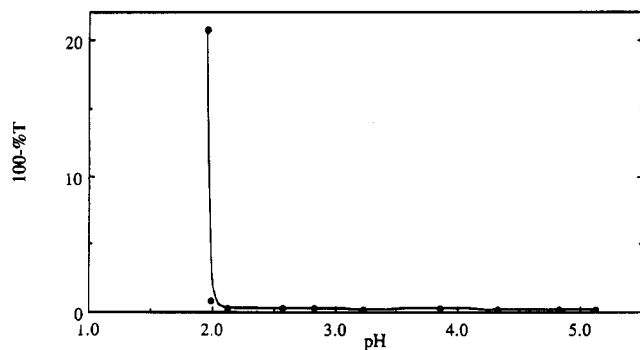


Figure 2. Turbidimetric plot for the solutions of PVPNO (0.4%)–SDS (60 mM) in 0.1 M NaCl as a function of pH.

saturation of PVPNO molecules with bound SDS aggregates; any further increase in C_s leads to the formation of free SDS micelles, with no change in γ .

It is important to point out that PVPNO is completely nonionic under the conditions employed for surface tension measurements (the pK_b is very small). Therefore, we cannot visualize an electrostatic interaction between polymer and surfactant. However, similar behavior in the surface tension of SDS solutions has been observed in the presence of other nonionic interacting polymers like PEO,⁵ PVP,¹⁴ and PVA.¹⁵ The two transition points commonly detected (cac and saturation point) are observed at C_s below and above the cmc, respectively. Their positions depend on the polymer structure, concentration, and molecular weight; the temperature; and the presence of added salt.^{5,14,15} Despite these similarities, it is noteworthy that maxima in γ with C_s have not been previously observed. These correspond to a decrease in surface activity upon addition of SDS and can be explained by highly cooperative binding of SDS by PVPNO. Interestingly, the maximum occurs prior to the cmc in pure water, but after the cmc in 0.1 M NaCl. This is because the effect of ionic strength on the cac and the saturation point is modest compared to the effect on the cmc. Since, as mentioned above, the polymer is uncharged under these conditions, the effect of ionic strength cannot be ascribed to screening of polyion–surfactant interactions. It is certainly conceivable that added salt could stabilize the structure of polymer-bound aggregates to a different degree than it stabilizes free micelles, but such analysis would be rather speculative at the current stage.

The turbidity of solutions containing 0.4% PVPNO and SDS (60 mM) was measured at different pH values. A representative plot at ionic strength 0.1 M is shown as 100 – % T versus pH in Figure 2 which reveals that the solutions remain optically clear down to pH 1.97 (as shown by % $T \approx 100$) but develop a bluish tint thereafter, with a sharp increase in turbidity. These solutions turn to milky opaque on standing, eventually leading to bulk phase separation. Such a phase transition is a typical feature of polyelectrolyte–oppositely charged micellar systems.^{30,31} Though the turbidity data do not provide information on the interaction of SDS with PVPNO at high pH, where the polymer behaves as an uncharged species, they do provide evidence for strong complex formation upon polymer protonation in highly acidic solutions at a well-defined “ pH_c ,” identified as the pH at the onset of turbidity. The low pH_c is evidence for the

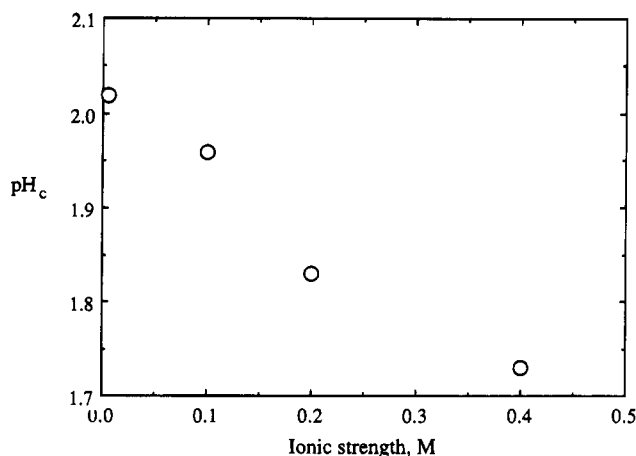


Figure 3. Critical pH versus ionic strength plot for PVPNO (0.4%)–SDS (60 mM).

