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Surfactant/Polymer Assemblies. 2. Polyelectrolyte Properties

Edson Minatti, David P. Norwood,[†] and Wayne F. Reed*

Department of Physics, Tulane University, New Orleans, Louisiana 70118

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ABSTRACT: The polyelectrolyte nature of the aggregates formed between neutral polymer, poly(vinyl pyrrolidone) (PVP) and anionic surfactant, sodium dodecyl sulfate (SDS) is demonstrated via their light scattering behavior. Adding SDS to neutral PVP is similar to electrostatically charging a neutral polymer, thereby increasing electrostatic excluded volume effects and decreasing osmotic compressibility and light scattering. Similarly, once formed, the behavior of these aggregates with respect to ionic strength resembles that of normal linear polyelectrolytes; namely, increasing ionic strength decreases their interactions, as measured by A_2, and decreases their R_g. Using combined electrostatic persistence length and excluded volume models, the main features of these phenomena are semiquantitatively described. Because SDS exists in multiple equilibria in the PVP/SDS solutions, the system is more complex than normal linear polyelectrolytes, and so the PVP/SDS aggregates also evidence behavior distinct from traditional polyelectrolytes.

Introduction

The companion paper previous to this work focused on the binding properties of the anionic surfactant sodium dodecyl sulfate (SDS) to a neutral polymer poly(vinyl pyrrolidone) (PVP). The main issues were what fraction of SDS binds to PVP, how this could be assessed by static light scattering (SLS), and what deductions about the binding energy and mechanisms could be made. It was shown that, consistent with many other references cited in the foregoing article, a significant fraction of SDS binds to PVP to form aggregates of SDS/PVP. These appear to consist of a single strand of PVP with multiple SDS micelles attached. Curiously, no evidence for anticooperativity of binding was found; i.e., as SDS is added to a PVP solution below the polymer saturation point (PSP), the fraction of added SDS which binds to the PVP remains constant.

This work follows up on the binding issues by investigating what polyelectrolytic properties are conferred on these SDS/PVP aggregates by virtue of the net charge acquired through SDS binding. An attempt is made to highlight the similarities and differences of these polyelectrolytic aggregates with conventional linear polyelectrolytes and to rationalize some of the behavior in the light of existing polyelectrolyte theory.

Although conflicting claims have often been made concerning the equilibrium properties of solutions of linear polyelectrolytes, some properties appear to be now well established. Among these is the fact that the presence of electric charge on a polymer increases its static dimensions with respect to the equivalent neutral polymer or highly screened equivalent polyelectrolyte, and that decreasing solution ionic strength also leads to expansion of the polyelectrolyte coil size. Furthermore, as ionic strength decreases, interparticle repulsions between polyelectrolytes increase, leading to an increasing second virial coefficient, A_2, and a decrease in total light scattered.[1,2]

On the basis of approximations which are often reasonable in the range of moderate ionic strengths (e.g. roughly 0.001−1.0 M), the Electrostatic Persistence Length (EPL) model[3,4] was developed, based on statistical thermodynamic notions summarized by Landau and Lifschitz.[5] This deals with the local stiffening of a flexible or semiflexible chain due to electrostatic repulsions between neighboring charged monomers on the chain. On the basis of work regarding neutral polymers by Yamakawa[6] and others, the idea of interchain excluded volume was developed to include electrostatic effects[7,8] from monomers distant along the chain, under the notion of electrostatic excluded volume (EEV). Taken together, EPL and EEV effects have successfully been used to rationalize experimental results on polyelectrolyte dimensions and interactions.[9−11] Monte Carlo simulations have also been performed to assess these effects,[12−14] and numerical approaches to the Poisson−Boltzmann equation have also been used.[9]

Another theoretical notion which has often been invoked in studying highly charged polymers is that of the condensation of counterions,[10] which for monovalent charges sets a maximum linear charge density for a polyelectrolyte of about one elementary charge every 7.2 Å of polymer length in pure water at 25 °C. In the previous companion work it was shown that the equivalent charge density was fairly close to this value. It is still a matter of conjecture whether this is fortuitous, since the model of charged spheroidal micelles attached at intervals is far from the infinitely thin, charged thread model of Manning.[16]

In this study investigations center on showing that the general polyelectrolyte properties of increasing A_2 and decreasing scattering with increased charge density and/or less screening are observed for the SDS/PVP aggregates but that relatively little intermolecular stiffening takes place. This is consistent with the peculiar lack of anticooperativity seen in the binding properties of the previous work. An attempt is made to apply EPL/EEV model concepts to the polyelectrolytic aggregates of SDS/PVP.

