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Sodium Chloride and Ethanol Induced Sphere to Rod Transition of Triblock Copolymer Micelles

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Dynamic light scattering (DLS), small-angle neutron scattering (SANS), and viscosity studies have been carried out to examine the influence of NaCl and ethanol on the structure of triblock copolymer $[(EO)_{20}(PO)_{70}(EO)_{20}]$ (EO = ethylene oxide; PO = propylene oxide) micelles in aqueous medium. The studies show that while the pure triblock copolymer solutions do not show any significant growth of the micelles on approaching the cloud point, the presence of a small amount of ethanol (5−10%) induces a sphere to rod shape transition of micelles at high temperatures. Interestingly, this ethanol induced sphere to rod transition of micelles can be brought down to room temperature (25 °C) with the addition of NaCl. It is also found that NaCl alone cannot induce such sphere to rod transitions and excess ethanol suppresses them by increasing their transition temperature.

Introduction

Self-assembly behaviors of (EO)−(PO)−(EO) (EO = ethylene oxide; PO = propylene oxide) based triblock copolymers have been studied extensively in view of their rich structural polymorphism and numerous applications in industries.[1−12] Amphiphilic character of these copolymers arises from a difference in the solubilities of EO and PO blocks in polar and nonpolar solvents. In aqueous medium, both the EO and PO blocks remain hydrated below a characteristic temperature called the critical micellar temperature (CMT). A drastic decrease in the solubility of the PO block at the CMT leads to the formation of micelles comprising PO blocks as the core and the hydrated EO blocks as the corona.[13] CMTs of triblock copolymers are concentration-dependent and decrease with an increase in the copolymer concentration.[14] Above the CMT, the micellar size increases progressively with an increase in temperature before being phase-separated at the cloud point (CP). The influence of temperature,[15−24] various water-soluble electrolytes,[25−35] and solvents[36−39] on the self-assembly behavior of these copolymers in water are well-documented. Many of these copolymer solutions exhibit sphere to rod transitions of the micelles on approaching their cloud points.[15−24] Since the maximum size of a spherical block copolymer micelle in water is limited by an entropically unfavorable stretching of the PO block, an increase in aggregation number with increase in temperature, above the CMT, leads to a change in shape of the block copolymer micelles.

The influences of cosolutes and cosolvents on the micellar and liquid crystalline behavior of (EO)−(PO)−(EO) based block copolymer aqueous solutions are diverse in nature.[25−39] Inorganic salts such as KCl, NaCl, and KF dehydrate the chains of PO and EO blocks and reduce CMT, the critical micelle concentration (cmc), the cloud point, and the liquid crystalline

onset temperature of the copolymer solutions, whereas salts such as KSCN have exactly the opposite effects.[25−35] The presence of KF even facilitates the sphere to rod transition of copolymer micelles by reducing the transition temperature to a significant extent.[16] A limited number of studies on the effect of addition of cosolvent shows that highly polar solvents such as glycerol stay away from the interior of the micelles and prefer to remain in a polar domain comprising water molecules.[36−39] This leads to de-swelling of the copolymer micelles as the weight fraction of water available for swelling the micellar corona decreases in the presence of glycerol. Solvents with less polarity like ethanol and methanol, etc., on the other hand, are known to be good solvents for both PO and EO blocks and lead to an increase in CMT, cmc, and the cloud point.[36−39]

In this paper, we report a sphere to rod transition of triblock copolymer $[(EO)_{20}(PO)_{70}(EO)_{20}]$ micelles in aqueous medium. Usually, such micellar transitions in the aqueous solutions of triblock copolymers are observed at high temperatures. Here, we observe that, in the presence of ethanol, aqueous solutions of this triblock copolymer show sphere to rod transition at high temperature and addition of NaCl decreases the transition temperature to 25 °C.

