Structure of Polymer−Surfactant Complexes by Static Light Scattering

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ABSTRACT: Light-scattering studies of the structure of macromolecular complexes formed between poly(ethylene oxide) [PEO] and a cationic surfactant, hexadecyltrimethylammonium chloride [HTAC], in aqueous solution, are reported. Analysis of the angle dependence of the scattered intensity indicates that binding of HTAC micelles is accompanied by an increase in radius of gyration (R_g), up to the maximum binding point. From measurements of the molecular weight of the PEO−HTAC complex, accounting for preferential binding of surfactant, we deduce that, at the maximum binding condition, 0.12 mol of HTAC is bound per mol of EO. In addition, evaluation of the PEO molecular weight, using equilibrium dialysis, indicates approximately 2.0 ± 0.3 PEO chains are incorporated in the complex. Beyond maximum binding, electrostatic screening induces the PEO chain to contract, evidenced by a reduction in R_g. Measurements of R_g at the maximum binding point for three different PEO molecular weights indicate that the relative chain expansion is comparable, $R_{g,\text{complex}}/R_{g,\text{PEO}} \sim 1.9$. The results provide insight into earlier observations of a viscosity maximum, when titrating dilute solutions of PEO with HTAC.

Introduction

The formation of complexes between water-soluble polymers and surfactants is of considerable technological importance, and has been the subject of intense study in recent years.[1] Abundant evidence[1−4] indicates that complex formation involves association of the polymer with surfactant micelles above the critical aggregation concentration (cac). The binding of ionic surfactants to nonionic polymers has been demonstrated to cause a characteristic change in the hydrodynamic properties of the solution. Specifically, on addition of anionic surfactant, sodium dodecyl sulfate (SDS), to poly(ethylene oxide) (PEO), the specific viscosity increases to a maximum value and then decreases slightly.[1,5−7] Measurements of the radius of gyration and hydrodynamic radius, by static and dynamic light scattering, indicate this phenomenon occurs because of expansion of the polymer coil due to electrostatic repulsions between bound micelles.[6,7] The maximum corresponds to the point of saturation of bound micelles, and the subsequent decrease in viscosity on further addition of surfactant is interpreted as due to screening of the charge interactions by excess counterions.[6,7] Recently, we observed a similar viscometric effect on mixing cationic surfactants, hexadecyltrimethylammonium chloride (HTAC) with PEO,[8] and hexadecyltrimethylammonium bromide (HTAB) with hydroxypropylcellulose (HPC),[9] and further showed that a maximum in hydrodynamic radius, R_h, measured by dynamic light scattering, correlates with the viscosity maximum. The existence of a maximum in viscosity has also been linked[10] to surfactant-induced interchain interactions, i.e., the formation of multichain complexes. However, no quantitative evidence for the existence of such species in solutions, which exhibit a viscosity maximum, has been reported. It is of interest, therefore, to obtain further insight into the structure of the complex formed between PEO and HTAC and surfactant through direct measurements of molecular weight.

Static light scattering is a well-established method to determine the molecular weight, radius of gyration, and state of aggregation of macromolecules in solution. The thermodynamic basis has been extended to incorporate the preferential binding interactions in solutions of macromolecules dissolved in mixed solvents.[11,12] Application of light-scattering methodology to characterize binding of surfactant to water-soluble synthetic polymers[7,13−19] and proteins[20,21] has been described. Boscher et al.[13] obtained evidence for preferential adsorption of surfactant to hydroxyethylcellulose (HEC) in water, determining the molecular weight of the complex, by an approximate method, treating the solution as a pseudo-two-component system. A similar approach was taken by Fundin et al.[14] to evaluate the molecular weight of complexes formed between poly(styrenesulfonate) (PSS) and cetyltrimethylammonium bromide (CTAB), and by Norwood et al.[18] to demonstrate binding of SDS to poly(vinylpyrrolidone) (PVP). Light-scattering measurements, using refractive index increments at constant chemical potential, were combined with evaluation of the amount of bound surfactant by dialysis equilibrium, to determine the molecular weight of complexes formed between poly(vinylpyrrolidone) and SDS.[19] Light-scattering analysis using refractive index increments measured at dialysis equilibrium has been applied to determine the number of protein chains in protein−SDS complexes.[20,21] Various studies[7,17−19] have reported changes in apparent radius of gyration on formation of polymer−surfactant complexes from analysis of the angle dependence of scattered light.