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* Author for correspondence.

[†] Current address: Department of Chemistry and Physics, Southeastern Louisiana University, Hammond, Louisiana 70402.

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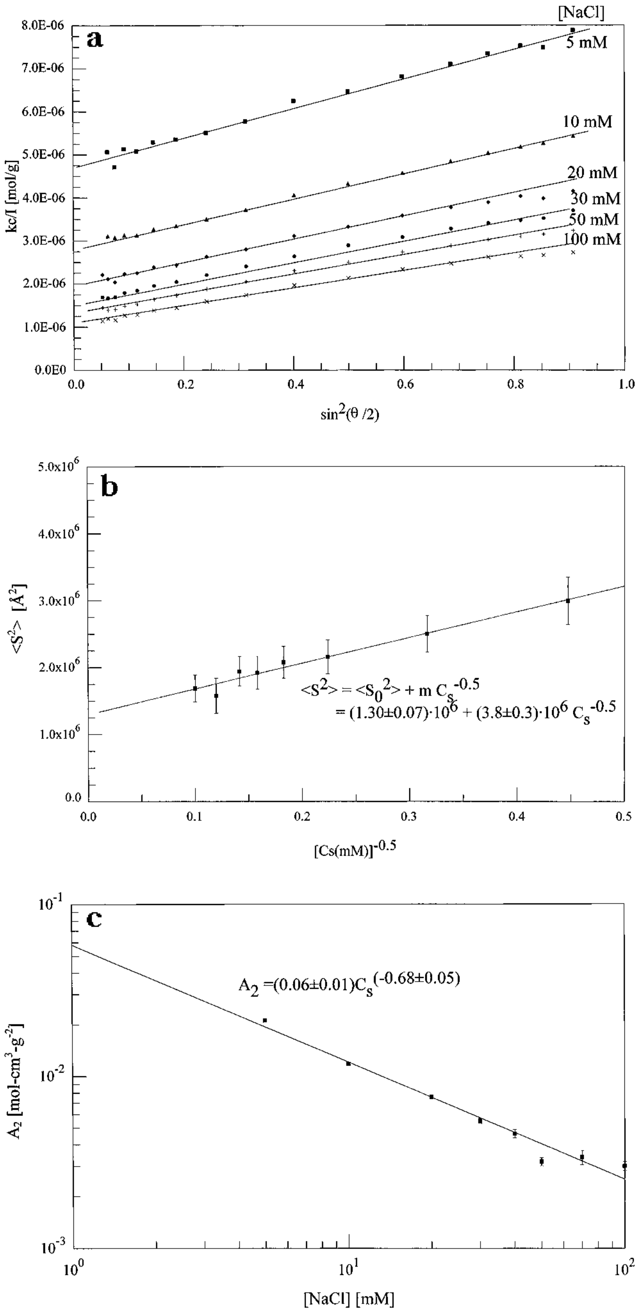

Figure 1. (a) $Kc/I(q)$ vs q^2 for various C_s for a linear polyelectrolyte, hyaluronate (HA). This illustrates "good" polyelectrolyte behavior which can be fairly well described quantitatively with electrostatic persistence length (EPL) and electrostatic excluded volume (EEV) theories. (b) $\langle S^2\rangle$ vs C_s for HA. (c) A_2 vs C_s for HA.

Materials and Methods

The samples used and their preparation, as well as the experimental apparatus and techniques used are identical to those in the accompanying work, and the reader is referred to it for details.

Results

Behavior of a Typical Linear Polyelectrolyte vs Ionic Strength. Figure 1a shows the SLS behavior for a typical linear polyelectrolyte, hyaluronate (HA) of mass $M_w = 1.5$ Mg/mol as a function of added salt. $Kc/I(q)$ is shown for various values of added salt C_s, where [HA] = 0.1 mg/mL. The main features are that (i) the $q = 0$ intercept decreases with increasing C_s, corresponding to the increased scattering intensity as A_2 decreases due to increased intra- and intermolecular shielding, and (ii) the slope, which is proportional to $\langle S^2\rangle$, decreases as the same shielding effect decreases the intramolecular electrostatic repulsion, letting the hyaluronate coil relax to smaller dimensions. Parts b and c of Figure 1 show, respectively, $\langle S^2\rangle$ and A_2 vs C_s for the data from Figure 1a. Analyses of R_g and A_2 for HA have been previously carried out.[11] Similar behavior is found if C_s is held constant and ξ is varied, as found by Reed et al.[10,12]