Experimental Section

The triblock copolymer $(EO)_{20}(PO)_{70}(EO)_{20}$ was purchased from Aldrich, ethanol was procured from Fluka, and sodium chloride was purchased from Merck. The copolymer solutions were prepared by weighing required amounts of solvents, copolymer, and NaCl (when needed) and keeping them in a refrigerator in tightly closed glass-stoppered vials for 1 week. The relative viscosities of the solutions were measured at 25 °C by using an Ostwald viscometer. Dynamic light scattering (DLS) measurements of the solutions were performed using a Malvern 4800 Autosizer employing a 7132 digital correlator. The light source was an argon ion laser operated at 514.5 nm with a maximum output power of 2 W. The average decay rate was obtained from the electric field autocorrelation function, $g^1(\tau)$, using the method of cumulants.[40] Measurements were

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made at five different angles ranging from 50 to 130°. For all solutions the average decay rate (Γ) from the second-order cumulant expansion of the electric field correlation function [$g^1(\tau)$] varies linearly with q^2, indicating translational diffusion of the scatterers (q being the magnitude of the scattering vector given by $q = [4\pi n \sin(\theta/2)]/\lambda$, where n is the refractive index of the solvent, λ is the wavelength of laser light, and θ is the scattering angle). From the slope of the Γ vs q^2 plots, the apparent diffusion coefficient values were estimated, and from these values the apparent equivalent hydrodynamic radii of the micelles were calculated using the Stokes–Einstein relationship. For anisotropic micelles where the solutions showed an abrupt increase in the relative viscosity, the lengths of the micelles were estimated from the translational diffusion coefficient employing Perrin's formula.[41] For prolate ellipsoids, the diffusion coefficient (D) is related to the axial ratio (ρ) and semimajor axis (a) of the micelles, by the relation

$$D = kT[G(\rho)]/6\pi\eta a$$

$$G(\rho) = (1 - \rho^2)^{-1/2} \ln[\{1 + (1 - \rho^2)^{1/2}\}/\rho]$$

where D is the translational diffusion coefficient, ρ is the ratio of the semimajor axis to the semiminor axis with a value > 1, and η is the viscosity of the medium.

The semiminor axis is fixed as the radius of the spherical micelle before the onset of growth. A linear variation of Γ vs q^2 indicates negligible contribution of the rotational diffusion coefficient of the rods.

SANS measurements were carried out on samples prepared in D_2O at the SANS facility at DHRUVA reactor, Trombay. The incident wavelength was 5.2 Å with $\Delta\lambda/\lambda = 15\%$. The magnitude of the scattering vector was varied from 0.02 to 0.2 Å^{-1}. The spectra were corrected for background, empty cell contributions, transmission, and detector efficiency and were placed on absolute scale using standard protocols. Correction due to instrumental smearing was taken into account throughout the data analysis. The qualities of the fits were assessed from the reduced χ^2 values.

The differential scattering cross-section per unit volume [$d\Sigma/d\Omega$] for monodisperse isotropic scatterers can be written as

$$d\Sigma/d\Omega = (\Delta\rho)^2 v^2 N P(q) \, S(q)$$

where $\Delta\rho^2$ is the contrast factor, N is the number density of scatterers, v is the volume of the scatterer, $P(q)$ is the form factor characteristic of the specific size and shape of the scatterers, and $S(q)$ is the structure factor that accounts for the interparticle interaction.

The block copolymer micelles can be considered as a spherical core shell particle with differing scattering length densities of hydrophobic core and hydrophilic shell. The scattering from the shell of the micelle depends on its thickness as well as its scattering length density. Due to the high degree of solvation, the scattering length density of the shell will not be significantly different from that of the solvent, and it was found difficult to get a unique value of the thickness of the shell when the thickness and contrast of the shell were used as an adjustable parameter. Thus, to limit the number of unknown parameters in the fit, we assumed that, for all practical purposes, the scattering in SANS mainly arises from the core of the micelles. To describe the core radius (r), we used a form factor for monodisperse spheres as