This paper reports a static light-scattering study of the interaction between PEO and HTAC in aqueous solution at 30 °C. First, we combine light-scattering measurements on ternary PEO−HTAC solutions with differential refractometry at dialysis equilibrium to determine the number of PEO chains involved in complex formation between PEO and HTAC. These light-scattering measurements are then combined with

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differential refractometric evaluation of the preferential binding of surfactant to obtain the molecular weight of the PEO−HTAC complex. Finally, we investigate the dependence of R_g on HTAC/PEO ratio and on PEO molecular weight. These results provide insight into the origin of the previously published viscometric data.[8]

Theoretical Background

The light intensity scattered by a binary polymer solution may be interpreted by the Zimm-Debye equation

$$\frac{Kc_2}{\Delta R_\theta} = [1 + q^2\langle R_g{}^2\rangle_z/3]\left[\frac{1}{M_w} + 2A_2c_2\right] \tag{1}$$

where K is the optical constant ($K = 4\pi^2n^2(\mathrm{d}n/\mathrm{d}c_2)^2/N_A\lambda^4$ for vertically polarized light), n is the refractive index of the solvent, c_2 is the polymer concentration (g/mL), λ is the wavelength of incident light, and $\mathrm{d}n/\mathrm{d}c_2$ is the refractive index increment (mL/g). $q = (4\pi n/\lambda)\sin(\theta/2)$ is the scattering vector with θ the scattering angle. ΔR_θ is the excess Rayleigh ratio: $\Delta R_\theta = \Delta i_\theta r^2/I_o$, where Δi_θ is the excess scattered light intensity per unit volume of the scattering solution, I_o is the incident light intensity, and r is the distance from the sample to the detector. M_w is the weight-average molecular weight, A_2 is the second osmotic virial coefficient, and $\langle R_g{}^2\rangle_z$ indicates the z-average mean-square radius of gyration, whose square root we designate hereafter as R_g.

The theory of light scattering from a polymer in a mixed solvent system was first developed by Kirkwood and Goldberg[11] and Stockmayer[12] to account for preferential binding of one solvent species to the polymer. In the system of interest in the present study, viz. a polymer dissolved in water containing a nonaqueous solvent, designating water as component 1, polymer as component 2, and nonaqueous solvent as component 3, the theory leads to the following equation

$$\left[\frac{K'c_2}{\Delta R_\theta}(\partial n/\partial c_2)_{T,P,c_3}{}^2\right] = [1 + q^2R_g{}^2/3]\left[\frac{1}{(1+D)^2}\right]\left[\frac{1}{M_w} + 2B^o c_2\right] \tag{2}$$

with

$$D = \left[\frac{(\partial n/\partial c_3)_{T,P,c_2}}{(\partial n/\partial c_2)_{T,P,c_3}}\right]\left(\frac{\partial c_3}{\partial c_2}\right)_{T,P,\mu_1,\mu_3} \tag{3}$$

and

$$K' = \frac{4\pi^2n^2}{N_A\lambda^4} \tag{4}$$

Here c_i is the mass concentration of component i (g/mL of water), T is the thermodynamic temperature, P is the pressure, and μ_i is the chemical potential of component i, M_w is the molecular weight of component 2, and B^o is an apparent second virial coefficient involving the interactions between the component 1 and the component 2. Now defining D' as the preferential interaction of nonaqueous component (surfactant) with polymer, in grams of surfactant per gram of polymer:

$$D' = \left(\frac{\partial c_3}{\partial c_2}\right)_{T,P,\mu_1,\mu_3} \tag{5}$$

In such systems, a plot of $Kc/\Delta R_\theta$ as a function of concentration extrapolates not to the true molecular weight of the macromolecules, but to an apparent molecular weight, $M_{w,app}$ which is a function of the interaction with the solvent components, and can be expressed as

$$M_{w,app} = M_w\,(1 + D)^2 \tag{6}$$

where M_w is the true molecular weight of the macromolecular solute. The deviation of the apparent molecular weight ($M_{w,app}$) from M_w is a measure of the extent of the preferential interaction.

As shown by Casassa and Eisenberg[22] and Overbeek and Vrij,[23] measurement of the true M_w in the binary solvent (water + nonaqueous solvent) requires determination of $(\mathrm{d}n/\mathrm{d}c_2)_{T,P,\mu_1,\mu_3}$, the refractive index increment of the solution at constant chemical potential of the solvent, i.e., the differential refractometry experiments must be performed under conditions where the chemical potential of the solvent components is identical in the solution and in the reference solvent. This is accomplished by performing equilibrium dialysis, and measuring the refractive index increment between the dialyzed solution and the dialyzate. Under such conditions the system can be treated as a pseudo-two component system, and eq 2 becomes, in the small-angle limit $q = 0$

$$\left[\frac{K'c_2}{\Delta R_\theta}(\partial n/\partial c_2)_{T,P,\mu_1,\mu_3}{}^2\right] = \frac{1}{M_w}(1 + 2B'c_2) \tag{7}$$

where B' is the corresponding second virial coefficient, and the intercept of the light-scattering plot gives directly M_w. Using eqs 3 and 5, eq 2 can be written in the limit of $q = 0$ and $c_2 = 0$ as

$$\lim_{c_2\to 0}\left[\frac{K'c_2}{\Delta R_\theta}\left\{\left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_3} + D'\left(\frac{\partial n}{\partial c_3}\right)_{T,P,c_2}\right\}^2\right] = \frac{1}{M_w} \tag{8}$$

