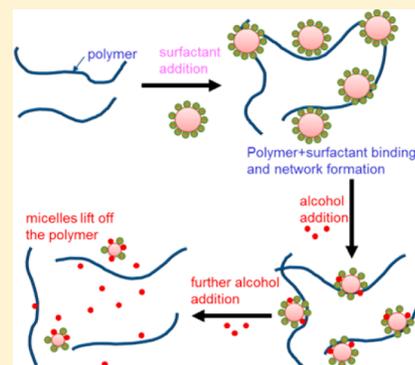


Charging and Uncharging a Neutral Polymer in Solution: A Small-Angle Neutron Scattering Investigation

Ankitkumar I. Fajalia and Marina Tsianou*

Department of Chemical & Biological Engineering, University at Buffalo, The State University of New York (SUNY), Buffalo, New York 14260-4200, United States

ABSTRACT: Aqueous formulations containing polymers and surfactants find several applications in pharmaceuticals, coatings, inks, and home products. The association between polymers and surfactants contributes greatly to the function of these complex fluids, however, the effects of polar organic solvents, ubiquitous in formulations, remain mostly unexplored. We have analyzed small angle neutron scattering (SANS) data to determine the conformation of a “model” nonionic polymer, poly(ethylene oxide) (PEO), in aqueous solutions as affected by the presence of an ionic surfactant, sodium dodecyl sulfate (SDS), and subsequent addition of short-chain alcohol (ethanol or 2-propanol). PEO chains ($M_V = 90\,000$) are Gaussian in dilute aqueous solutions, but become polyelectrolyte-like upon the addition of 30 mM SDS, with about 6 SDS micelles bound to each PEO chain. Micelles associated with polymer are similar in structure and interactions to micelles that form in aqueous solutions in the absence of polymer. Addition of alcohol alters both the polymer and micelle structure and interactions, leads to detachment of micelles from the polymer, and the PEO chains regain their Gaussian conformation. 2-Propanol is more effective than ethanol in influencing the polymer conformation and the properties of SDS micelles in aqueous solutions, either in the presence or in the absence of PEO. This study contributes fundamental insights on polymer and surfactant organization in solution, as well as new, quantitative information on systems that are widely used in practice.



1. INTRODUCTION

Nonionic polymers can interact with ionic surfactants and organize themselves to form various structures in aqueous media.¹ Interactions between polymers and surfactants depend on solution conditions such as temperature, pH, and ionic strength. Addition of polar organic solvents influences these interactions and affords additional control over self-assembly^{2–16} which is a major reason for its implementation in a wide range of industrial formulations.^{1,17–22}

Proper characterization of the interactions and the phase behavior and structure of aqueous polymer–surfactant mixtures in the presence of cosolvents such as alcohols is thus important. While a qualitative picture of how alcohols can affect polymer or surfactant aqueous solution properties has emerged, a quantitative understanding on the role of alcohol on surfactant-bound polymer chains is lacking. For example, it is not clear how alcohol molecules affect the conformation and association of polymer chains that participate in polymer–surfactant complexes. Further, how alcohol affects the bound surfactant: To what extent can alcohol change the micelle shape, size, and intermicellar interactions? Last, in what manner alcohol affects polymer–surfactant binding: Does alcohol displace polymer chains from the micelles? What is the molecular-level explanation of the changes observed upon addition of an alcohol?⁸

These questions have been addressed in the literature to varying degrees by using various experimental techniques such as viscosity,^{8,23} conductivity,⁸ fluorescence,⁵ potentiometry,²

tensiometry,³ turbidimetry,³ dynamic light scattering (DLS),³ scanning electron microscopy (SEM),³ nuclear magnetic resonance (NMR),⁸ and isothermal titration calorimetry (ITC),^{3,7} as well as with molecular simulations.^{24–26} Reports using structural characterization techniques such as small-angle neutron scattering (SANS) are less common. This is despite the fact that SANS offers the unique capability to provide structural information on a certain domain of an overall structure by matching the scattering contrast of other domains to that of the solvent. SANS investigations on polymer–surfactant complexes formed in aqueous solutions have been pioneered by Cabane et al.^{27,28} who, for the case of the nonionic polymers poly(ethylene oxide) (PEO) or ethyl(hydroxyl ethyl)cellulose (EHEC) in the presence of sodium dodecyl sulfate (SDS), have shown a polyelectrolyte-like behavior of the polymer chains due to bound surfactant micelles. Using SANS, Chari et al. reported on the micelle dimensions and intermicelle spacing of SDS bound to PEO at different salt concentrations.²⁹ To our best knowledge, the only SANS study that examined polymer–surfactant aqueous solutions in the presence of an alcohol is that by Griffiths et al.⁵ who considered ethanol effects on interactions between poly(vinylpyrrolidone) (PVP) and SDS in terms of changes in the polymer conformation, surfactant

Received: March 6, 2014

Revised: June 14, 2014

Published: July 11, 2014

micellization, polymer–surfactant binding, and polymer–polymer/polymer–micelle interactions.

The major objective of the present study is to address fundamental questions on how short-chain alcohols affect the conformation of polymer chains and the structure of micelles incorporated in polymer–surfactant complexes in aqueous solutions, and to provide molecular-level interpretation of the reported changes in bulk solution properties upon addition of alcohol. To this end, we selected the nonionic polymer PEO and the ionic surfactant SDS as “model” ingredients,^{17,29–33} and we utilized SANS with contrast variation as the most appropriate technique to access the information that we seek. Short chain alcohols are known to influence the solvent quality of water for PEO³⁴ and the bulk solution properties of PEO–SDS complexes.⁸ At lower concentrations in aqueous media, short-chain alcohols can act as cosurfactants and localize in micelles, and at higher concentrations as cosolvents, affecting primarily the solvent phase (e.g., increasing its hydrophobicity).^{35–41} Accordingly, in the present study, we have investigated the effects of both ethanol and 2-propanol, over a wide concentration range.

In what follows, we first examine polymer–water–alcohol and surfactant–water–alcohol solutions, where the polymer or surfactant is hydrogenous and the solvent (water and alcohol) deuterated, to establish the effect of alcohol on the conformation of the polymer and the structure of the micelles separately. We then consider polymer–surfactant–water–alcohol solutions, with scattering contrast between the hydrogenous polymer and surfactant and the deuterated solvent, to reveal the structure of the polymer + surfactant association as affected by alcohol type and concentration. We also analyze solutions with deuterated surfactant in order to directly assess the conformation of (hydrogenated) polymer involved in polymer + surfactant associations.

To the best of our knowledge, this is the first SANS study on PEO–SDS–water–alcohol systems, only the second paper that utilizes SANS for the study of polymer–surfactant–water–alcohol solutions, and one of just four reports on alcohol effects on PEO–SDS–water systems. SANS data on PEO with MW 90 000 at the solvents and polymer concentration range considered here have not been previously reported. And while SDS–water–*n*-propanol solutions have been studied by SANS,^{36,37} the effect of 2-propanol on SDS micelles has not been investigated by this technique yet. Thus, this investigation provides fundamental insights on polymer and surfactant organization in solution, and needed structural information for widely used systems.