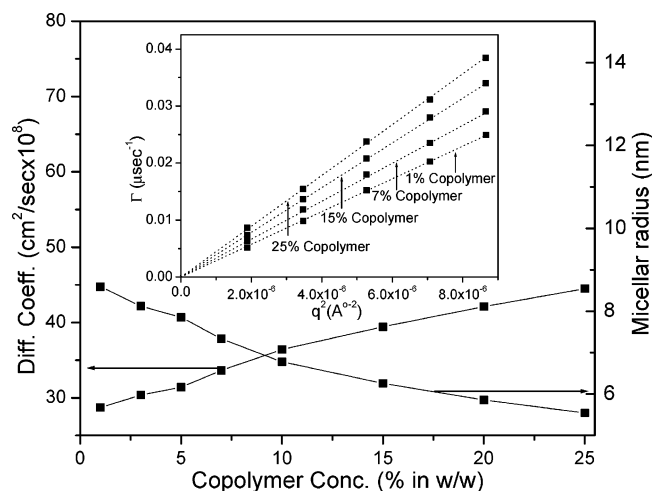$$P(q) = [3\{\sin(qr) - qr\cos(qr)\}/(qr)^3]^2$$

Figure 1. Variation of the translational diffusion coefficient and hydrodynamic radius of the micelles with concentration of the triblock copolymer, $(EO_{20})(PO_{70})(EO_{20})$, at 30 °C. Inset shows the corresponding relaxation rate (Γ) vs q^2 plots.

The interparticle interaction was captured from the analytical solution of the Ornstein–Zernike equation in the Percus–Yevick approximation employing hard sphere potential.[42] The total volume fraction of the micelles and the overall core and shell radius of the micelles were used as variables in $S(q)$ calculation. A similar approach has been employed in the literature for the analysis of SANS data of block copolymer micelles.[19]

Results and Discussion

(1) Effect of Copolymer Concentration. To investigate the structural changes in micelles by the addition of salt and ethanol, we begin with a two-component system of copolymer and water at 25 °C. Figure 1 shows the concentration dependence of the diffusion coefficient of the block copolymer micelles as determined by DLS in the concentration range 1–25% (w/w), which is well above the cmc (0.025%) of this copolymer at 25 °C.[43] Truly the translational diffusion nature of the micelles is evident from the linear dependence of Γ on q^2 (inset of Figure 1). The slope of this plot steadily increases with an increase in the copolymer concentration, indicating an increase in the diffusion coefficient of the micelles. This increase in diffusion coefficient reflects a decrease in the apparent hydrodynamic radius of the micelles with an increase in copolymer concentration. The hydrodynamic radius of the micelles in 1% solution is consistent with the micellar radii observed in the aqueous solutions of block copolymers of similar molecular weights.[24,31] Thus, it is very likely that there is negligible intermicellar interaction at this concentration. However, at higher polymer concentrations intermicellar interaction becomes important. The variation of diffusion coefficient with volume fraction of the copolymer, ϕ, can be expressed as,

$$D_{eff} = D_0(1 + k_0\phi)$$

where D_{eff} is the effective diffusion coefficient at any volume fraction, ϕ, D_0 is the diffusion coefficient at infinite dilution, and k_0 is the diffusion virial coefficient that has a value of 1.56 for colloids with hard sphere interaction. In the present case, considering the volume fraction of the polymer (ϕ) to be proportional to the mass fraction, a linear variation of D_{eff} with ϕ is observed up to a ϕ value of 0.1. A linear regression to the data gives a value of $D_0 = 27.7$ cm^2/s and $k_0 = 3.08$. The observed value of k_0 is twice what is expected for hard sphere

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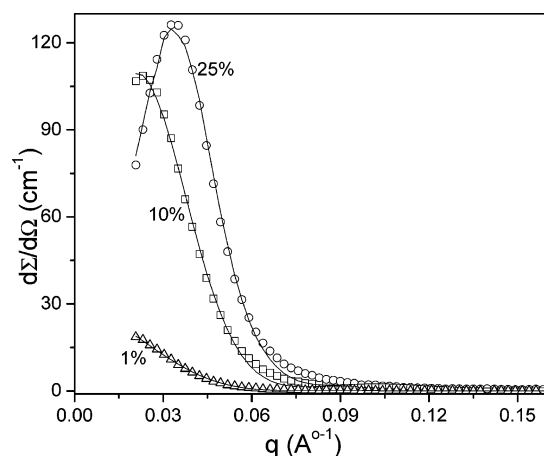*J. Phys. Chem. B, Vol. 109, No. 12, 2005* **5655**

Figure 2. SANS patterns of 1, 10, and 25% aqueous copolymer solutions at 30 °C. The solid lines are fit to the data using a model for interacting hard sphere colloids.