From eq 7, we may write in the limit of $q = 0$ and $c_2 = 0$

$$\lim_{c_2\to 0}\left[\frac{K'c_2}{\Delta R_\theta}\left(\frac{\partial n}{\partial c_2}\right)_{T,P,\mu_1,\mu_3}^{2}\right] = \frac{1}{M_w} \tag{9}$$

Comparing eqs 8 and 9, we find that the amount of preferential binding of surfactant to polymer can be calculated from the following equation:

$$D' = \left[\left(\frac{\partial n}{\partial c_2}\right)_{T,P,\mu_1,\mu_3} - \left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_3}\right]\Big/\left(\frac{\partial n}{\partial c_3}\right)_{T,P,c_2} \tag{10}$$

It follows then that the molecular weight of the polymer−surfactant complex, $M_{w,com}$ can be obtained as

$$M_{w,com} = M_w\,(1 + D') \tag{11}$$

Here, M_w is the molecular weight of polymer in the complex, obtained via eq 9.

Experimental Section

Materials and Sample Preparation. Three poly(ethylene oxide) (PEO) specimens with different molecular weights were utilized: ($M_w = 1 \times 10^5$, 6×10^5, 9×10^5), designated PEO(1), PEO(2), and PEO(3), respectively. The PEO samples were polydisperse, having normalized second cumulants, $\mu_2/\Gamma^2 \sim 0.5$, estimated by dynamic light scattering.[8] All PEO samples were dried in a vacuum oven for 1 day at room temperature before preparing solutions for light-scattering analyses. Sterile, deionized water, purchased from the Thai Pharmaceutical Organization, was used as a solvent, after filtration through a 0.2 μm Millipore membrane. The aqueous polymer solutions were gently stirred for several hours until homogeneous. The polymer stock solutions were placed in an oven for about 1 h at 50 °C to ensure complete dissolution. Hexadecyltrimethylammonium chloride (HTAC) was provided by Unilever Holding Inc. and used as received. Polymer and surfactant solutions were mixed at the appropriate ratio and diluted with filtered sterile water. The polymer–surfactant solutions were gently stirred before light-scattering measurements were performed. All solutions were centrifuged at 8000 rpm for 1 h, and then filtered directly into the light-scattering cell through 0.22 or 0.45 μm Millipore membranes, depending on the molecular weight of polymer. All measurements were carried out at a temperature of 30 °C, where previous work[8] established that complex formation between HTAC and PEO occurs, as evidenced by a substantial decrease of the cac below the cmc of pure HTAC.

Methods. Dialysis Experiments. Ternary PEO–HTAC solutions with different concentration ratios were dialyzed against surfactant solution to obtain chemical potential equilibrium. Regenerated cellulose, with a molecular weight cutoff of 8000, from Spectrum Medical Industries, was used as a membrane. A dialysis bag filled with polymer–surfactant solution was immersed in a beaker containing surfactant solution of the same concentration as inside the bag. The duration of dialysis was at least 1 week with 2–3 exchanges of surfactant solution. A previous report[21] found that very long dialysis times (several weeks) were required to achieve equilibrium in protein–SDS solutions. In our study, the dialysis time was varied from 1 week to 3 weeks and we found $(dn/dc)\mu_3$ to be constant within experimental error (±2% deviation) over this time period.

Refractive Index Increment. Refractive index increments of solutions of pure PEO and of PEO–HTAC complex were measured by a Dawn Optilab interferometric refractometer. In what follows, we use the designations c_2 for PEO concentration (g/100 mL), c_3 for HTAC concentration (g/100 mL), and c_3/c_2 for the HTAC to PEO ratio. It was determined that $dn/dc_2 = 0.136$ mL/g for the binary PEO solution, which is in good agreement with values cited in the literature.[24] Measurements were performed on dialyzed solutions, at various HTAC to PEO concentration ratios, to obtain $(dn/dc_2)\mu_3$, where we have used the abbreviation μ_3 to designate constant chemical potential of all solvent components (i.e., constant μ_1 and μ_3). We also determined the change in refractive index of the ternary solution when varying PEO concentration at fixed HTAC concentration, viz.

$$[dn/dc_2]_{c_3} = \left[\frac{n(\text{ternary})_{c_3} - n(\text{H}_2\text{O} + \text{HTAC})}{c_2}\right] \qquad (12)$$

Finally, the change in refractive index when varying the HTAC concentration, keeping the PEO concentration constant, was obtained:

$$[dn/dc_3]_{c_2} = \left[\frac{n(\text{ternary})_{c_2} - n(\text{H}_2\text{O} + \text{PEO})}{c_3}\right] \qquad (13)$$

Static Light Scattering. Measurements of light-scattering intensity were performed at 30 °C over the angular range 30–120° with a Brookhaven instrument, equipped with a 15 mW He – Ne laser emitting vertically polarized light at wavelength $\lambda = 632.8$ nm. The sample cell was mounted at the center of a temperature-controlled, refractive index matched bath. The intensity measurements were calibrated against toluene (Rayleigh ratio: 1.4×10^{-5} cm^{-1}).[25] Measurements were performed at 30° C. Radii of gyration (R_g) were determined from the angular dependence of the reduced scattering intensity ($Kc/\Delta R_\theta$) via eq 1.