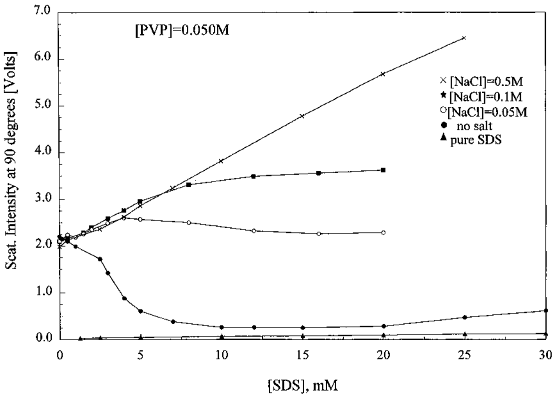

Figure 2. V_{11} vs [SDS] for [PVP] = 50 mM and C_s = 0, 0.05, 0.1, and 0.5 M (using NaCl). This shows the sharp reduction in scattering with added SDS at low added salt C_s, which shows that the PVP is becoming electrically charged, and hence polyelectrolytic, so that the EPL and EEV effects are becoming important.

Scattering from PVP/SDS Aggregates vs Ionic Strength and Charge Density Resembles That of Typical Linear Polyelectrolytes. In several of the following curves we have chosen to represent raw scattering voltage at $\theta = 90°$ on the ordinate, usually referred to as V_{11}, rather than Kc/I or other quantity requiring data reduction, so that the immediately observable, empirical effects being introduced are highlighted. Unless stated otherwise the [PVP] concentrations were kept constant in the following experiments where [SDS] was varied, by maintaining the fixed [PVP] in the [SDS] or salt stock solution which was used to titrate the solutions.

The first demonstration of the polyelectrolyte behavior of the aggregates formed by SDS and PVP is given in Figure 2. This shows raw scattering voltage at $\theta = 90°$ vs [SDS] for [PVP] = 0.05 M and C_s = 0, 0.05, 0.1, and 0.5 M. For $C_s = 0$ the striking trend is that as SDS is added the scattering, after first increasing slightly, *decreases* with increasing [SDS]. This is clear evidence that the PVP is becoming increasingly charged by the presence of the SDS, which strongly increases A_2 leading to decreased scattered intensity, *even though both the molecular weight of the PVP/SDS aggregate and the total solute concentration of the sample are increasing.* If SDS were merely forming micelles not interacting with PVP, highly charged and scattering little light of their own, the scattered intensity would have to increase or at least stay the same. In fact, it was recently shown[13] that the main effect of mixing nonassociating neutral polymer and polyelectrolyte (dextran and xanthan in the case of Norwood et al.), was to increase the overall scattering level.

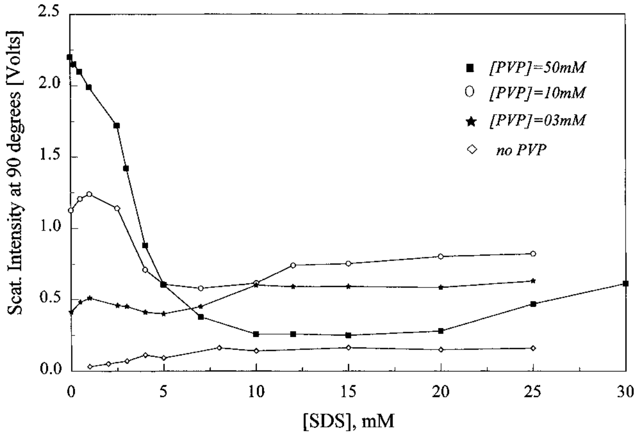

Figure 3. V_{11} vs [SDS] for $C_s = 0$ and [PVP] = 0, 3, 10, and 50 mM. This shows the suppression of scattering due to the electrostatically enhanced A_2 as [PVP] increases.