TABLE 1: Hydrodynamic Radius (R_H) Measured from DLS Technique, Core Radius (R_C), Hard Sphere Radius (R_{HS}), and Aggregation Numbers Calculated from the SANS Study for Different Copolymer Solutions

composn	R_H (nm)	R_C (nm)	aggregation no.	R_{HS} (nm)
1% copolymer				
(a) 0% ethanol	8.8	6.2	149	
(b) 20% ethanol	–	5.0	78	
(c) 30% ethanol	–	4.1	43	
10% copolymer				
(a) 0% ethanol	6.8	6.4	164	8.1
(b) 20% ethanol	–	4.8	70	8.1
25% copolymer				
(a) 0% ethanol	5.7	5.7	116	8.1
(b) 10% ethanol	–	4.3	50	8.0

colloids, suggesting that the effective volume fraction of solvated micelles is twice the mass fraction of the polymer. This result is consistent with the recent report of Lindner et al. on the concentration dependence of the diffusion coefficient of P-94 block copolymer micelles.[24]

Figure 2 shows the SANS spectra of the block copolymer micelles in D$_2$O at 298 K at three different polymer concentrations together with their model fits. For 1% (w/w) polymer concentration, no correlation peak is observed indicative of the absence of any intermicellar interaction. Thus, the data were analyzed without considering any intermicellar interaction (i.e. $S(q) = 1$). From analysis using a monodisperse spherical core and neglecting the shell contribution due to very low contrast with the solvent, a core radius of 6.2 nm is observed. With an increase in the copolymer concentration (10%), a correlation peak develops, which shifts to higher q values with further increase in the polymer concentration (25%). This is consistent with the expectation that an increase in the number density of micelles leads to a decrease in the average intermicellar distance, as the position of the correlation peak (q_{max}) can be approximated to the interparticle distance, d, by the relation $d \approx 2\pi/q_{max}$. The spectra for the 10 and 25% (w/w) copolymer solutions were analyzed by taking into consideration the intermicellar interaction in terms of hard sphere potential. The intraparticle form factor ($P(q)$) will capture the micelle core, whereas the interparticle interaction ($S(q)$) is governed by the total volume fraction and overall dimension of the micelle. The micellar parameters obtained from the model fits are summarized in Table 1. The aggregation numbers of the micelles were calculated from the core radius and the volume of PO units (95.4 Å^3), assuming that the core comprises only of PO units. Evaluation of the data at high polymer concentration enables
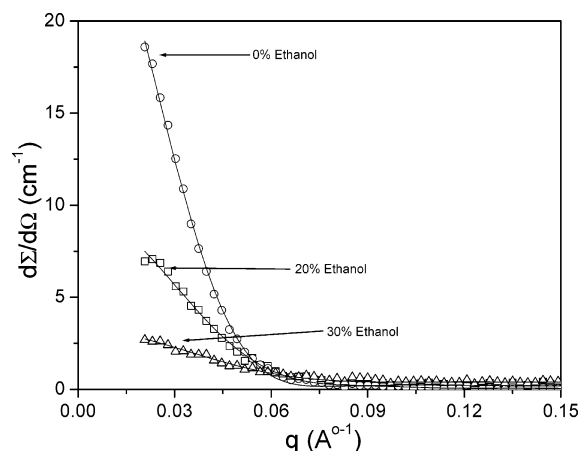

Figure 3. SANS patterns of 1% aqueous copolymer solutions with different ethanol concentrations at 30 °C. The solid lines represent fits to the data using the spherical form factor.

us to obtain the micellar core radius as well as the total core and shell radius. The overall hard sphere radius of the micelles obtained from the $S(q)$ terms in the scattering spectra is 8.1 nm. This is consistent with the hydrodynamic radius of the micelles observed from DLS measurement (8.8 nm) in the dilute copolymer solution containing 1% copolymer. The slightly higher value of the hydrodynamic radius of the micelles as compared to the hard sphere radius could arise from diffusions of the micelles along with a sheath of associated solvent molecules. Both the core and the shell dimensions of the micelles are practically independent of polymer concentration up to 25% (w/w) of polymer, which is in agreement with the reports for other block copolymer micelles.[1]