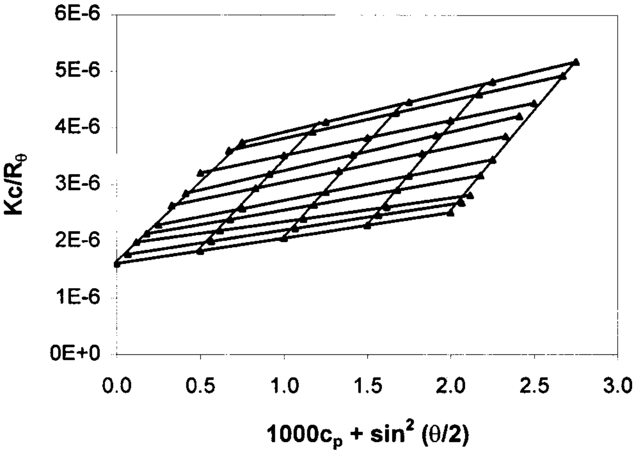

Figure 1. Typical Zimm plot for PEO(2) in water at 30 °C. The lines drawn represent least-squares fits to the data.

Table 1. Zimm Plot Results for PEO in Water at 30 °C

polymer[a]	M_w[b] × 10^5	R_g (nm)	A_2 (mL mol/g^2)
PEO(1) *1×10^5 M_w*	1.23 ± 0.08 (1.04 ± 0.15)	41.6 ± 2.8	0.0002
PEO(2) *6×10^5 M_w*	6.08 ± 0.13 (5.97 ± 0.11)	86.8 ± 3.2	0.0002
PEO(3) *9×10^5 M_w*	9.04 ± 0.32 (8.86 ± 0.10)	97.7 ± 2.7	0.0005

[a] Molecular weight values in italics were provided by the supplier. [b] Results in parentheses were obtained by intrinsic viscosity measurements.[8]

Results and Discussion

Binary Solutions of PEO in Water. Figure 1 shows a representative Zimm plot for the binary system of PEO(2) in water at polymer concentration ranging from 0.05 to 0.2 g/100 mL. The weight-average molecular weight (M_w), radius of gyration (R_g), and second virial coefficient (A_2) were obtained from dual extrapolations following eq 1. Table 1 summarizes the results and also shows values obtained from intrinsic viscosity measurements.[8] The light-scattering molecular weight values are in good agreement with the values quoted by the suppliers and are also consistent with the values obtained from intrinsic viscosity measurements.[8] Our values of A_2 are in good agreement with results reported by Devanand et al.,[26] but the measured R_g values are larger. The larger R_g values are attributed to the fact that our PEO samples have substantially wider molecular weight distributions ($\mu_2/\Gamma^2 \sim 0.5$).[8]

Ternary System of PEO–HTAC in Water. As noted above, we have previously demonstrated[8] that when HTAC is mixed with PEO in salt-free water, chain expansion occurs due to electrostatic repulsions between HTAC micelles bound to PEO, as evidenced by a pronounced viscosity maximum when the HTAC concentration is increased at fixed PEO concentration. The viscosity maximum occurs at the maximum binding condition, above which chain contraction occurs, due to screening of the electrostatic repulsions by excess counterions. To gain insight into the structure of the complex formed during titration of a PEO(2) solution with HTAC, light-scattering measurements were performed at con-

Table 2. Refractive Index Increments and Molecular Weight Obtained by Full Thermodynamic Treatment Method

c_3/c_2	$(dn/dc_2)_{\mu_3}$ (mL/g)	$(dn/dc_2)_{c_3}$ (mL/g)	$(dn/dc_3)_{c_2}$ (mL/g)	D' (g of HTAC/g of PEO)	D' (mol of HTAC/mol of EO)	$M_w \times 10^{-5}$	$M_{w,com} \times 10^{-5}$
0	0.1362	0	0	0	0	6.08 ± 0.13	6.08 ± 0.13
0.1	0.1440	0.1346	0.1362	0.069	0.009	6.25 ± 0.13	6.54 ± 0.20
0.5	0.1480	0.1202	0.1302	0.214	0.030	6.64 ± 0.18	8.06 ± 0.31
1.0	0.1540	0.1120	0.1173	0.358	0.049	6.80 ± 0.26	9.24 ± 0.50
1.75	0.1880	0.1002	0.1005	0.874	0.121	12.07 ± 1.39	22.62 ± 1.68
2.5	0.1860	0.1012	0.1160	0.731	0.101	11.07 ± 1.30	17.93 ± 1.44
3.0	0.1930	0.1105	0.1214	0.680	0.094	9.47 ± 0.47	15.91 ± 1.12