2. MATERIALS

Poly(ethylene oxide) of $M_w = 90\,000$ ($M_w/M_n = 1.09$) was obtained from Polymer Source Inc. (Dorval, Quebec, Canada). Hydrogenous sodium dodecyl sulfate (SDS) was purchased from Sigma and deuterated sodium dodecyl sulfate ($(CD_3(CD_2)_{11}OSO_3Na)$ (D2S, 98%) from Cambridge Isotope Laboratories, Tewksbury, MA. Heavy water (D_2O), deuterated ethanol (C_2D_5OD) (D, 99%), and deuterated 2-propanol ($(CD_3)_2CDOD$) (D, 99%) were purchased from Cambridge Isotope Laboratories, Tewksbury, MA. All chemicals were used as received. The deuterated chemicals were stored in a desiccator or ampules to prevent contamination with H_2O from the atmosphere. Stock solutions of polymer or surfactant in heavy water were first prepared, and then mixed with each other and with deuterated alcohol, where appropriate, to

prepare the desired final concentrations. Adequate time for equilibration was allowed.

SANS measurements of PEO aqueous (D_2O) solutions with polymer concentrations of 0.2, 0.5, 1, and 2 wt % were first performed in order to investigate the effect of polymer concentration on chain conformation covering the dilute up to semidilute range. In subsequent experiments with samples containing SDS and/or alcohol, the PEO was kept at 0.5 wt %, which is well below the overlap concentration,⁴² in order to reduce the influence of large clusters.

We then investigated surfactant–water–alcohol solutions to assess the effect of alcohol on “free” micelles (in the absence of polymer) in terms of changes in the onset of micellization, micelle structure, localization of alcohol, and intermicellar interactions. The deuterated ethanol concentrations used were 10 and 20 wt %, while deuterated 2-propanol varied from 5 to 20 wt % in the present study. At any alcohol concentration used in our study, the SDS concentration was 30 mM which is well above the critical micelle concentration (CMC) values.^{39,43}

We have performed SANS of PEO+SDS aqueous solutions in the absence of added alcohol in order to establish the reference case for the subsequent study on alcohol effects. In particular, we examined dilute PEO solutions (0.5 wt %) in the presence of hydrogenous SDS at a lower concentration (8 mM) and at a higher concentration (30 mM). To reveal the polyelectrolyte-like nature of the PEO chains in the presence of bound SDS, we have investigated aqueous 0.5 wt % PEO with 30 mM deuterated SDS. In the absence of alcohol, the addition of small amount of SDS ($C_{SDS} < \sim 10$ mM) to a dilute PEO solution leads to formation of a small number of micelles on the each PEO chain which are not sufficient to bridge adjacent PEO chains.²⁹ However, above 10 mM SDS, the increased number of micelles enhances interpolymer chain bridging and causes an increase in the solution viscosity up to a saturation surfactant concentration (~ 75 mM).²⁹

Finally, having established the conformation of PEO in water and in water + alcohol solutions, the structure and interactions of SDS micelles in water and in water + alcohol solutions, and the structure of PEO bound with SDS in water, we focus to the main object of this investigation, the effects of alcohol on the polymer conformation in the presence of bound SDS. To this end, we carried out SANS on solutions containing 0.5 wt % PEO and 30 mM h-SDS or 0.5 wt % PEO and 30 mM d-SDS in the presence of 20 wt % ethanol-*d* or 2-propanol-*d*. The alcohol concentration (20 wt %) was selected such that it is not too high to completely dis-assemble micelles, but sufficient to have an effect on polymer–surfactant interactions.

3. METHODS

Small-Angle Neutron Scattering (SANS): Method of Approach. Scattering data obtained from SANS measurements were analyzed using various structural models in order to extract information regarding polymer conformation, micelle structure, and polymer–polymer/polymer–micelle/micelle–micelle interactions.

In dilute solutions of water and short-chain alcohol, PEO exhibits random coil or swollen conformation.^{34,42} At higher polymer/alcohol concentrations, a decreased polymer solvency leads to formation of large clusters. To describe the above, we first invoke the correlation length model to analyze SANS data for PEO–water, PEO–water–alcohol or PEO–SDS-*d*–water–alcohol systems. We found nearly random coil conformation of individual PEO chains at the conditions examined. Sub-

sequently, we derive conformation-related parameters of PEO chains, such as contour length, end-to-end distance, and monomer length, using the Debye + power law model.

Bound micelles have a profound effect on PEO conformation. Scattering from D₂O solutions of PEO with deuterated SDS shows a strong interaction peak at intermediate q that is reminiscent of scattering from a polyelectrolyte. We thus invoke the polyelectrolyte model^{44,45} to capture the scattering in the intermediate q range. From fittings to this model we were able to obtain the effective monomer length and the fractional charge for a polymer chain which are important in determining the number of micelles bound to each chain. The overall scattering from SDS micelles depends on the micelle shape and size captured by the prolate core–shell form factor^{36,46} and the micelle interactions expressed by a Hayter–Penfold-type structure factor.^{36,46,47}

SANS Data Collection and Reduction. SANS measurements were performed on the 30 m spectrometer (NG3) at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. Neutrons with wavelength of 6 Å and wavelength spread ($\Delta\lambda/\lambda$) of 14.3% were focused on the sample kept in 4 mm quartz cell at 25 ± 0.1 °C. All data are for this temperature. Sample-to-detector distances of 2 and 10 m were used for each of the samples to cover the wave-vector (q) range of $0.005 \text{ \AA}^{-1} < q < 0.3 \text{ \AA}^{-1}$. The beam time was between 180 and 4800 s for each of the measurements. Scattering data were corrected for the scattering from background, empty cell, and detector sensitivity. Absolute scale intensity was obtained by normalizing the scattered intensity with a well characterized polystyrene/deuterated polystyrene standard by NIST-supplied data reduction tools.⁴⁸ Absolute intensity data were then corrected for incoherent solvent scattering. Reduced SANS data were fitted to the various models described below using a nonlinear least-square method based on the Levenberg–Marquardt algorithm to obtain appropriate values of the fitting parameters. The uncertainties in the fitting parameters are specified as one standard deviation in the fitting coefficient, and are automatically calculated from the fitting function of the IGOR PRO software which estimates these values using the measurement errors assuming normally distributed errors.

SANS Data Analysis: Polymer Conformation. We have utilized three different types of models to describe the polymer conformation, depending on the scattering profile. The correlation length and the Debye + power law models were invoked to describe the scattering behavior of polymer in water–alcohol solution, either in the absence of surfactants or when the surfactant effect on the polymer conformation is negligible (i.e., at high amount of alcohol present). The scattering profiles in these cases reflect random coil conformation of individual chains at intermediate q , along with some low q features indicative of large clusters with no interaction peak. To obtain physically more appropriate radii of gyration for the individual polymer chains, compared to the values estimated from correlation length model fits, we have utilized the Debye model which analytically represents the scattering behavior of Gaussian polymer chains. In polymer–surfactant solutions with surfactant concentrations above the critical aggregation concentration, micelles bind along the polymer chain in a “bead-on-necklace” manner.^{27,49} Because of this, the nonionic polymer exhibits scattering behavior similar to that of a charged polymer or polyelectrolyte, i.e., the scattering profile shows an interaction peak because of charge–charge repulsions between micelles along the polymer

chain.^{27,50} The polyelectrolyte + power law model was thus used to describe scattering that includes a distinct interaction peak due to bound micelles (polymer–surfactant solutions with deuterated surfactants in the absence of alcohol or at low alcohol concentrations).