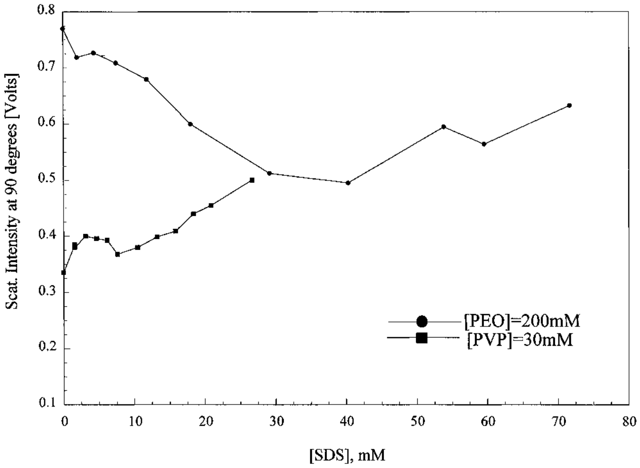

Figure 4. Same as Figure 2 but for low molecular weight PVP and/or POE, to show the expected dependence of the $2A_2c$ effect on M and the independence of the effect from the chemical identity of the neutral polymer.

In Figure 2 it is seen that as C_s is increased, the electrostatic charging of the PVP by the SDS becomes increasingly shielded, until at $C_s = 0.5$ M the intensity increases monotonically with [SDS]. It is clear that the electrostatic shielding at this high ionic strength reduces A_2 sufficiently that the increasing scattering with [SDS] reflects the increase of the mass of the PVP/SDS aggregate.

Figure 3 shows curves similar to Figure 2, but for a variety of [PVP] at $C_s = 0$. As expected, the higher values of [PVP] lead to more pronounced decreases in scattering as [SDS] increases and increases A_2. The eventual upturn in the curves in Figure 3 after a certain [SDS], which increases with increasing [PVP] shows the “self-salt” effect of the SDS and its counterions and presumably the effect of saturating the PVP with SDS (related to the so-called polymer saturation point, PSP). That is, free counterions and monomeric surfactant add to the ionic strength of the solution. As [SDS] increases, the ionic strength increases, which shields the increasingly charged PVP/SDS aggregates, which counteracts increases in R_g and A_2, and after saturation of the PVP, adding more SDS charges the PVP no further but does continue to increase ionic strength and shielding.

Figure 4 shows V_{11} vs [SDS] for low molecular mass PVP and poly(ethylene oxide) (PEO) in the absence of salt. The PEO is at 200 mM (8.8 mg/mL) and shows the same decrease in scattering as [SDS] increases as high molecular mass PVP. Thus, the effect is specific neither to PVP nor to high molecular weights. Rather it is a general effect that should be expected whenever a charged surfactant associates with any neutral polymer. The 10K PVP, at a relatively low concentration of 30 mM (3.4 mg/mL), shows scattering increasing with [SDS]. This illustrates the effect of M_w on the scattering, as seen in eq 4 of the companion paper, which is that the scattering will decrease as [SDS] increases only if the $2A_2c$ term grows more quickly than the $1/M_w$ term decreases.

Figure 5a shows V_{11} vs C_s for [PVP] = 30 mM and [SDS] = 7 mM. This is above the critical aggregation concentration (CAC). First of all, it is seen that, to within experimental error, pure PVP with no SDS is not appreciably affected by C_s, as is expected for a neutral polymer. For the case where the 30 mM PVP is charged (at [SDS] well above the CAC) a very strong dependence of scattering on C_s is seen, exactly as expected for a polyelectrolyte. In Figure 5a one clearly sees the suppression of light scattering at low ionic strength, due to the electrostatically enhanced A_2. The scattering up to about $C_s = 25$ mM is below the scattering of the pure PVP, even though the mass of the aggregate is greater. Using the results of the accompanying paper, the mass of the PVP/SDS aggregate at a salt concentration of 10 mM is at least 7% greater than the mass of a bare polymer molecule and would scatter more light, rather than less. As ionic strength increases beyond this, the scattering gradually levels off to a level well above that of pure PVP, reflecting the greater mass of the PVP/SDS aggregate.

Figure 5b shows $Kc/I(q)$ derived from the raw scattering voltages from the full angular range of detection. Figure 5b is to be compared directly with Figure 1a for HA, a linear polyelectrolyte. Again, the striking drop in $Kc/I(q)$ with increasing C_s shows A_2 diminishing with increasing salt. A significant difference is that the slope of $Kc/I(q)$, which is proportional to $\langle S^2 \rangle = R_g^2$, is not very sensitive to ionic strength for the PVP/SDS aggregates, whereas it is for the HA. We take this as evidence that (i) there are not strong interactions between micelles in a given PVP/SDS aggregate, which was also reflected in a lack of anti-cooperativity of binding, and (ii) even at $C_s = 0$ there is considerable ionic strength due to the SDS. This latter conclusion is reinforced by the following analysis of the electrostatically enhanced A_2 of the aggregates, which suggests that only a small fraction of added SDS is both bound and ionized.