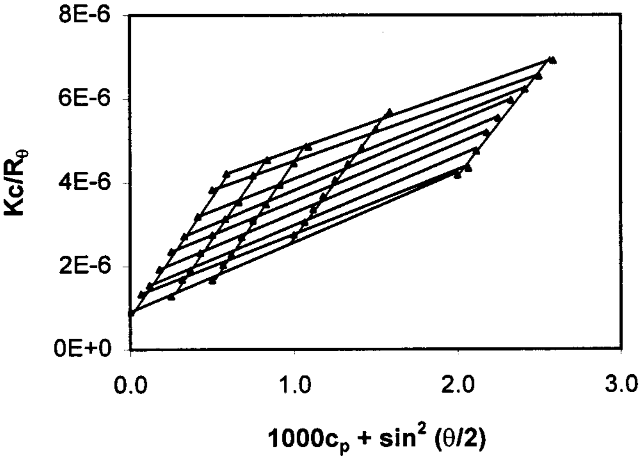

Figure 2. Zimm plot for the PEO(2)−HTAC ternary solution in water at 30 °C, at the maximum binding point ($c_3/c_2 = 1.75$), constructed by application of eq 7. The lines drawn represent least-squares fits to the experimental data.

stant ratio of HTAC to PEO(2) (i.e., constant c_3/c_2). The maximum binding ratio of HTAC to PEO(2), which has $M_w = 6.08 \times 10^5$, occurs at $c_3/c_2 \sim 1.75$, as evaluated by dynamic light scattering and viscometry.[8]

First, we measured the molecular weight, M_w, of PEO in the PEO−HTAC complex by light-scattering analysis via eq 7, using the $(dn/dc_2)\mu_3$ values after equilibrium dialysis listed in Table 2. The corresponding Zimm plot for the PEO(2)−HTAC complex at $c_3/c_2 = 1.75$, constructed following eq 7, is shown in Figure 2 as an example. As evident in Table 2, M_w increases up to the maximum binding point at $c_3/c_2 = 1.75$, indicative of an increasing level of interpolymer complex formation. Above $c_3/c_2 = 1.75$, M_w levels off, indicative that excess surfactant does not reduce the tendency that PEO chains share micelles.

Next, we determined D', the preferential interaction of HTAC with PEO(2), using eq 10, combining values of $(dn/dc_2)\mu_3$ with $(dn/dc_2)_{c_3}$ and $(dn/dc_3)_{c_2}$ values obtained, respectively, from eqs 12 and 13. Subsequently, $M_{w,com}$ was computed through eq 11. The corresponding values of $(dn/dc_2)\mu_3$, $(dn/dc_2)_{c_3}$, $(dn/dc_3)_{c_2}$, M_w, D' (in g of HTAC/g of PEO, and in mol of HTAC/mol of EO), and $M_{w,com}$ are each displayed in Table 2. Above the cac ($c_3/c_2 \sim 0.1$), $M_{w,com}$ increases steeply with added HTAC up to the maximum binding point, where it levels off. This increase derives from two sources, an increase in D', and the previously mentioned increase in M_w. From the latter, we deduce that, on average, 2.0 ± 0.3 PEO chains are involved in formation of the PEO−HTAC complex at maximum binding. In addition, $N_{3,b}/N_2$, the number of bound HTAC molecules per PEO(2) chain, can be determined from eq 11 as $N_{3,b}/N_2 = D'M_{w,PEO}/M_{HTAC}$, where $M_{w,PEO} = 608\,000$, and $M_{HTAC} = 319$ is the molecular weight of HTAC. The results are shown in Table 3 and compared with N_3/N_2, the total number of HTAC molecules (bound + free HTAC molecules) per PEO(2) chain. We also list $N_{3,f}/N_2$ the number of free HTAC molecules per PEO chain, and $n_{3,b}$, the number of bound HTAC micelles, the latter computed from the aggregation number of free HTAC micelles, reported by Zana et al.[4] Note that this estimate may be inaccurate, since the aggregation number of bound micelles is lower than that of free micelles,[4] although it is reported to approach the latter as the surfactant-to-polymer ratio increases.[27] At maximum binding ($c_3/c_2 = 1.75$), only 50% of the available surfactant molecules are bound to the polymer chain (see Table 3), thus the complex coexists with free surfactant micelles. This relatively weak binding affinity of HTAC for PEO may be the driving force for PEO chains to share micelles when forming complexes. In particular, multipolymer sharing of bound micelles facilitates reduction of the strong electrostatic repulsions between surfactant headgroups at low ionic strength, and the corresponding translational entropy loss is compensated by the entropy of the free micelles.