Correlation Length Model. The correlation length model consists of a combination of Lorentzian and power law terms:⁵⁰

$$I(q) = \frac{I_p}{q^P} + \frac{I_L}{1 + (q\xi)^m} + B \quad (1)$$

The second term in eq 1 describes the scattering behavior of polymer chains or network for polymer concentrations below or above the overlap concentration, respectively. The Lorentzian exponent m was fixed³⁴ at $m = 2$, assuming a Gaussian nature of PEO chain at that length scale. The first term in eq 1 describes the Porod scattering from large objects (clusters) with the power law exponent P capturing the scattering behavior at low q values.

The correlation length ξ describes the average distance between two polymer chain intersections in the case of semidilute solution, and is related to the radius of gyration of a single Gaussian polymer chain at intermediate q values: $R_g = \sqrt{2}\xi$. The scale factor I_L captures the solvation scattering of the polymer: a lower I_L value indicates more effective solvation.³⁴ The power law exponent P reflects the mass fractal dimension of the clusters, and I_p the scattering contribution of clusters. P , ξ , I_p , I_L , and incoherent background B are fitting parameters.

Debye + Power Law Model. The Debye + power law model for scattering of a polymer solution is described by the following equation:⁵¹

$$I(q) = \frac{I_p}{q^P} + I_D \left[\frac{2(e^{-x} + x - 1)}{x^2} \right] + B \quad (2)$$

The second term in eq 2 represents the scattering from individual polymer chains at intermediate q values, while the first term represents the scattering from large clusters at low q . The variable x is related to the radius of gyration R_g : $x = (qR_g)^2$, I_D represents a scale factor corresponding to Debye scattering, while I_p represents a scale factor for clustering.

The power law exponent P , radius of gyration R_g , scale factors I_p and I_D , and incoherent background B are the fitting parameters. The chain end-to-end distance R_0 can be obtained from R_g : $R_0^2 = 6R_g^2$. The Debye intensity factor I_D is related to the polymer volume fraction ϕ_p , scattering contrast $\Delta\rho$, degree of polymerization Z_p , and volume of a monomer v_m by the relation: $I_D = \phi_p(\Delta\rho)^2 Z_p v_m$, where $\Delta\rho$ is the difference between the scattering length densities of the polymer and solvent. The clustering strength I_p/q^P at low q values reflects polymer–polymer association related to phase separation.³⁴

Polyelectrolyte + Power Law Model. In the case of PEO chains bound to SDS micelles in the absence of alcohol, we have utilized the polyelectrolyte + power law model:^{44,45}

$$I(q) = \frac{I_p}{q^P} + \frac{K}{4\pi L_B \alpha^2} \frac{(q^2 + \kappa^2)}{1 + R_0^2(q^2 + \kappa^2)[q^2 - (12hC/a_m^2)]} + B_{inc} \quad (3)$$

The second term in eq 3 represents the polyelectrolyte structure factor^{44,45} and the first term represents the power-law type scattering at low q due to large clusters present in the solution. κ is the Debye length and L_B is the Bjerrum length. K

is the scattering contrast factor for the polymer and was calculated from $K = (b_p - v_p b_s / v_s)^2$, given the scattering lengths of the monomer b_p and solvent b_s , along with specific volumes of the monomer v_p and solvent v_s . C is the molar concentration of the polymer (number of moles of monomers present in a unit volume) and h a virial parameter which is a function of the second and third virial coefficient for monomer–monomer interactions.^{44,45} The radius R_0 was calculated from $R_0^2 = (1/\alpha\sqrt{C}) (\alpha_m/(48\pi L_B)^{1/2})$.⁴⁵ To reduce the number of fitting parameters K was calculated from the molecular volumes and scattering lengths of the monomer and solvent. h was fixed at 12 \AA^3 .⁴⁵

The main fitting parameters are the polymer degree of ionization α , effective monomer length a_m , power law intensity I_p , and power law exponent P_e . The extracted values of α and a_m are important in the determination of the total number of charges present on a polymer chain.

A schematic for polymer conformation without or with bound surfactant micelles is shown in Figure 1. Given the

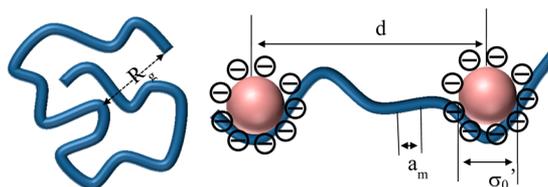


Figure 1. Schematic of polymer conformation without/with bound surfactants: Random coil (left) in the absence of bound surfactants, and extended, polyelectrolyte-like conformation with bound micelles (right). R_g is the polymer coil radius of gyration, a_m the effective monomer length between two charges on a chain, d the intermicelle distance, and σ_0' the effective micelle diameter.

surfactant aggregation number and the number of charges present on each micelles (obtained separately from fitting SANS data of polymer bound surfactants as described below), the number of micelles bound per polymer chain, and thereby the amount of bound surfactants per polymer chain, can be estimated.

SANS Data Analysis: Micelle Structure and Interactions. A charged core–shell ellipsoid^{36,47} (Figure 2) is used here to describe the SDS micelles. The overall scattering intensity $I(q)$ is given by

$$I_{micelle}(q) = A \cdot \phi \cdot P(q) \cdot S(q) + B_{inc} \quad (4)$$

The form factor $P(q)$ calculated using eqs 5 and 6 represents the shape and structure of a micelle, while the structure factor $S(q)$ represents the intermicelle interactions and arrangement of micelles in the solution. ϕ is the volume fraction of the micelles, which in turn depends on the overall surfactant concentration. The parameters A and B_{inc} account for additional contributions due to absolute scaling and incoherent noise, respectively.

$$P(q) = \frac{1}{V_{TOT}} \int_0^{\perp} |F(q, a, b, \delta, \beta)|^2 d\beta \quad (5)$$

$$F(q, a, b, \delta, \beta) = V_C(\rho_1 - \rho_2) \frac{3j_1(u_C)}{u_C} + V_{TOT}(\rho_2 - \rho_s) \frac{3j_1(u_T)}{u_T} \quad (6)$$

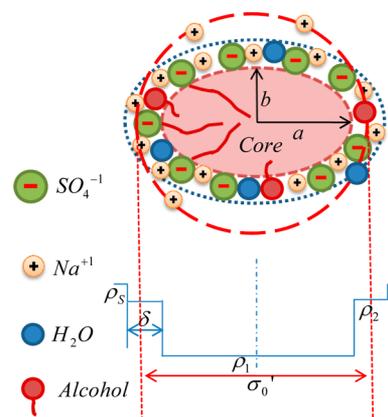


Figure 2. SDS micelle represented as a core–shell prolate ellipsoid. The core has a major axis a and minor axis b , and comprises of hydrophobic alkyl tails of surfactants and alcohol. The shell has thickness δ and consists of surfactant head groups, associated water molecules, counterions, and hydroxyl groups of alcohols. ρ_1 , ρ_2 , and ρ_s are the scattering length density of core, shell, and solvent, respectively. σ_0' is the equivalent spherical diameter of the ellipsoid.