Figure 5c shows the second virial coefficient, A_2, obtained from the data of Figure 5b, plotted (on a log–log plot) as a function of the concentration of added salt. Also shown are two calculations using a combined electrostatic persistence length (EPL) and electrostatic excluded volume (EEV) model which has had some success in describing polyelectrolyte conformations and interactions at moderate to high ionic strengths. The model is based on the EPL and EEV theories of Odijk[7] and Fixman and Skolnick,[8] combined with theories of general excluded volume of Yamakawa[6] and Gupta and Forsman.[14] The ad hoc combination of these theories has been previously presented in detail and is not presented here.[10,11,18] This combined model gave a good quantitative description of polyelectrolyte interactions and conformations for HA,[17] proteoglycans, and copolymers of polyacrylate and poly(acrylic acid). Here we use

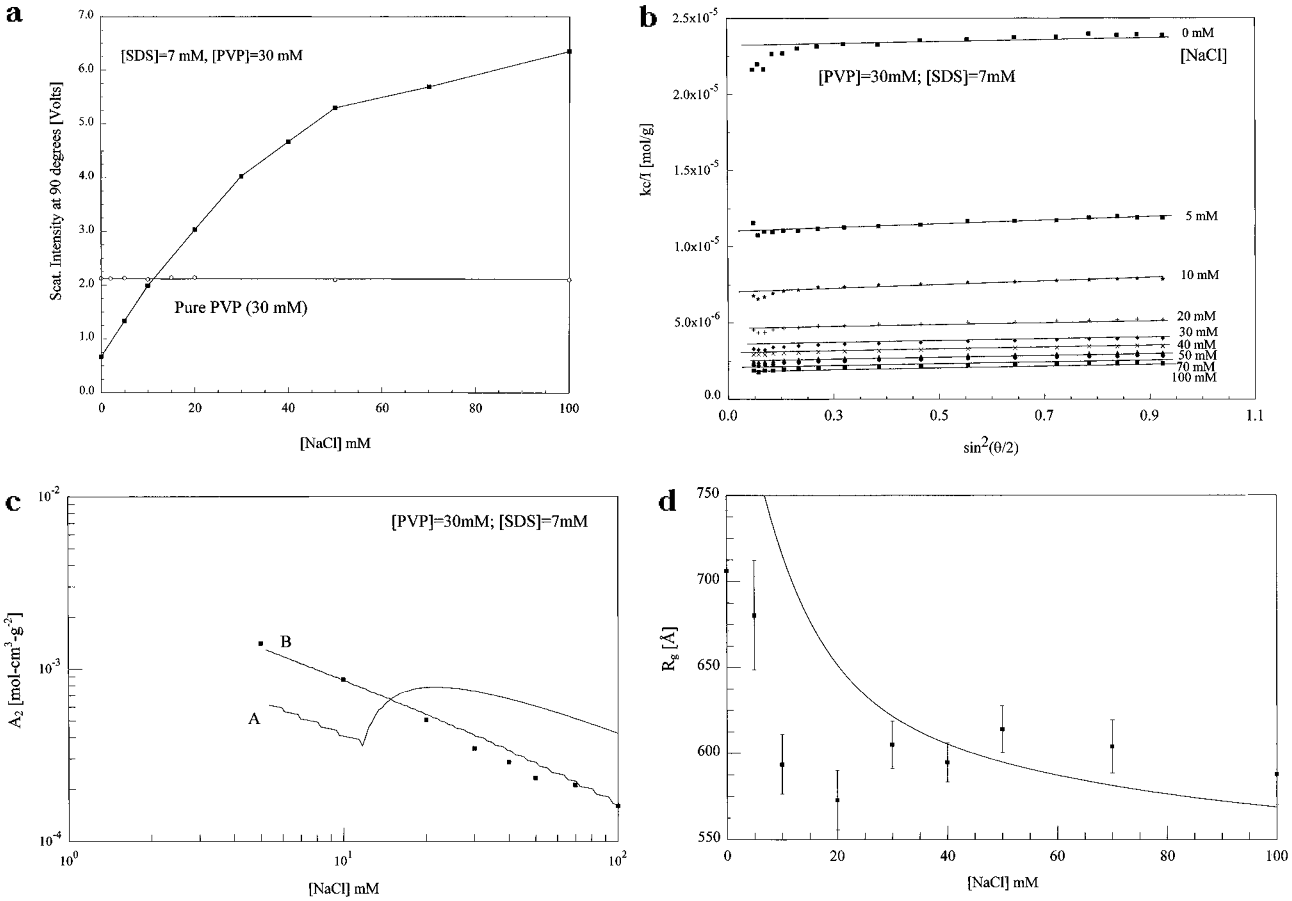

Figure 5. (a) V_{11} vs C_s for [SDS] = 7 mM and [PVP] = 30 mM. The increase in V_{11} vs C_s shows how A_2 decreases due to increased shielding. Pure [PVP] = 30 mM scattering data, not appreciably affected by C_s, are also shown for comparison. (b) $Kc/I(q)$ derived from the raw scattering voltages for [SDS] = 7 mM and [PVP] = 30 mM. The behavior resembles that of a simple linear polyelectrolyte (compare Figure 1a). (c) A_2 from the data of part b as a function of added salt for [SDS] = 7 mM and [PVP] = 30 mM. Also shown are two computations using a combined electrostatic persistence length (EPL) and electrostatic excluded volume (EEV) model (see text). (d) R_g from the data in Figure 5b, plotted in a log–log plot as a function of added salt. A computed curve is shown which used the fixed value of αf obtained from part c in the EEV/EPL computation.

it to interpret the electrostatic interactions in PVP/SDS aggregates. The difference between the two consists of assumptions made concerning the behavior of the bound fraction, f, and the fraction of SDS molecules ionized, α, as a function of added salt.

In the case of curve A, which provides a result that is both quantitatively and qualitatively poor, it was assumed that α remained fixed and f varied as determined from the Zimm plot data, presented in the accompanying paper. Curve B provides a much better fit. In this case, the product of α and f was held fixed and αf adjusted to produce a best fit. (This is in contrast to previous EEV/EPL calculations, where all the polyelectrolyte parameters were well-known, so there were *no* adjusted parameters[9–11,13,18]). Since f is known from the Zimm plot results to increase with added salt, this implies that