(2) Effect of Ethanol. Unlike water, which is an EO-block selective solvent, ethanol is known to be a good solvent for both EO and PO blocks of the EO−PO−EO based triblock copolymers. Addition of ethanol thus has significant influence on the self-assembly behavior of these block copolymers in aqueous medium. An increase in ethanol concentration in the aqueous copolymer solutions leads to an increase in CMT and cmc and a decrease in the aggregation number of the copolymer micelles.[38] Figure 3 shows the evolution of the SANS spectra of 1% copolymer solutions at different ethanol concentrations. A drastic decrease in intensity at low q values with addition of ethanol suggests a decrease in the size of the micelles. Since interparticle interactions are absent in the 1% copolymer solution, the solutions with varying ethanol concentrations could be analyzed in terms of spherical form factors of the hydrophobic core of the micelles. Analysis of the data shows that indeed the core size and subsequently the aggregation number of the micelles decrease steadily with an increase in the ethanol concentration (Table 1). Figure 4 shows the effect of ethanol on the SANS spectra of 10 and 25% copolymer solutions at 30 °C. Data Analysis by incorporating the interparticle interaction term $S(q)$ shows that in both cases the core radius and the aggregation number of the micelles decreases upon addition of ethanol but their hard sphere radius remains almost unchanged. A shift of the correlation peak positions (q_{max}) to higher q values indicates that the intermicellar distance decreases upon addition of ethanol. This could be attributed to an increase in the number density of the micelles resulting from a decrease in their aggregation number upon addition of ethanol. Similar results were reported in the SDS−F127 mixed micellar systems, where addition of SDS (sodium dodecyl sulfate) in the aqueous solution of F127 (EO$_{99}$PO$_{69}$EO$_{99}$) leads to a decrease in the aggregation number of the micelles and subsequently shifts the peak position

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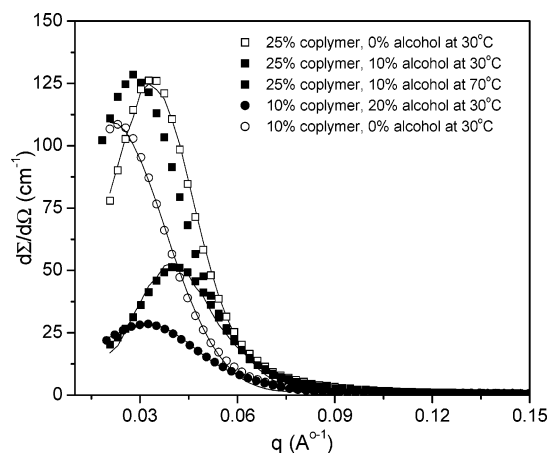
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Figure 4. SANS patterns of 10 and 25% aqueous copolymer solutions with and without ethanol at 30 °C. The solid lines represent a fit to the data using the spherical form factor.

Figure 5. Variation of the cloud point and gelation point of 25% aqueous copolymer solutions as a function of ethanol and NaCl concentrations.

of the SANS spectra to higher q values.[44] The observed results indicate that, in the presence of ethanol, an increased swelling of the EO blocks in the corona region compensates for the decrease in the aggregation number of the micelles.