The first term in eq 6 represents scattering due to the micelle core with volume $V_C = (4\pi/3) ab^2$, where a is the major and b the minor core radius. The second term in eq 6 signifies scattering due to the micelle shell (constant shell thickness δ) of the micelle with volume $V_{TOT} = (4\pi/3)(a + \delta)(b + \delta)^2$. $j_1(u)$ denotes first order spherical Bessel function of first kind expressed by $j_1(u_i) = (\sin u_i - u_i \cos u_i)/u_i^2$, where $u_i = q [a_i^2 \beta^2 + b_i^2(1 - \beta^2)]^{1/2}$. ρ_1 , ρ_2 , and ρ_s are the scattering length densities of the micelle core, micelle shell, and solvent, respectively.⁴⁶

The structure factor $S(q)$ was calculated using a Hayter–Penfold-type potential,⁵² with mean spherical approximation and rescaling corrections for low volume fractions, given the micelle volume fraction, charge on a micelle, and ionic strength of the solution.

The major fitting parameters to describe scattering from micelles in the absence of added polymer are the surfactant aggregation number η , micelle volume fraction ϕ , charge on a micelle Z , and number of alcohol molecules per micelle η_E . The micelle core radius b was obtained from the Tanford formula for a fully stretched alkyl chain⁵³ $b = 1.5 + 1.265N_C$ (\AA) where N_C is the number of carbon atoms in the chain ($N_C = 12$ for SDS). The core volume V_C (\AA^3) was calculated given the surfactant aggregation number and number of alcohol molecules per micelle using $V_C = \eta V_{t_{SDS}} + \eta_E V_{t_{Alcohol}}$ where $V_{t_{SDS}}$ and $V_{t_{Alcohol}}$ are the volume of hydrocarbon chains of the surfactant and alcohol molecules present in the micelle core, obtained from Tanford's formula $V_{t^*} = 27.4 + 26.9N_C$ (\AA^3) using $N_C = 12$ for SDS, $N_C = 2$ for ethanol, and $N_C = 3$ for 2-propanol. The major micelle core radius a was determined using the core volume, from which the major to minor axis ratio ϵ was determined. In the occasion (at high alcohol content) where fixing $b = 16.7 \text{ \AA}$ would result in $\epsilon < 1$, the data were fitted using core–shell sphere ($\epsilon = 1$) with equivalent spherical radius calculated using the same core volume V_C as determined before. The total volume of a micelle was calculated from the core volume V_C and the shell volume V_{Shell} considering volume contributions from head groups, counterions, water molecules, and polar –OD groups of alcohol present in the shell, using $V_{TOT} = \eta (V_{OSO_3^-} + (1 - \alpha) V_{Na^+} + N_H V_{D_2O}) +$

$k(V_{OD} + N_{HE}V_{D_2O}) + V_C$ where α is the fractional charge on a micelle defined as Z/η . N_H and N_{HE} are hydration numbers, number of water molecules associated per molecule of surfactant headgroup or ethanol, respectively, and were fixed at $N_H = 10$ and $N_{HE} = 2$, following reference 36. $V_{OSO_3^-}$, V_{Na^+} , V_{D_2O} , and V_{OD} are the molecular volume of head groups, counterions, deuterated water molecule, and polar $-OD$ group of the alcohol molecule, respectively. The shell thickness δ was calculated iteratively using the total micelle volume and micelle core volume.

Table 1 presents values of molecular parameters used for SANS data fittings. Scattering length densities of the core ρ_1

Table 1. Scattering Lengths and Parameters Used for Fitting SANS Data of SDS Solutions^a

species	$10^3 \times \Sigma b_i$ (Å)	v_i (Å ³)	$10^5 \times \rho_i$ (Å ⁻²)	n_i ³⁶
Na ⁺	0.0363	8.99 ^b	0.4038	6
OSO ₃ ⁻	0.2602	49.80 ^b	0.5224	4
OD	0.1247	15.80 ^c	0.7895	2
D ₂ O	0.1915	30.19 ^d	0.6341	
ethanol- <i>d</i>	0.5913	96.99 ^d	0.6097	
CH ₃	-0.0457	54.30	-0.0841	
CH ₂	-0.0083	26.90	-0.0307	
CD ₃	0.2666	54.30	0.4911	
CD ₂	0.1999	26.90	0.7432	
H ⁺	-0.0374	-	0.0000	

^a Σb_i is the scattering length of species i (sum of the scattering lengths of atoms present in the group⁵⁵), v_i is the molecular volume of species i , and n_i is the number of water molecules associated with each of the species i . ^bMolecular volumes from ref 46. ^cMolecular volume of $-OH$ group in ethanol was calculated by subtracting volume of CH_3-CH_2 from the volume of an ethanol molecule. ^dMolecular volumes were calculated from bulk density at 25 °C. Molecular volumes of CH_3 , CH_2 groups are calculated from the Tanford formula.⁵³

and the shell ρ_2 were calculated by the addition of scattering length contributions of the groups/atoms present (given in Table 1) and the molar volumes of the micelle core V_C and the shell V_{shell} respectively. The scattering length density of solvent ρ_s was calculated utilizing the scattering lengths of alcohol and heavy water, mole fractions of alcohol present, and the bulk densities of the solution. The scattering length density of deuterated alcohol is almost similar to that of D₂O. The dielectric constant values used for different water–alcohol mixtures were obtained from the literature.⁵⁴

The form factor, structure factor, and, thereby, the overall scattering intensity profile were calculated using all the fitting parameters, fixed parameters, calculated micelle dimensions, and scattering length densities. The fitting procedure, we have followed is similar to that by Caponetti et al.³⁶ except the fact that in our study we varied the number of alcohol molecules per micelle as a fitting parameter, whereas they have deduced the aggregation number of alcohol from the increase in the volume fraction of the dispersed (micellar) phase in the presence of alcohol as compared to that in the “plain” surfactant case.

SANS Data Analysis: Polymer in the Presence of Hydrogenous Surfactant. The overall scattering intensity of polymer + surfactant solution was taken as the additive contribution of polymer scattering and of surfactant micelle scattering as shown in eq 7.⁵

$$I(q) = I_{polymer}(q) + I_{micelles}(q) \quad (7)$$

The first term in eq 7 represents the scattering due to polymers associated with surfactants in the case where the surfactants are deuterated to match out their scattering contrast with that of the deuterated solvent. The second term represents scattering due to surfactant micelles either bound to the polymers or free, depending on the alcohol concentration. At higher alcohol concentration (20 wt %), micelles detach from the polymer chains, and the polymer regains its original random coil conformation which has been captured using the “Debye + power law model”. The scattering contribution of the hydrogenous surfactant micelles $I_{micelles}(q)$ was calculated by subtracting the polymer scattering $I_{polymers}(q)$ from the measured overall intensity $I(q)$, and was fitted to the “charged prolate core-shell model” described in the preceding section.

4. RESULTS AND DISCUSSION

4.1. Polymer in Solution: PEO Conformation. We first analyze the conformation and clustering of PEO in water (D₂O) in the absence and in the presence of alcohol, but in the absence of any added surfactant.

Conformation of PEO in Water (No Alcohol). Scattering profiles from aqueous PEO solutions at room temperature are shown in Figure 3. With an increase in polymer concentration,

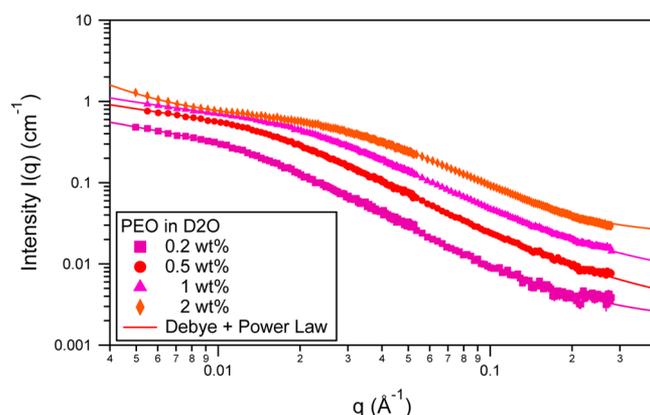


Figure 3. Effect of polymer concentration on SANS intensity profiles from aqueous (D₂O) solutions of PEO. Markers are experimental data and solid lines represent fits using the Debye + power law model.

the Guinier region near $q = 0.01$ shifts toward higher q values indicating smaller coil dimensions. At 2 wt % polymer, the low q features become stronger, indicative of formation of larger clusters.