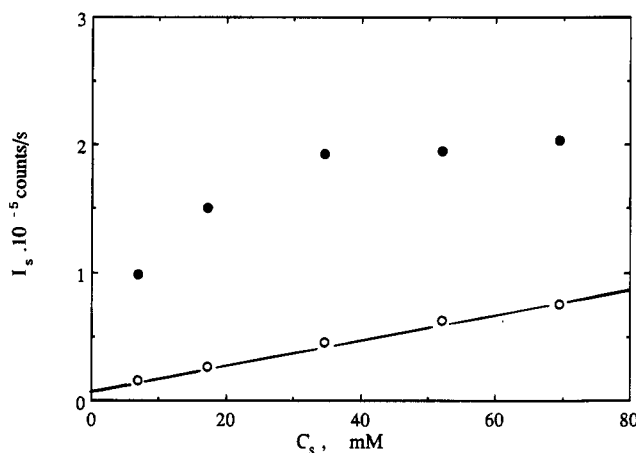


Figure 4. Intensity of scattered light as a function of SDS concentration in 0.1 M NaCl: open circles, in the absence of PVPNO; solid circles, in the presence of 0.2% PVPNO.

absence of vinylpyridine residues in the polymer which, if present, would lead to positive charges at higher pH. Figure 3 shows the decrease in pH_c with increase in ionic strength. This effect corresponds to the attenuation, by the small ions, of Coulombic interactions between the anionic micelles and the cationic form of $PVPNOH^+$, so that a higher polymer charge (lower pH) is needed to compensate for the screening by NaCl. It is thus clear that electrostatic interactions are responsible for phase separation. We may suggest that the complex between neutral PVPNO and SDS micelles retains the Na^+ counterions and corresponding hydration, whereas charge neutralization in the $PVPNOH^+$ –SDS complex leads to the elimination of these counterions and concomitant loss of solubility. An alternative viewpoint is that the longer-range Coulombic forces for the $PVPNOH^+$ –SDS complex facilitate interpolymer aggregation. The abrupt phase separation accompanying the onset of protonation of PVPNO resembles similar behavior for SDS/TX-100 micelles in the presence of linear poly(ethyleneimine) when a critical degree of polymer protonation is reached.³²

The effect of PVPNO on the scattering of SDS solutions at neutral pH and 0.1 M ionic strength as observed from the photon count rate, I_s , provides further evidence for the interaction between PVPNO and SDS. Figure 4 shows an almost linear increase in I_s with C_s for polymer-free solutions, which suggests that the aggregation number of micelles is independent of C_s , in the concentration range

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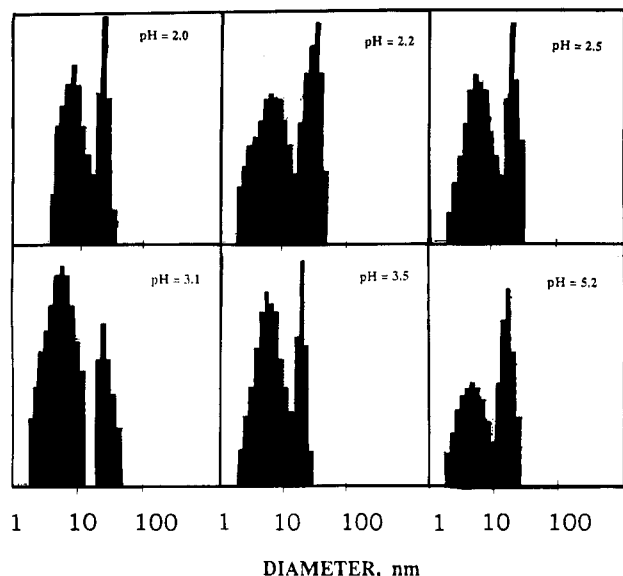


Figure 5. QELS distribution profiles for PVPNO (0.4%)–SDS (60 mM) in 0.1 M NaCl at different pH.

of the present study. However, in the presence of PVPNO, an increase in photon counts, with much higher values than for the corresponding polymer-free solutions, reflects the PVPNO–SDS interaction. I_s is virtually constant above 30 mM SDS concentration, indicating saturation of PVPNO with SDS.