The cloud points of aqueous solutions of triblock copolymers are related to the dehydration of EO blocks with an increase in temperature. Addition of ethanol to these solutions increases the solvation of the EO blocks and leads to an increase in the cloud point.[36] In the present study, the CP of aqueous copolymer solutions remains nearly constant ($\approx$50 °C) in the concentration range 1−25% (w/w). It increases significantly with the addition of ethanol, and in the copolymer solutions with 20% ethanol it is not observed up to 100 °C. In the absence of ethanol, the copolymer solutions do not show any gelation with an increase in temperature up to their respective cloud points. Such gelations, which are observed in aqueous solutions of other copolymers at temperatures above 60 °C, have been explained on the basis of sphere to rod transitions of the copolymer micelles.[16−24] In the present case, the absence of any gelation in pure block copolymer solutions could be because of low CP ($\approx$50 °C) of the solutions, which arises from a low EO/PO ratio (0.57) of the copolymer. The cloud points of the aqueous solutions of triblock copolymers decrease with a decrease in the molecular weight and the EO/PO ratio of the copolymers.[10] As the CP of copolymer solutions increase with the addition of 5% ethanol, an increase in the viscosity of the solutions is observed on approaching the respective cloud points. For solutions containing 15−25% copolymer and 5% ethanol, a thermoreversible gel is formed on approaching the CP. This suggests that the microstructure of the micellar assemblies changes on approaching the respective cloud points. The temperatures at which such gels (for 15−25% copolymer concentration) are formed are henceforth referred to in this paper as gelation points. The effect of the addition of ethanol and NaCl on the gelation point and CP of 25% block copolymer aqueous solution is depicted in Figure 5. The cloud points were measured by DLS technique as the temperatures at which a sharp increase in light scattering intensity is observed. The gelation points were measured in a temperature-controlled water bath as the temperatures at which the solutions became gels and flow only as a lump. The stiffness of this gel is less than that observed in the case of isotropic liquid crystalline gels containing cubically arranged spherical micelles. Such liquid crystalline gels do not flow and are observed when the volume fraction of the spherical micelles in the micellar solutions becomes more than 53%.[9] As shown in Figure 5a, the cloud point increases
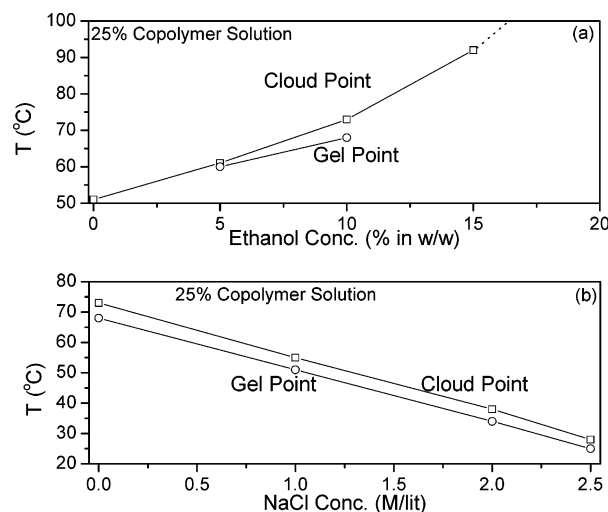
monotonically with an increase in ethanol concentration. The gelation point increases from 60 to 68 °C with an increase in ethanol concentration from 5 to 10% and is not observed with a further increase in alcohol concentration to 15%. This suggests that excess addition of ethanol destabilizes the process of gelation. A comparison of the SANS patterns of 25% copolymer solution with 10% ethanol, recorded at different temperatures (Figure 4), reveals that an increase in temperature from 30 to 70 °C leads to a large increase in scattering intensity and a shift of q_{max} to lower q values. This is an indication of the growth of the micelles with an increase in temperature. The SANS data at 70 °C could not be fitted with a model of interacting spherical micelles, suggesting a nonspherical growth of micelles. Considering the fact that the structure factor still dominates the scattering function, detailed information on the form of the nonspherical aggregates could not be gained from the present data. As the viscosity of the solution increases drastically with an increase in temperature, it is likely that the micelles develop into prolate ellipsoids at higher temperature. The observed increase in the gelation point with an increase in the ethanol concentration suggests that the role of ethanol in inducing gelation is probably to increase the cloud point of the copolymer solutions to temperatures above their possible gelation points.

(3) Effect of NaCl. Inorganic salts such as NaCl, KCl, and KF are, in general, known to have effects opposite to that of ethanol on the aggregation behavior of the triblock copolymer micelles in water.[16,25,38] It has been reported that 1 M KF reduces the sphere to rod transition temperature of the micelles in the aqueous solution of the copolymer $(EO)_{29}(PO)_{40}(EO)_{29}$ (with a cloud point of 90 °C), from 70 to 37 °C.[16] In view of this, we studied the influence of NaCl on gelation characteristics of copolymer solutions. In the absence of ethanol, addition of NaCl decreases the cloud point of the aqueous copolymer solutions without inducing any gelation. In 25% copolymer solution containing 10% ethanol, however, the gelation point and cloud point of the solution decreases with the addition of NaCl (Figure 5b). This facilitated the formation of a thermoreversible gel with a transition temperature of 25 °C at 2.5 M NaCl.