α must decrease with added salt. This behavior is consistent with a mass-action type of behavior, which would predict that as the ambient concentration of sodium ions increases (due to added salt), the tendency of SDS molecules to ionize would decrease. Note that this assumption of fixed αf means that the net bound charge remains fixed, as does the average linear charge density. This can be calculated from known parameters; the total charge bound (in elementary charges) is αf[SDS], and the average charge bound per monomer of [PVP] is αf[SDS]/[PVP]. For the conditions of Figure 5c, [SDS] = 7 mM and [PVP] = 30 mM, and the fitted parameter, $\alpha f = 0.06$, the average bound elementary charge per monomer is 0.014. Using a monomer–monomer length of 2.52 Å, we obtain a linear charge density of 0.0056 charges/Å, which corresponds to 0.04 charges /Bjerrum length, well below the Manning condensation limit. This value is significantly smaller than the value quoted in the accompanying paper because (a) the concentration of SDS is smaller relative to that of PVP and (b) the product of αf is smaller than that used previously. The former condition is trivial and simply reflects that we are well below the saturation of PVP by SDS. The latter is of more significance, since it implies that were we to go to saturation in SDS, the linear charge density would be 0.22 elementary charges per Bjerrum length. This is smaller than the estimate in the accompanying paper, but still suggests the saturation may be analogous to Manning condensation.

Figure 5d shows the radius of gyration, R_g, obtained from the data in Figure 5b, again plotted in a log–log plot as a function of added salt. Again we show a computed curve using the same EEV/EPL theories discussed above. The product αf is again held fixed, at the value 0.06 found from the A_2 fit. In addition, the high salt persistence length is set at 46 Å, considerably higher than the apparent persistence length value of about 25 Å determined from the GPC data. This higher persistence length is an artifact of using batch light scattering results to obtain R_g. Since light scattering from a polydisperse system returns the Z-average of R_g and the weight-average of the molecular weight, the corresponding apparent persistence length is artificially high. While the fit follows the data qualitatively, it is hardly quantitative. The deviation could also be due to other effects of polydispersity, but the current circumstances are sufficiently different from the assumptions of the EEV/EPL models being used that such a supposition is hard to defend. Further data using a monodisperse system would more cleanly resolve this issue.