Quasielastic light scattering (QELS) measurements and the corresponding CONTIN analyses were performed on solutions of SDS, polymers, and polymer–SDS mixtures. These provide interesting information on polymer–surfactant interaction. Solutions of SDS (50 mM) in 0.1 M NaCl show a single distribution peak with an apparent Stokes diameter d_s^{app} of 4 nm over the concentration range 10–50 mM. At these concentrations in 0.1 M NaCl micelles retain spherical geometry.⁷ QELS data on solutions of PVPNO in 0.1 M NaCl also reveal only one kind of species centered around $d_s^{app} = 8$ nm over the polymer concentration $C_p = 1$ –4%. This value is quite reasonable for a polymer with $MW \approx 10^4$. The hydrodynamic size of PVPNO molecules in 0.1 M NaCl remains unchanged with pH over the range 6–3, also indicating the absence of vinylpyridine in the polymer. Mixed PVPNO–SDS systems ($C_p = 0.2\%$, $C_s = 50$ mM), examined over a wide pH range, showed two peaks in the distribution profiles; one around 3–5 nm (corresponding to free SDS micelles) and the other around 20–25 nm, corresponding to the PVPNO–SDS complex. No change in peak positions was observed at lower pH, even close to pH_c . These QELS results are shown in Figure 5.

Since uncharged PVPNO forms a complex with SDS, it was of interest to compare the interaction strength with the most intensely studied related system, PEO–SDS. Qualitative comparisons could be accomplished by QELS studies on mixtures of SDS, PVPNO, and PEO. The samples of PEO with MW 900K and 4000K used had sufficiently large molecular dimensions to be clearly resolved from PVPNO or its complexes. The concentrations of SDS and PVPNO were 50 mM and 0.2%, respectively, as used before, but the concentration of PEO was kept low (0.02%) in order to prevent the complex of SDS and high molecular weight PEO from overwhelming the scattering spectra. The CONTIN distribution diagrams for different mixtures are shown in Figure 6 while the mean Stokes diameters obtained from the distribution peaks are recorded in Table 1. A perusal of Figure 6 and Table 1 clearly shows single peaks for solutions of SDS,

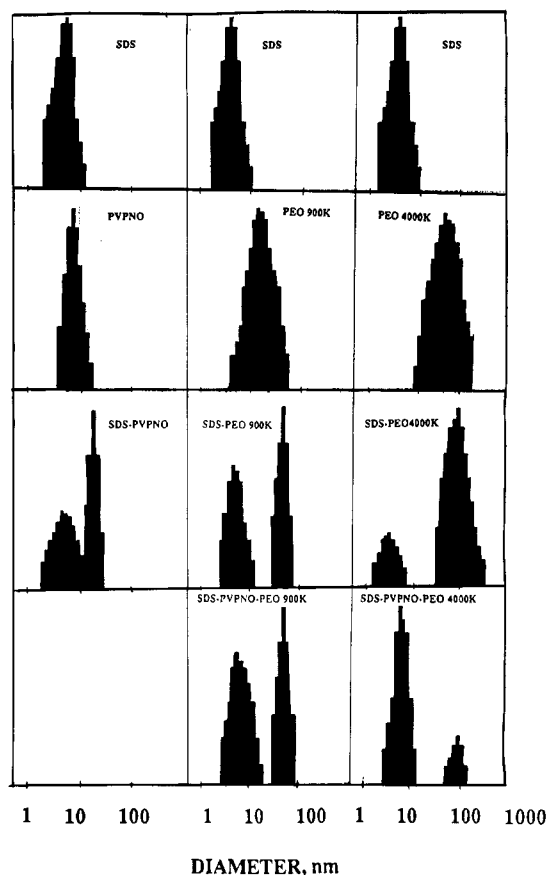


Figure 6. QELS distribution profiles for SDS, PVPNO, PEO900, PEO4000, and their mixtures in 0.1 M NaCl.