Table 2 shows the parameters extracted from the SANS data when fitted with the correlation length model. The Lorentzian screening length ξ decreases with an increase in polymer concentration. The Lorentzian exponents are found in all samples close to 1.94 reflecting the Gaussian nature of the individual PEO chains at the temperature considered (25 °C). In this case, values of radius of gyration for individual polymer coils (shown in Table 2) can be estimated from ξ using $R_g^0 = \sqrt{2}\xi$. Using the radius of gyration value (122 Å) obtained for 0.2 wt % PEO solution we estimated the overlap concentration $C^* = MW/(4\pi R_g^3 N_{AV}/3) \times 100 = 2.02$ wt %, which indicates that all the samples of Figure 3 fall in the dilute concentration range for which the Debye model can be applied. On the other end, the extent of clustering, as indicated by values of the

Table 2. PEO Concentration Effect on Parameters Extracted from SANS Data Fits Using the Correlation Length Model.^a

	PEO concentration (wt %)			
	0.2	0.5	1	2
power law scale	1.37×10^{-05} ($\pm 1.30 \times 10^{-6}$)	2.71×10^{-05} ($\pm 1.65 \times 10^{-6}$)	3.58×10^{-05} ($\pm 1.22 \times 10^{-6}$)	5.29×10^{-08} ($\pm 3.60 \times 10^{-08}$)
power law exponent n	1.65 (± 0.00)	1.65 (± 0.01)	1.66 (± 0.00)	3.05 (± 0.13)
Lorentzian scale	0.470 (± 0.005)	0.717 (± 0.004)	0.765 (± 0.002)	0.754 (± 0.007)
Lorentzian screening length (\AA)	87 (± 0.0)	66 (± 0.0)	47 (± 0.1)	31 (± 0.3)
Lorentzian exponent m	1.99 (± 0.01)	1.94 (± 0.00)	1.94 (± 0.00)	1.94 (± 0.01)
estimated R_g^0 (\AA)	122	94	67	44
clustering strength at $q = 0.004 \text{ cm}^{-1}$	0.124	0.245	0.342	1.075
reduced χ^b	1.11	1.14	1.01	1.03

^aValues of uncertainties in the fitting parameters are shown below the parameters in parentheses in *italics*. ^bReduced χ values⁵⁶ were calculated using $\chi = ((1/(N - N_p + 1)) \sum_{i=1}^N [(y_i - y_i^m)/\sigma_i]^2)^{1/2}$ where y_i is the experimental data, y_i^m is the model prediction, σ_i is the standard deviation of the measurement, N is the number of data points, and N_p is the number of fitting parameters.

Table 3. PEO Concentration Effect on Parameters Extracted from SANS Data Fit Using the Debye + Power Law Model

	PEO concentration (wt %)			
	0.2	0.5	1	2
scale	0.358 (± 0.010)	0.545 (± 0.003)	0.559 (± 0.002)	0.640 (± 0.002)
R_g (\AA)	121 (± 1.4)	94 (± 0.3)	66 (± 0.1)	43 (± 0.0)
clustering coefficient, A	1.32×10^{-4} ($\pm 9 \times 10^{-6}$)	7.59×10^{-4} ($\pm 3 \times 10^{-5}$)	1.60×10^{-3} ($\pm 2 \times 10^{-5}$)	1.06×10^{-5} ($\pm 1 \times 10^{-6}$)
cluster power exponent n	1.34 (± 0.02)	1.13 (± 0.01)	1.06 (± 0.02)	2.06 (± 0.00)
clustering strength at $q = 0.004 \text{ cm}^{-1}$	0.222	0.390	0.554	0.941
reduced χ	1.10	1.04	1.12	2.91

clustering strength calculated at very low q value ($q = 0.004 \text{ \AA}^{-1}$), increases with an increase in polymer concentration. Hence, data were also fitted with the Debye + power law model which can provide physically more appropriate values of radius of gyration of Gaussian coils (Table 3). The obtained radius of gyration depends on polymer concentration as $R_g \sim C_p^{-0.45}$. A similar trend of radius of gyration decrease with increase in PEO concentration in aqueous solutions has been reported by Hammouda et al.⁴² for shorter chain PEO molecules (MW 41 500). A decrease in the Lorentzian screening length and an increase in clustering with polymer concentration were also observed.⁴²

Effect of Alcohol on Conformation of PEO. Figure 4 shows the effects of alcohol addition on the scattering profiles of 0.5 wt % PEO aqueous solutions. The PEO concentration selected was 0.5 wt %, well below the overlap concentration where the clustering strength is relatively low, so that we focus on the effect of alcohol on individual polymer chains rather than on the clusters. Whereas the addition of 20 wt % ethanol-*d* does not change much the PEO scattering compared to that in plain water, the addition of similar amount of 2-propanol does. To our best knowledge, no SANS data for PEO in 2-propanol-water solutions have yet been reported in the literature.

Scattering data were fitted with the correlation length model as well as the Debye + power law model, and the extracted parameters are listed in Table 4 and 5, respectively. Ethanol does not change much the conformation of individual polymer

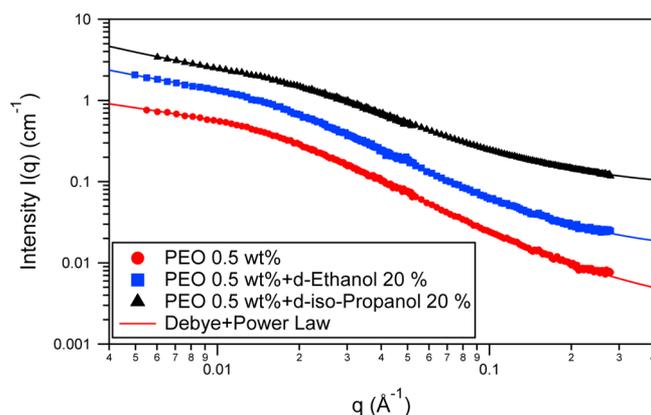


Figure 4. SANS intensity profiles from aqueous (D_2O) solutions of PEO (0.5 wt %) in the presence of 20 wt % deuterated ethanol or 2-propanol. Markers represent experimental data and solid lines represent the corresponding model fits using Debye + power law model. (Note: An intensity offset of 10 and 100 has been applied to SANS data and fits of the ethanol- and 2-propanol-containing solutions, respectively.)

chains, as seen by minor deviation in radius of gyration or Lorentzian screening length values from the corresponding values in the absence of alcohol. 2-propanol on the other hand, decreases the PEO radius of gyration to 66 from 94 \AA , which may indicate local dehydration because of the competitive

Table 4. Alcohol Concentration Effect on Parameters Extracted from SANS Data Fits Using the Correlation Length Model for 0.5 wt % PEO Aqueous Solutions^a

	no alcohol	ethanol- <i>d</i>	2-propanol- <i>d</i>
power law scale	2.71×10^{-05} ($\pm 1.65 \times 10^{-6}$)	3.3×10^{-05} ($\pm 2.30 \times 10^{-6}$)	0.0013 ($\pm 1.50 \times 10^{-5}$)
power law exponent	1.65 (± 0.01)	1.65 (± 0.00)	1.06 (± 0.00)
Lorenzian scale	0.717 (± 0.004)	0.662 (± 0.010)	0.269 (± 0.002)
Lorenzian screening length (Å)	66 (± 0.0)	67 (± 0.5)	46 (± 0.2)
Lorenzian exponent	1.94 (± 0.00)	1.94 (± 0.00)	2.0 (± 0.00)
estimated R_g^0 (Å)	94	95	66
clustering strength at $q = 0.004 \text{ cm}^{-1}$	0.245	0.300	0.516
reduced χ	1.14	1.04	1.79

^aValues of uncertainties in the fitting parameters are shown below the parameters in parentheses in *italics*.