Scattering of PVP/SDS Aggregates at No Added Salt Is *Unlike* Most Polyelectrolytes. In contrast to the resemblance of the behavior of linear polyelectrolytes and SDS/PVP aggregate interactions vs ionic strength and charge density, it is nonetheless remarkable that none of the scattering experiments with no added salt showed the typical hallmarks of salt-free polyelectrolyte behavior. Often, in the no added salt regime (or at very little added salt), the interparticle correlations are strong enough to produce a high contrast peak in the angular distribution of scattered intensity $I(q)$. Such a peak has been observed, for example, for such polyelectrolytes as poly(styrenesulfonate),[15] xanthan,[19] succinoglycan,[16] proteoglycan,[17] and DNA.[18] This peak, occurring in the dilute regime, has been interpreted in terms of average interparticle distances corresponding to energy minima in a damped, quasi-periodic interparticle potential energy function.[19] When such polyelectrolytes are measured in more concentrated solution, the peak usually shifts to higher values of q, inaccessible with visible light, in which case $Kc/I(q)$ becomes a monotonically *decreasing* function of q, rather than the normal increasing type seen here or for neutral polymers, or polyelectrolytes at moderate to high ionic strengths. Another type of scattering behavior observed at no added salt is that of hyaluronate, for which there is no peak in $I(q)$, but instead the scattering signal is so suppressed by a large, electrostatically enhanced A_2 that the signal is virtually the same as that of pure water. The fact that the SDS/PVP aggregates never manifest these types of behavior is because there is always appreciable ionic strength in the solutions, even with no added salt. This is a direct consequence of the aggregate multiple equilibria of the SDS; i.e., there are always some free SDS monomers in solution, and these contribute appreciable ionic strength, in addition to osmotically free counterions from PVP-bound and micelle-bound SDS.

Evidence for Association of SDS and PVP below the CAC. Figure 6a shows representative V_{11} vs C_s (using NaCl) for [SDS] = 2 mM and [PVP] = 0.01, 0.03, 0.05, and 0.10 M. Also shown is the same control as in Figure 5a, namely 0.03 M PVP with no SDS. In this latter case, again, it is seen that pure PVP is not appreciably affected by C_s, as is expected for a neutral polymer. [SDS] = 2 mM is below the critical aggregation concentration (CAC), but it is clear that the SDS associates with the PVP, causing it to become electrically charged and hence increasing A_2 and decreasing light scattering. This can be seen by considering [PVP] = 0.03 M in Figure 6a. With [SDS] = 2 mM, the scattering is appreciably less than the pure PVP scattering at $C_s = 0$, attesting to the effect of charging the PVP by the SDS. As C_s ([NaCl]) increases, the pure PVP scattering stays the same, whereas that for the PVP with [SDS] = 2 mM monotonically increases, as the SDS-charged PVP is progressively screened and A_2 decreases.

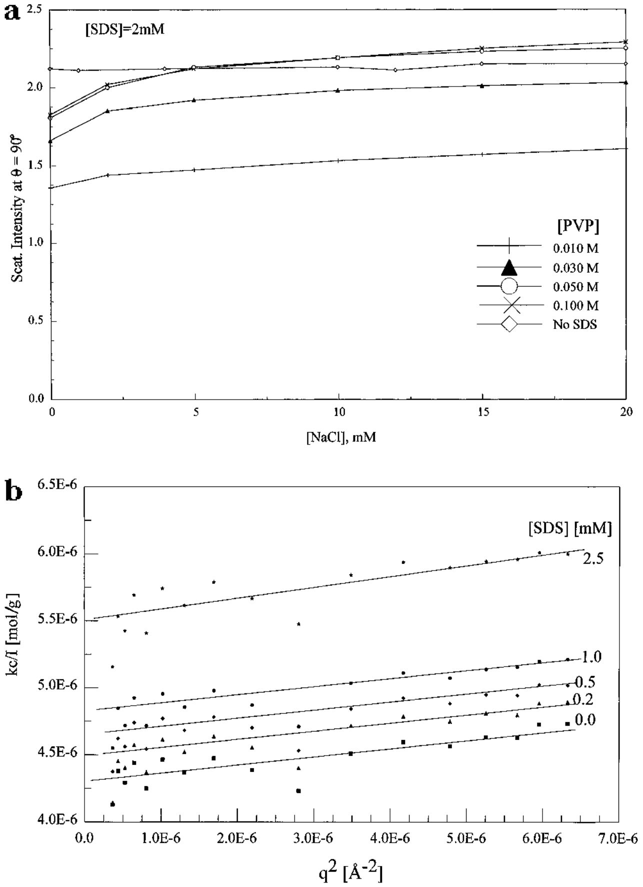

Figure 6. (a) Evidence of SDS/PVP association below the CAC. V_{11} vs C_s for [PVP] = 10, 30, 50, and 100 mM and [SDS] = 2 mM. Data for [PVP] = 30 mM and [SDS] = 0 are also shown, as an important control that there is no appreciable effect on scattering of PVP in absence of SDS. (b) Further evidence of electrostatic charging of PVP by SDS below the CAC. Kc/I vs q^2.