Figure 6 (a and b) shows a study on the effect of the addition of NaCl on the micellar size and viscosity in 10% block copolymer solution containing 20% ethanol. The diffusion coefficient of the micelles and the relative viscosity of the copolymer solutions were monitored systematically as a function of NaCl concentration at 30 and 25 °C, respectively. The chosen
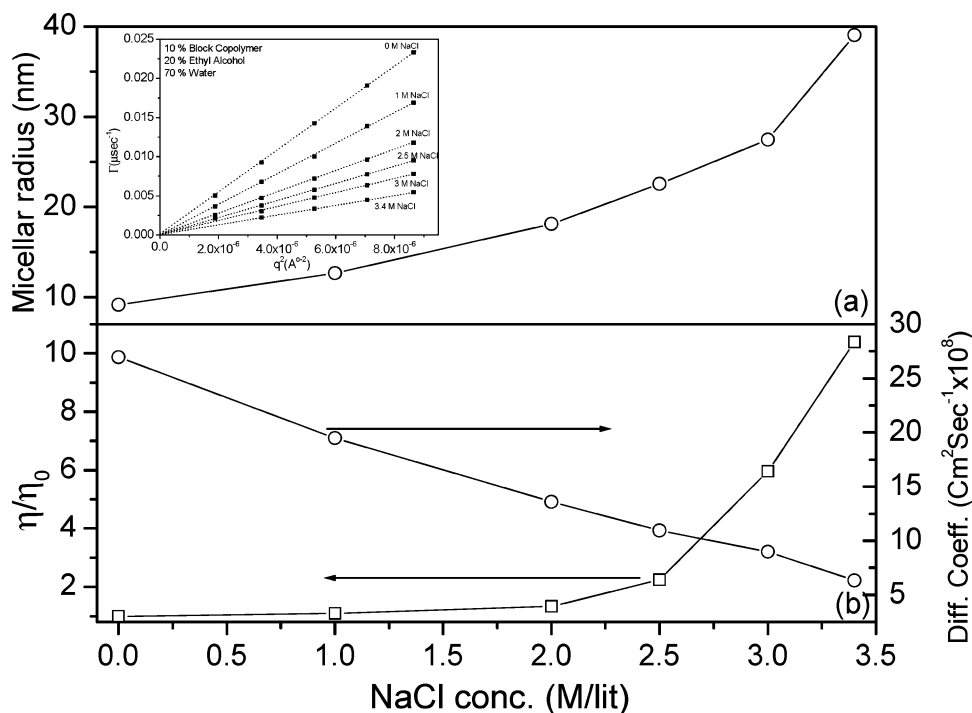
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Figure 6. (a) Variation of apparent hydrodynamic radius of the micelles with NaCl concentration for the solutions containing 10% copolymer and 20% ethanol (inset shows the corresponding relaxation rate (Γ) vs q^2 plots). (b) Relative viscosity and translational diffusion coefficient as a function of NaCl concentration.

TABLE 2: Micellar Rod Length as a Function of NaCl Concentration for the 10% Aqueous Solution with 20% Ethyl Alcohol Content

NaCl concn (mol/L)	rod length (nm)	NaCl concn (mol/L)	rod length (nm)
1	40.8	3	156.8
2	80.4	3.4	262.6
2.5	115.5		

alcohol concentration (20%) gives a high cloud point (>100 °C), and at 10% copolymer concentration no gelation is observed that will hinder the measurement of flow viscosities using capillary viscometers. The relaxation rate vs q^2 plots of the copolymer solutions (inset of Figure 6a) reflect the translational diffusive nature of the micelles. As shown in Figure 6a, the apparent micellar radius increases steadily with an increase in NaCl concentration and reaches about 39 nm at 3.4 M NaCl. Figure 6b shows that this increase in the micellar size is accompanied by a large increase in the relative viscosity of the solution. For the present block copolymer, as the maximum extended length of PO and EO chains is much less than 39 nm, it is unrealistic to have a spherical micelle of 39 nm radius. This suggests that the micelles of apparent radius of 39 nm may have either a prolate or an oblate ellipsoidal shape. At a given volume fraction, the relative viscosity of a suspension is sensitive to the shape of the colloid. A comparison of the shape factors for spheres and prolate and oblate ellipsoids suggests that the relative viscosity of prolate ellipsoids is much higher than that of oblate ellipsoids having the same equivalent hydrodynamic diameter and volume fraction.[45] Thus, it is very likely that the observed large increase in viscosity (Figure 6b) arises from sphere to prolate ellipsoidal transition of the block copolymer micelles. Similar changes in the viscosity as a result of a change in shape of the micelles from spherical to prolate ellipsoidal shape has been observed in the triblock copolymer aqueous solutions with an increase in temperature.[16] A progressive increase in the viscosity with NaCl concentration suggests that the length of the prolate ellipsoidal micelles increases with an increase in the NaCl concentration. Analysis of the diffusion