Table 5. Alcohol Concentration Effect on Parameters Extracted from SANS Data Fits Using the Debye + Power Law Model for 0.5 wt % PEO Aqueous Solutions

	no alcohol	ethanol- <i>d</i>	2-propanol- <i>d</i>
scale	0.545 (± 0.003)	0.473 (± 0.009)	0.210 (± 0.002)
R_g (Å)	94 (± 0.3)	93 (± 0.9)	65 (± 0.1)
clustering coefficient, A	7.59×10^{-4} ($\pm 3 \times 10^{-5}$)	5.46×10^{-4} ($\pm 4.2 \times 10^{-5}$)	0.0015 ($\pm 2.0 \times 10^{-5}$)
cluster power exponent n	1.13 (± 0.01)	1.23 (± 0.02)	1.1 (± 0.01)
clustering strength at $q = 0.004 \text{ cm}^{-1}$	0.390	0.484	0.516
reduced χ	1.04	1.03	1.78

hydrogen bonding of 2-propanol with water present in the hydration shell of PEO chains.⁹ A similar decrease in the PEO radius of gyration has been reported in water–methanol solutions.⁵⁷ The observed decrease in solvation intensity (Lorenzian scale) in the water–alcohol system (Table 4) indicates the water–2-propanol mixture as a more effective solvent for PEO chains.³⁴

Alcohol addition increases PEO clustering as evident from higher values of the clustering strength. The amount of clusters is higher for 2-propanol–water system compared to ethanol–water. Addition of alcohol enhances hydrophobic interactions between chain ends which are responsible for higher amount of clustering.⁵⁸ The effect of ethanol on the solvation and clustering of semidilute 4 wt % PEO (MW 42900) solutions have been studied by Hammouda et al.³⁴ who reported a better solvency of PEO in water–alcohol mixtures, similar to our study.

4.2. Surfactant in Solution: SDS Micelles. In order to establish the effect of alcohol on structure and interactions of “free” (i.e., not bound to polymer) micelles, we have performed SANS on deuterated water–alcohol solutions containing 30 mM hydrogenous SDS but no polymer. To the best of our knowledge, SANS data on SDS in aqueous 2-propanol solutions have not been previously reported.

Effect of Ethanol on SDS Micelle Structure and Intermicellar Interactions. Ethanol effects on SANS data for

aqueous SDS solutions are shown in Figure 5. The correlation peak reflects repulsive interactions between micelles. The

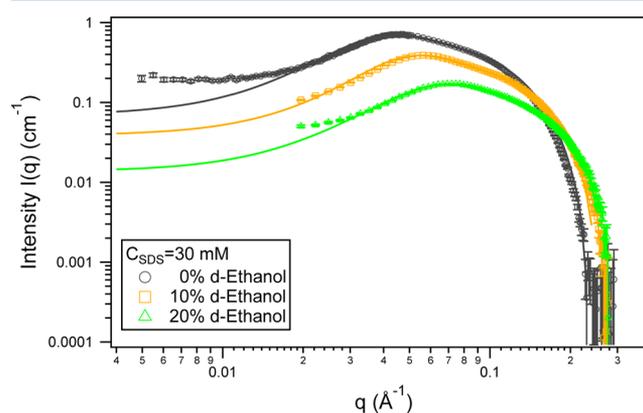


Figure 5. Effect of deuterated ethanol on SANS intensity profiles from 30 mM SDS in D_2O . Markers indicate experimental data and solid lines represent fits based on the core–shell prolate ellipsoid form factor and Hayter–Penfold-type structure factor.

intermicelle distance d can be estimated from the q value at the peak maximum $d = 2\pi/q_{\text{max}}$. As the ethanol concentration increases, the intermicelle distances decrease. Since the surfactant concentration has been kept constant, such a decrease in d reflects an increase in the micelle number density which is possible only if the micelles become smaller. The peak intensity decreases strongly with the addition of ethanol, indicating weaker electrostatic repulsions between the micelles.

Table 6 summarizes some of the important parameters obtained by the SANS data fits. Addition of 20 wt % ethanol leads to a sharp decrease by $\sim 72\%$ of the aggregation number η (number of surfactants per micelle), eventually, leading to a disassembly of the micelles. The micelle size is also reduced as evident by decreasing values of effective micelle diameter σ and shell thickness δ . Further, the micelle shape changes from an elongated prolate to a sphere upon addition of ethanol. The average surface area per surfactant headgroup in a micelle drops from its initial value of 92.7 \AA^2 , in the absence of alcohol, to 72.5 \AA^2 at 10 wt % ethanol, and then again increases to around 94.3 \AA^2 at 20 wt % ethanol. These changes suggest denser packing of surfactants in the micelle owing to the “co-surfactant effect” at lower alcohol concentrations, but less dense packing

Table 6. Parameters Obtained by Fitting SANS Data of 30 mM SDS in D₂O + Ethanol-*d* Solution (in the Absence or the Presence of PEO) Using the Form and Structure Factors Described in the Text^a

C_E (wt %)	η	α	$\phi \times 10^3$	η_E	b (Å)	ϵ	δ (Å)	Γ_k	κ^{-1} (Å)	d (Å)	red. χ
No PEO											
0	76.0 (± 0.1)	0.14 (± 0.04)	9.43 (± 0.004)	0.0	16.7	1.4	4.9	0.45	76.4	178.8	10.60
10	44.3 (± 0.2)	0.25 (± 0.06)	11.96 (± 0.018)	20.0 (± 0.9)	16.0	1.0	4.2	0.40	52.2	142.4	5.94
20	21.2 (± 0.1)	0.36 (± 0.06)	11.82 (± 0.025)	12.0 (± 0.1)	12.6	1.0	3.3	0.29	41.9	112.6	5.33
With PEO (0.5 wt %) (Fittings for $I_{\text{Subtract}} = I_{\text{PEO+h-SDS}} - I_{\text{PEO+d-SDS}}$) ^b											
0	79.4 (± 0.1)	0.08 (± 0.02)	9.43 (± 0.004)	0.0	16.7	1.4	4.9	0.30	100.9	181.5	6.74
20	26.0 (± 0.1)	0.28 (± 0.06)	11.82 (± 0.036)	12 (± 0.3)	13.4	1.0	3.5	0.29	47.6	119.8	5.18