Table 3. Physical Parameters of PEO(2)−HTAC Complexes Obtained from Light-Scattering Measurements

c_3/c_2	N_3/N_2	$N_{3,b}/N_2$	$N_{3s,f}/N_2$	$n_{3,b}$
0.1	191	132	59	~1
0.5	953	408	545	5
1.0	1906	682	1224	9
1.75	3335	1666	1669	22
2.5	4765	1393	3372	19
3.0	5718	1296	4422	17

Above maximum binding, the amount of bound surfactant appears to decrease significantly. The reason for this is not clear at present. However, Zimm plot analysis of the light-scattering intensities also indicates that the radius of gyration, R_g, of the complex increases with added surfactant up to $c_3/c_2 = 1.75$, and then decreases significantly, as shown in Table 4. Thus, we speculate that the decrease in D' and $N_{3,b}/N_2$ above $c_3/c_2 = 1.75$ may reflect some change in structure of bound micelles which accompanies the decrease in R_g. Also presented, for reference, in Table 4 are values of the hydrodynamic radius, $R_{h,f}$, and polydispersity, μ_2/Γ^2, obtained in an earlier dynamic light-scattering study,[8] as well as approximate values of the viscometric hydrodynamic radius, $R_{h,\eta}$, obtained by combining the previous viscosity data[8] and the present molecular weight information as $\eta_{sp}M_{w,com}/c_2(1+D') \sim 2.5\ N_AV_h$. As evident in Table 4, and further exhibited in Figures 3 and 4, maxima in $R_{h,f}$ and $R_{h,\eta}$ at the maximum binding point at $c_3/c_2 = 1.75$ correlate to those observed in $M_{w,com}$ and R_g. The decreases in R_g, $R_{h,f}$, and $R_{h,\eta}$ at large c_3/c_2 presumably arise because excess added surfactant results in screening of electrostatic interactions between bound micelles and therefore, chain contraction occurs. Note that the

Table 4. Variation of $M_{w,com}$, R_g, $R_{h,f}$, and $R_{h,\eta}$ with Addition of HTAC

c_3/c_2	$M_{w,com} \times 10^5$	polydispersity (μ_2/Γ^2)	R_g (nm)	$R_{h,f}^{app}$ (nm)	$R_{h,\eta}^{app}$ (nm)
0	6.08 ± 0.13	0.47 ± 0.01	86.8 ± 3.2	40.4 ± 3.0	35.7 ± 0.2
0.1	6.54 ± 0.20	0.50 ± 0.01	86.9 ± 5.3	56.9 ± 3.8	34.9 ± 0.4
0.5	8.06 ± 0.31	0.59 ± 0.02	95.1 ± 4.9	60.8 ± 3.6	37.4 ± 1.1
1.0	9.24 ± 0.50	0.67 ± 0.01	106.7 ± 7.1	73.6 ± 1.7	41.1 ± 1.5
1.75	22.62 ± 3.68	0.71 ± 0.02	169.8 ± 6.4	81.4 ± 0.4	47.0 ± 3.0
2.5	17.93 ± 1.44	0.69 ± 0.01	151.4 ± 9.1	60.0 ± 4.0	45.1 ± 1.8
3.0	15.91 ± 1.12	0.66 ± 0.02	148.3 ± 1.8	58.0 ± 1.3	44.4 ± 2.0

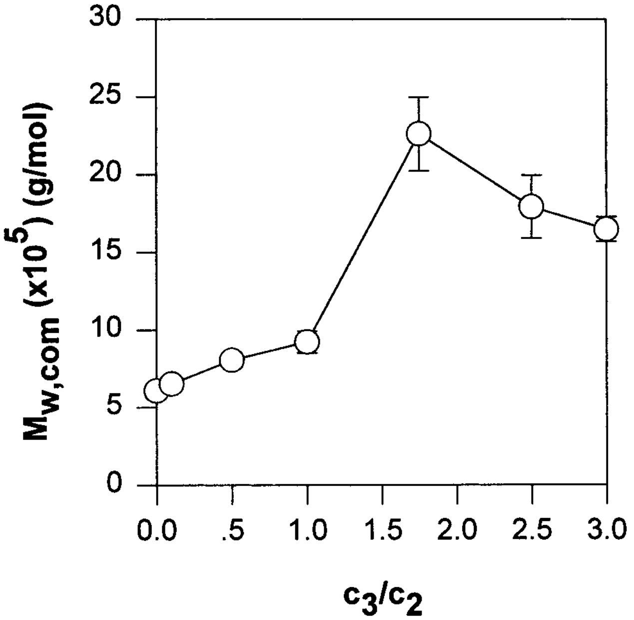

Figure 3. Molecular weight of PEO(2)−HTAC complex as a function of surfactant to polymer concentration ratio in ternary solution at 30 °C.

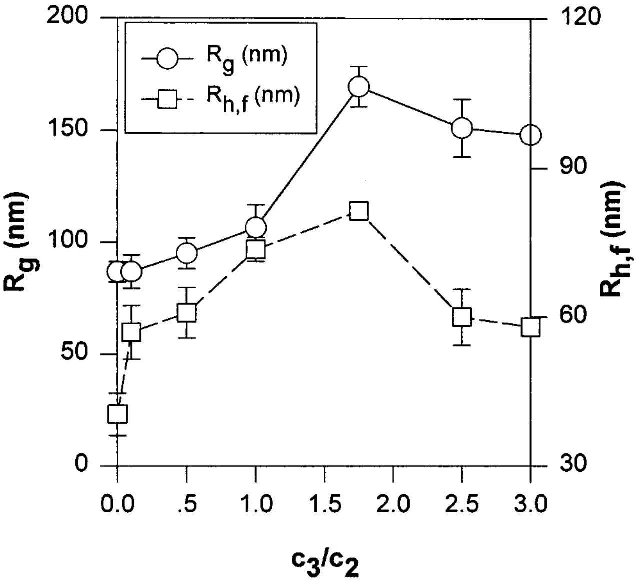

Figure 4. Radius of gyration and apparent hydrodynamic radius as a function of surfactant to polymer concentration ratio for PEO(2)−HTAC complex in ternary solution at 30 °C.