coefficient data using Perrin's formula (for prolate ellipsoid) yields an estimate of the average length of the micelles, which is summarized in Table 2. The viscosity and DLS data thus suggest that observed NaCl induced gelation results from sphere to rod growth of the copolymer micelles.

To get further evidence about the role of sphere to rod growth of the copolymer micelles in inducing gelations in the copolymer solutions, we carried out SANS studies (Figure 7) on a 10% copolymer solution containing 20% ethanol, before and after addition of 3 M NaCl at 30 °C. A large increase in the scattering intensity and disappearance of the correlation peak upon addition
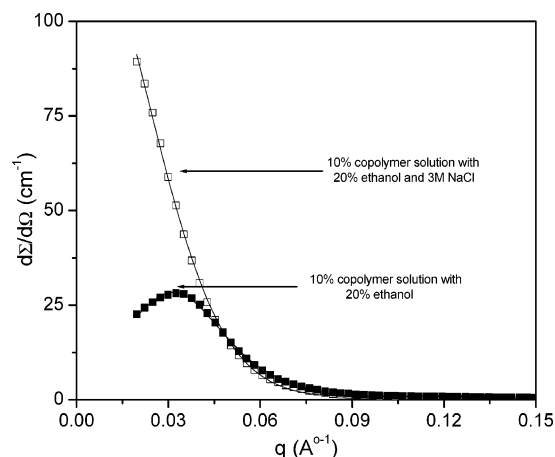

Figure 7. SANS spectra of 10% copolymer solutions with 20% ethanol in the presence and absence of 3 M NaCl at 30 °C. The solid lines represent fits to the data.

of 3 M NaCl again suggest growth of the copolymer micelles with the addition of NaCl. The data for the solution containing 3 M NaCl could be best described in terms of the prolate ellipsoidal shape of the micelles. From such an analysis, the length of the micelles present is found to be 14.3 nm with a radius of 4.8 nm. The length obtained from SANS spectra is much smaller than that calculated from DLS data. The observed difference in the length of the micelles as obtained from SANS and DLS measurements possibly arise from the limit of SANS measurement up to the lowest q value of 0.015 Å^{-1}. Accurate estimates of the lengths of the larger micelles can only be detected from measurement at still lower q values. Thus, the length obtained from SANS data reflects only the minimum length of the micelles. However, the changes in the shape of the micelles from sphere to prolate ellipsoids and subsequent growth of the micelles are evident in the SANS spectra.

Conclusion

Sodium chloride (NaCl) and ethanol (C$_2$H$_5$OH) induced sphere to rod growth of triblock copolymer [(EO)$_{20}$(PO)$_{70}$(EO)$_{20}$] micelles has been studied in aqueous medium by dynamic light scattering, neutron scattering, and viscosity measurements. The pure aqueous copolymer solutions do not show any significant growth of the micelles below their cloud points. Addition of 5−10% ethanol increases the cloud points of the solutions and induces a high-temperature gelation on approaching the cloud point. The transition temperature of such gelation increases in the presence of excess ethanol but decreases upon addition of NaCl. Systematic DLS and SANS studies on the NaCl induced growth of the copolymer micelles in 10% copolymer solutions containing ethanol suggests that the observed NaCl induced gelation in the copolymer solutions results due to sphere to rod growth of the copolymer micelles. To the best of our knowledge, this is the first observation of salt induced sphere to rod shape transition of micelles in the triblock copolymer aqueous solutions at temperatures as low as 25 °C.

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