^a C_E is the ethanol concentration, η the aggregation number (number of surfactant molecules per micelle), α the fractional charge or charge per surfactant molecule in a micelle, ϕ the volume fraction of the micelles, η_E the number of ethanol molecules per micelle, b the minor micelle core radius, ϵ the ratio of major to minor micelle core axis, δ the shell thickness, and Γ_k the coupling constant or dimensionless electrostatic interactions at inter-micelle distance, κ^{-1} Debye length, and d inter-micelle distance. Values of uncertainties in the fitting parameters are shown below the parameters in parentheses in *italics* font. ^bIn the presence of PEO, the scattering due to PEO-bound SDS micelles is obtained by subtracting (a) the scattering intensity from deuterated alcohol–water solutions containing hydrogenous PEO + deuterated SDS from (b) the scattering intensity of the corresponding solution containing hydrogenous PEO and hydrogenous SDS.

at higher alcohol concentrations because of a “co-solvent effect”.^{36,39,43,59}

Ethanol also affects electrostatic interactions between micelles as indicated by a decrease in Γ_k , intermicelle distances, and surface area per headgroup in a micelle (Table 6). The charge per surfactant molecule α increases by 157% with ethanol addition, comparable to the $\sim 130\%$ increase in the fractional charge α of SDS (45 mM) micelles upon 20 v/v% ethanol addition reported by Safarpour et al.³⁸ from potentiometric measurements. The effective Debye length of the medium also decreases with ethanol, allowing micelles to pack more densely.

At the same time as the intermicelle distances and thereby micelle number density increase with alcohol addition, the micelle volume fraction initially increases and then stabilizes at higher ethanol concentrations. Using the micelle volume fraction ϕ and total surfactant concentration C_{SDS} we can calculate the amount of surfactant molecules that are not part of micelles and, thereby, can obtain the critical micelle concentration $\text{CMC}_{\text{Model}}$ from the relation $\text{CMC}_{\text{Model}} = C_{\text{SDS}} - 1 \times 10^{30} \eta \phi / (N_{\text{AV}} V_{\text{TOT}})$ (mM), where N_{AV} is Avogadro's number. We have also determined CMC values independently using pyrene fluorescence. Table 7 shows very good agreement

Table 7. Comparison of CMC Values for SDS in Ethanol–Water Solutions Obtained from SANS Data Fittings and Fluorescence Measurements (Performed in Our Laboratory), and CMC Values Reported in the Literature³⁵

C_E (wt %)	$\text{CMC}_{\text{Model}}$ (mM)	$\text{CMC}_{\text{Fluorescence}}$ (mM)	$\text{CMC}_{\text{Literature}}$ (mM)
0	7.9	7.8	8.0
10	4.5	5.3	4.0
20	5.4	5.5	6.0

between CMC values obtained by SANS data fittings and by fluorescence. The main drop (by $\sim 32\%$) in CMC is observed at 10 wt % ethanol concentration, indicating the cosurfactant effect, while by 20 wt % ethanol, the CMC increases marginally (cosolvent effect).

Additional evidence of whether ethanol is acting as “co-surfactant” or as “co-solvent” is directly obtained from the changes in the number of ethanol molecules per micelle η_E reported in Table 6. The η_E values are in good agreement with the corresponding values (extrapolated for the surfactant/alcohol ratios used in our study) obtained by fluorescence

quenching.⁴³ As shown in Table 6, at 10 wt % ethanol the number of ethanol molecules that participate in a micelle is high, supporting the “co-surfactant” effect of ethanol for the surfactant. However, at 20 wt % ethanol, η_E decreases indicating a “co-solvent” effect.

The effect of short-chain alcohols on properties of SDS micelles has been previously studied with SANS by Caponetti et al.³⁶ and Førland et al.³⁷ but for much lower alcohol concentration (2% v/v and 7 wt %, respectively) than those considered in our study. A comparable decrease (about 41%) in aggregation number upon addition of 20 wt % ethanol in 75 mM SDS aqueous solutions has been reported by Griffiths et al.⁵ The higher % decrease in aggregation numbers observed in our study can be attributed to the lower SDS concentration that we used (30 mM) and correspondingly higher ethanol/SDS ratio. Similar trends of decreasing SDS aggregation numbers upon alcohol addition have been obtained by fluorescence.³⁵

Effect of 2-Propanol on SDS Micelle Structure and Intermicellar Interactions. Figure 6 shows SANS data and corresponding model fits for SDS aqueous solutions in the presence of deuterated 2-propanol. A 20 wt % 2-propanol-*d* sample shifts the peak maxima from $q = 0.044 \text{ \AA}^{-1}$ to $q = 0.079 \text{ \AA}^{-1}$, a higher shift compared to the case of 20 wt % ethanol-*d*.

Table 8 lists the parameters extracted by fits to the SANS data. The aggregation number decreases by 28% per mole of 2-

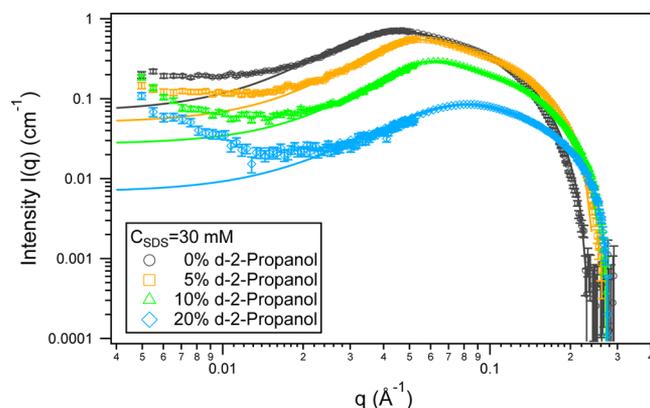
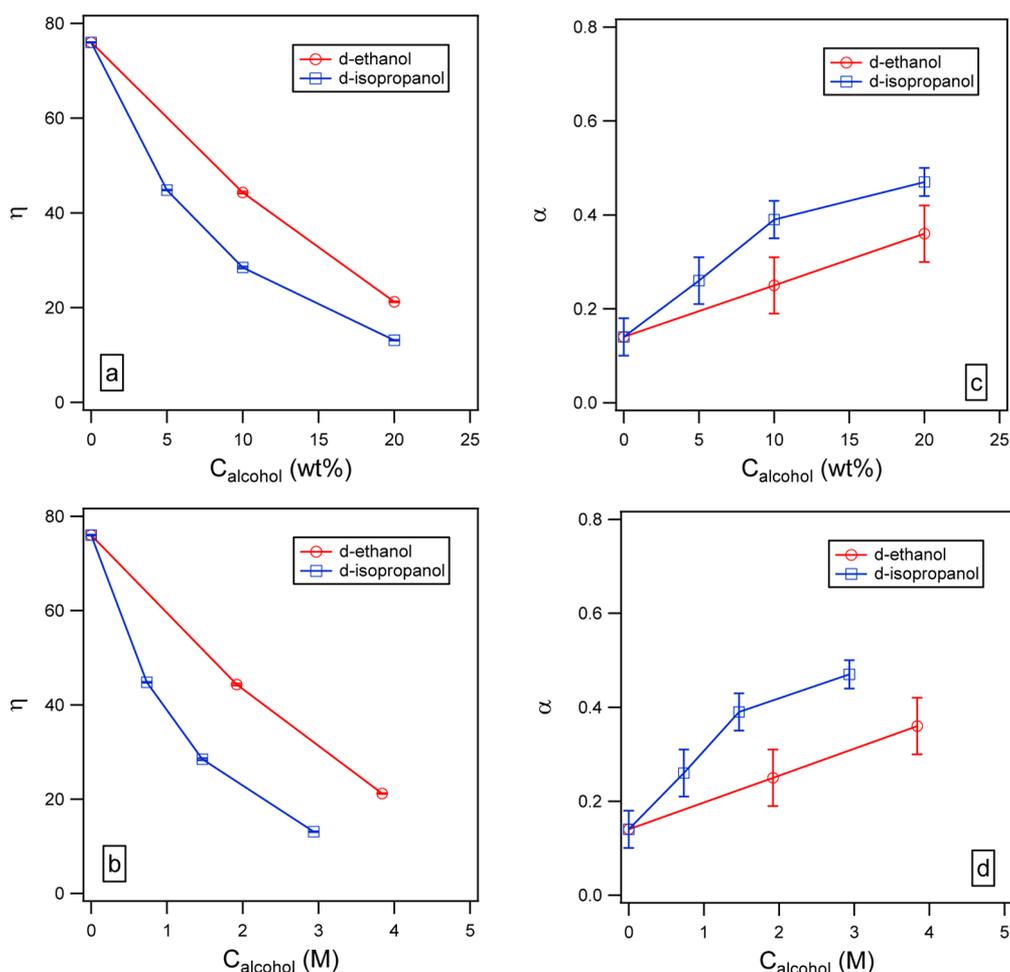
**Figure 6.** Effect of deuterated 2-propanol on SANS intensity profiles from 30 mM SDS in D₂O. Markers indicate experimental data and solid lines represent fits based on the core–shell prolate ellipsoid form factor and Hayter–Penfold-type structure factor.