apparent hydrodynamic radii, $R_{h,f}^{app}$ and $R_{h,\eta}^{app}$ obtained by dynamic light scattering and viscometry at finite concentrations, are not expected to be numerically accurate, because they will be strongly influenced by the effect of intermolecular electrostatic interactions on translational diffusion coefficient and viscosity. We also note that, consistent with our present analysis of light-scattering intensities, no fast micelle mode was observed in the earlier dynamic light-scattering studies[8] up to $c_3/c_2 = 3.0$.

To our knowledge, only one previous study[19] has utilized a similar combination of light scattering, with the refractive index increment measured at constant chemical potential, and independent evaluation of the preferential binding of surfactant to determine the molecular weight of polymer surfactant complexes. These authors[19] investigated complex formation between poly(vinylpyrrolidone) (PVP) and SDS in 0.1 M $NaNO_3$, and found only unipolymer complex formation occurs up to maximum binding, at which point essentially all of the surfactant is bound to the polymer.[19] In further contrast to our results for the HTAC/PEO system without added salt, SDS/PVP in 0.1 M $NaNO_3$ exhibits a minimum in viscosity, and a minimum in radius of gyration, on addition of surfactant.[19] Our results, however, are consistent with previous studies, which indicate that the maximum binding ratio increases with addition of inorganic salt. For example, Cabane and Duplessix[3] observed an increase in binding ratio of SDS to EO from 0.25, at zero salt, to 0.85, at ionic strength of 0.4. The small binding ratio of HTAC to EO at zero salt (0.12), compared to that of SDS to EO (0.25) is further consistent with expectation that binding of cationic surfactant to uncharged polymers is weaker than that of anionic surfactant.[1]

We also note certain similarities between our observations and studies of complex formation between SDS and protein chains. As mentioned above, Valstar et al.[21] determined that multichain complexes form between SDS and serum albumen, based on light-scattering data interpreted via eq 7. However, they further report that the number of protein chains decreases toward unity as the dialysis time increases. No such effect was observed in our study. Also, Greener et al.[28] observed a maximum in viscosity of alkali-processed gelatin on titration with SDS, interpreted as due to cross-linking of gelatin chains by SDS micelles. Finally, a recent study[17] of complex formation between cetyltrimethylammonium bromide (CTAB) micelles and poly(acrylic acid) (PAA) at low pH reports that maximum binding occurs when the CTAB/Acrylic acid mole ratio = 1.0, where essentially all surfactant is bound. In the CTAB/PAA system, significant ionization of PAA occurs on addition of surfactant,[17] hence the higher binding affinity likely occurs because electrostatic interactions between surfactant and acrylate monomer stabilize complex formation.

Finally, in Table 5, for three different molecular weights of PEO, we show values of $M_{w,com}$ and R_g at the maximum binding point, the former determined via eqs 7 and 11, with the assumption that the amount of bound surfactant, D', was the same for each polymer. This assumption is reasonable, based on previous studies,[10] for the PEO/SDS system that, above a PEO molecular weight of 4000, the free energy of interaction is inde-

Table 5. Light Scattering Results for Different Molecular Weights of PEO−HTAC Complexes at the Maximum Binding Point

polymer	M_w	$M_{w,com}$	R_g (nm)	$R_{g,complex}/R_{g,PEO}$
PEO(1)	123000 ± 8000	462000 ± 34600	70.3 ± 2.6	1.7 ± 0.05
PEO(2)	608000 ± 13000	2262000 ± 168000	169.8 ± 6.4	2.0 ± 0.01
PEO(3)	904000 ± 32000	3581220 ± 665000	182.8 ± 13.1	1.9 ± 0.08

pendent of molecular weight. The results in Table 5 indicate that the chain expansion on binding of micelles is comparable for each molecular weight, $R_{g,complex}/R_{g,PEO} \sim 1.9$. This is consistent with our previous observation[8] that the fractional increase in solution viscosity up to maximum binding is independent of molecular weight.