Table 1. Apparent Stokes Diameters Observed in Solutions of SDS Micelles, Polymers, and Mixtures Thereof, in 0.10 M NaCl^a

SDS	PVPNO	PEO		d_s^{app} , nm			
		900K	4000K				
X	—	—	—	—	—	—	4
—	X	—	—	—	—	—	8
—	—	X	—	—	—	23	—
—	—	—	X	—	56	—	—
X	X	—	—	—	—	25	5
X	—	X	—	—	45	—	3
X	—	—	X	85	—	—	3
X	X	X	—	—	45	—	8
X	X	—	X	92	—	—	7
—	—	—	—	—	—	—	—

^a "X" indicates component(s) present in sample.

PVPNO, PEO900, and PEO4000 with apparent Stokes diameters of 4, 8, 23, and 56 nm, respectively. All the mixed systems—PVPNO–SDS, PEO900–SDS, and PEO4000–SDS—clearly show two peaks; one around 3–5 nm (corresponding to free SDS micelles) and the other at 23, 45, or 85 nm, respectively. The latter peaks correspond to the complexes and are always greater in size than the corresponding surfactant-free polymers. Similar bimodal distributions for SDS–PEO systems have been observed before from QELS.^{7,8} Most interesting are the two distinct modes seen for solutions of PVPNO–PEO–SDS. In such mixtures of two polymers with SDS, the first peak was observed at 7–8 nm, and the other at almost the same d_s^{app} observed for the corresponding PEO–SDS system. The peak at 7–8 nm may be identified as that of free PVPNO. Evidently, the binding of SDS to PEO depletes the surfactant content to the point where formation of the PVPNO–SDS complex no longer takes place. These

Table 2. Electrophoretic Mobility of Solutions of PVPNO and Polymer-SDS Complexes in 0.1 M NaCl at Neutral pH

system	electrophoretic mobility, $\mu\text{m cm}/(\text{V/s})$
PVPNO	+0.3
PVPNO-SDS	-2.1
PEO-SDS	-2.6
PVPNO-PEO-SDS	-2.6, +0.2

experiments thus provide a clear indication that SDS binds more strongly to PEO than to PVPNO.

Electrophoretic mobilities of these solutions obtained from electrophoretic light scattering, recorded in Table 2, confirm the QELS results. The surfactant-free PEO solutions had zero mobility, whereas the surfactant-free PVPNO solution showed a very slightly positive mobility. SDS micelles in aqueous salt solutions have been reported to have a mobility of about -3 to $4 \mu\text{m cm}/(\text{V/s})$.³³ But no peak of corresponding mobility is observed in the presence of polymer, because complex formation leads to species whose strong scattering and charge dominates the ELS signal. The electrophoretic mobilities of the PVPNO-SDS, PEO900-SDS, and PVPNO-PEO900-SDS systems were -2.1 , -2.6 , and -2.6 , respectively. The identical mobility values for the last two systems reveal that SDS has a preference for binding to PEO. This may also be reflected in the lower mobility for PVPNO-SDS, which could correspond to a lower degree of micelle binding.

While the PEO-SDS complex has been observed by numerous techniques, the nature of the interaction

responsible for its formation has been the subject of conjecture and debate. It has been proposed that some hydrophobic interaction may take place between PEO residues and the hydrocarbon chain of SDS. It is surely easier to recognize hydrophobic character in the backbone of PVPNO than PEO, yet the latter apparently binds SDS more strongly. Dubin et al. suggested that coordination of Na^+ micelle counterions by PEO could promote binding⁸ but such a mechanism seems unlikely for PVPNO. Therefore, the results with PVPNO do not particularly lend support for either a dominant influence of hydrophobic interaction, or for a unique role of cation binding.

Conclusions

PVPNO forms complexes with SDS by two distinctly different mechanisms. At moderate pH, soluble complexes, presumably similar to other SDS-nonionic polymer complexes, are formed with dimensions some $3\times$ larger than for PVPNO itself, reflecting intramolecular repulsion. At very low pH, protonation of PVPNO to PVPNOH^+ leads to phase separation, as a consequence of polyelectrolyte-micelle interactions. The coexistence of these two types of interactions distinguishes the PVPNO-SDS complex from other SDS-nonionic polymer systems.

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