Figure 6b shows $Kc/I(q)$ for [PVP] = 50 mM and [SDS] in the range 0−2.5 mM, at no added salt. In this range of parameters, the concentration of SDS is again below the CAC. The increase in A_2 and R_g both constitute evidence that, even below the CAC, association of PVP and SDS occurs. The increase in A_2 is again due to charging of the PVP molecules and hence electrostatic enhancement of the virial coefficient. The increase in R_g, while again small, reflects some small degree of electrostatic stiffening of the PVP molecule.

Specificity and Sign of Charge in Polymer/Surfactant Aggregates. Consistent with many other reports, it was found that there is a large degree of chemical specificity in surfactant/polymer aggregate formation. Whereas PVP and SDS form aggregates, cationic cetyl trimethylammonium bromide (CTABr) surfactant does not aggregate with PVP. This lends strength to the argument that Na^+ or other positive ion is attracted to the partially negative ether oxygen on PVP, allowing the DS surfactant to attach. Br^- in this interpretation cannot form a "receptor site" for DS with the PVP ether oxygen. Further evidence of specificity is seen in the fact that, in this work, it was found that neutral dextran and SDS did not form aggregates. Specificity seems to extend beyond chemical identity of the neutral polymer (e.g., PVP and PEO vs dextran) and surfactant charge sign, to include surfactant chain length and even counterion.

The evidence in this work is that the PVP/SDS aggregate is a polyanion. This was deduced from the fact that mixing HA with PVP/SDS aggregates did not lead to any precipitation or even any especially strong interaction as measured by SLS. When a large polyanion is mixed with a large polycation, the result is inevitably the immediate formation of large microgels or outright, rapid precipitation.

The model we deduce from this builds off of the Dubin[19] model: The Na^+ may form the "receptor site" for DS, perhaps by interacting with a partially negative portion of PVP, such as the ether oxygen proposed by Dubin. Probably several of these Na^+ receptors then allow a micelle-like aggregate of SDS to become associated with the PVP. Since the PVP/SDS aggregate is a fairly highly charged polyanion, it seems that there are significantly more DS monomers in a bound micelle than Na^+ groups acting as "receptor sites". The rest of the Na^+ ions presumably are either condensed onto the micelle surface or are free and involved in the electrostatic double layer. Hence, in this picture the PVP/SDS aggregate is a *net polyanion*, whereas the counterions associated with neutral PVP in the Dubin model were said to comprise a *"pseudo-polycation"*.

Conclusions

PVP and SDS form negatively charged aggregates. Below the CAC these consist of SDS monomers associated with individual PVP chains, whereas above the CAC the aggregate is a single PVP chain with multiple SDS micelles attached. These aggregates exhibit properties similar to linear polyelectrolytes. Notably, A_2 is a sensitive function of the aggregate's charge density and solution ionic strength. When SDS is added to a PVP solution two effects occur; the PVP becomes electrically charged as SDS associates with it, and solution ionic strength increases as the population of both dissociated SDS counterions and unassociated SDS/counterion buildup. As a salt-free solution of fixed [PVP] is titrated up to a certain [SDS], the PVP becomes electrically charged, as manifested by a continuous decrease in scattering intensity. In this regime the charging effect is greater than the screening effect from increasing ionic strength due to increasing [SDS], and A_2 increases. After a certain [SDS], however, the scattering intensity increases. Here the shielding due to the increase in ionic strength is sufficient to lower A_2, whether the PVP may already be saturated by SDS or not.

Characteristic "very low salt" polyelectrolyte behavior (i.e. peak of $I(q)$, or a monotonically increasing $I(q)$, or just weak, noisy scattering) of the PVP/SDS is never observed. This is presumably due to the fact that charging PVP with SDS is always accompanied by a significant increase of ionic strength, and such "very low salt" effects for polyelectrolytes are usually destroyed by even submillimolar increases in ionic strength.

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