To conclude, it is interesting to discuss our observations in light of recent theoretical treatments of the viscosity of a dilute solution of strongly charged polyions.[29−31] In particular, we refer to an expression for the specific viscosity derived by Cohen et al.[30] in the strong coupling limit, omitting numerical prefactors

$$\eta_{sp} \approx R_H l_B^{\,2} c_{po}^{\,2} Z_p^{\,2}/\kappa^3 \tag{14}$$

where R_H is the hydrodynamic radius of the polyion, c_{po} is the polyion concentration in mol/L $= c_p/M_p$ where c_p is the polyion concentration in g/L and M_p is the polyion molecular weight, Z_p is the net charge on the polyion, and κ is the Debye length, given, for monovalent counterions, by $\kappa^2 = 4\pi l_B(c_{po}Z_p + 2c_s)$, where c_s is the concentration of added salt, and $l_B = e^2/\epsilon_o k_B T$ is the Bjerrum length, ϵ_o is the dielectric constant of the solvent, k_B is Boltzmann's constant, and T is the absolute temperature. Adapting eq 14 to our present system, viz. a polymer/micelle complex in equilibrium with free surfactant micelles, we equate $c_p \equiv c_2(1 + D')$, and $M_p \equiv M_w(1 + D')$, where D' is the amount of bound surfactant, and the net charge on the PEO/HTAC complex, $Z_p = D'M_w/M_3$, where M_3 is the molecular weight of the surfactant. We may also express $\kappa^2 = 4\pi l_B(c_{po}\alpha_p Z_p + c_{mo}\alpha_m Z_m)$, with $c_{po} = c_p/M_p = c_2/M_w$, and where $c_{mo} = (c_3\text{-}c_2D')/M_m$ is the molar concentration of free surfactant micelles, with c_3 being the total concentration of surfactant and $M_m \equiv M_3Z_m$, where Z_m is the net charge on the micelle and α_p and α_m refer to the fraction of dissociated counterions for polymer−micelle complex and free micelles, respectively. With these substitutions, we obtain a scaling relation for the dependence of η_{sp} on R_H, D', and the ratios c_3/c_2 and α_m/α_p:

$$\eta_{sp} \approx \frac{R_H c_2^{\,0.5} \alpha_m^{\,0.5} (D')^2}{M_3^{\,0.5} (c_3/c_2)^{1.5} (\alpha_m/\alpha_p)^2} \tag{15}$$

Since α_m, c_2, and M_3 are fixed, we may thus write

$$\eta_{sp} = \frac{K R_H (D')^2}{(c_3/c_2)^{1.5} (\alpha_m/\alpha_p)^2} \tag{16}$$

where K is a numerical constant. Using our experimentally determined values of R_H and D' (see Tables 2 and 4), we find that eq 16 indeed predicts a maximum in viscosity, which coincides with that observed[8] at $c_3/c_2 = 1.75$. However, to quantitatively match the observed change in viscosity, which increases from $\eta_{sp} \sim 0.4$ at $c_3/c_2 = 0.5$ to $\eta_{sp} \sim 0.6$ at $c_3/c_2 = 1.75$ and then decreases to $\eta_{sp} \sim 0.5$ at $c_3/c_2 = 3.0$, it is necessary, in eq 16, to allow that α_m/α_p varies with change in the surfactant-to-polymer ratio, c_3/c_2. In fact, an increase in α_m/α_p from around 0.5 at small c_3/c_2 to approximately unity at maximum binding was reported by Fundin et al.,[17] in their study of complexes formed between CTAB and poly(acrylic acid), i.e., at low c_3/c_2, counterion condensation on bound micelles is substantially diminished, and increases to a level comparable to that of free micelles at maximum micelle binding, where it levels off. Hence, if we assume $\alpha_m/\alpha_p = 1.0$ at $c_3/c_2 = 1.75$, then, from the viscosity values via eq 16, we deduce α_m/α_p increases from approximately 0.66 at $c_3/c_2 = 0.5$, to unity at maximum binding, and then decreases again to approximately 0.48 at $c_3/c_2 = 3.0$. It seems likely that the putative decrease in α_m/α_p above maximum binding is erroneous, perhaps signaling a breakdown of the strong coupling approximation,[30] or a crossover from dilute solution to semidilute solution behavior, where the theory no longer applies.

Conclusions

In this paper, we have determined the molecular weight and radius of gyration of PEO−HTAC complexes formed in dilute aqueous solution by static light-scattering analysis, as a function of HTAC concentration. The goal was to gain insight into the origin of the viscosity maximum observed when a dilute solution of PEO is titrated with HTAC. Our results show that HTAC binds to PEO as evidenced by increases in molecular weight and radius of gyration, which level off at the PEO/HTAC ratio where the viscosity maximum occurs. Measurement of the preferential binding of HTAC to PEO indicates that 0.874 g of surfactant is bound per g of PEO at the viscosity maximum. We further observe that on average 2.0 ± 0.3 PEO chains are involved in the formation of the complex. Moreover, the relative chain expansion produced by complex formation is comparable for three different molecular weights, consistent with our previous observation that the fractional increase in solution viscosity up to maximum binding is independent of molecular weight. Our observations support the earlier interpretation that the viscosity maximum occurs because of binding of surfactant micelles to the polymer, which is accompanied by a chain expansion, enhanced by the electrostatic repulsions between bound micelles, and formation of interpolymer complexes, up to the maximum binding point. Beyond this, the viscosity decreases because of contraction of the complex due to electrostatic screening from the accumulation of free micelles and counterions in the solution.

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