Table 8. Parameters Obtained by Fitting SANS Data of 30 mM SDS in D₂O + 2-Propanol-*d* Solution (in the Absence or the Presence of PEO) Using the Form and Structure Factors Described in the Text^a

C _A (wt %)	η	α	$\phi \times 10^3$	η_E	b (Å)	ϵ	δ (Å)	Γ_k	κ^{-1} (Å)	d (Å)	red. χ
No PEO											
0	76.0 (± 0.1)	0.14 (± 0.04)	9.43 (± 0.004)	0.0	16.7	1.4	4.9	0.45	76.4	178.8	10.60
5	44.8 (± 0.1)	0.26 (± 0.05)	11.10 (± 0.086)	16.5 (± 0.1)	16.1	1.0	4.2	0.42	53.3	146.3	8.75
10	28.5 (± 0.2)	0.39 (± 0.04)	12.51 (± 0.010)	28.5 (± 0.1)	14.6	1.0	3.6	0.37	43.0	126.7	7.85
20	13.1 (± 0.1)	0.47 (± 0.03)	12.78 (± 0.040)	15.4 (± 0.1)	11.4	1.0	2.8	0.23	37.5	98.2	4.02
With PEO (0.5 wt %) (Fittings for $I_{\text{Subtract}} = I_{\text{PEO+h-SDS}} - I_{\text{PEO+d-SDS}}$) ^b											
20	11.1 (± 0.1)	0.62 (± 0.03)	13.28 (± 0.086)	15.4 (± 0.2)	11.0	1.0	2.7	0.24	32.5	93.0	3.34

^aC_A is the 2-propanol concentration; the various other parameters are defined in Table 6. Values of uncertainties in the fitting parameters are shown below the parameters in parentheses in *italics* font. ^bIn the presence of PEO, the scattering due to PEO-bound SDS micelles is obtained by subtracting (a) the scattering intensity from deuterated alcohol–water solutions containing hydrogenous PEO + deuterated SDS from (b) the scattering intensity of the corresponding solution containing hydrogenous PEO and hydrogenous SDS.

**Figure 7.** Effect of alcohol concentration measured in (top panels) wt % and (bottom panels) M on surfactant aggregation number η (left panels) and on fractional charge α (right panels).

propanol-*d* added, as compared to a 19% reduction per mole of ethanol added (see Figure 7, panels a and b). Similar to the case of ethanol, addition of 2-propanol decreases the CMC (by $\sim 20\%$) at the lower concentration examined (5 wt %), but the CMC increases again (by $\sim 10\%$) at the higher 2-propanol concentration (20 wt %) (Table 9). The micelles decrease in size and change in shape from prolate to spheres as indicated by the axis ratio ϵ . The switch in micelle shape from prolate to sphere occurs at about 5 wt % (0.7 M) 2-propanol as compared to ~ 10 wt % (1.9 M) ethanol. Panels c and d of Figure 7 compare the variation in fractional charge (degree of

Table 9. Comparison of CMC Values for SDS in 2-Propanol–Water Solutions Obtained from SANS Data Fittings (This Study) and CMC Values Reported in the Literature.⁶⁰

C _A (wt %)	CMC _{Model} (mM)	CMC _{Literature} (mM)
0	7.9	8.1
5	6.3	6.3
10	6.7	6.8
20	7.0	7.0

ionization) on a SDS micelle as a function of ethanol-*d* or 2-propanol-*d* concentration. The fractional charge rises by ~78% per mole of 2-propanol-*d* added, which is much higher than the ~41% rise per mole of ethanol. This can be attributed to the lower dielectric constants in 2-propanol solutions.

The intermicelle distances decrease more sharply when 2-propanol is added compared to ethanol, along with lower electrostatic repulsions reflected in a drop in coupling constant (by ~16% per mole of 2-propanol-*d* added compared to ~10% for ethanol) and the Debye lengths.

4.3. Nonionic Polymer Affected by Ionic Surfactant. PEO + SDS Association in Aqueous Solutions. We first discuss aqueous polymer solutions in the presence of surfactant but in the absence of added alcohol. Figure 8 shows SANS profiles for

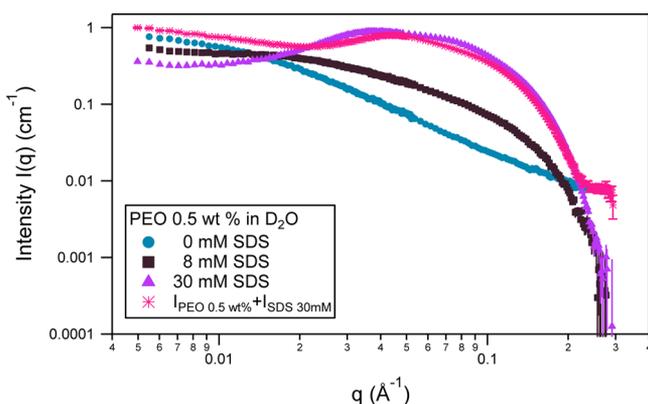


Figure 8. Effect of SDS on SANS intensity profiles for aqueous solutions of PEO (0.5 wt %).

dilute solution of PEO (0.5 wt %) in D₂O containing different amounts of hydrogenous SDS. In the absence of added surfactant, the scattering from PEO solutions does not show any correlation peak because of the nonionic nature of this polymer. However, upon addition of surfactant an interaction peak in the scattering profile emerges, indicative of surfactant micelle formation. For 0.5% PEO aqueous solution with 30 mM SDS, the peak maximum q_{peak} falls at 0.037 \AA^{-1} which corresponds to $\sim 170 \text{ \AA}$ distance between micelles either bound to the polymer chains or free in solution.

The overall scattering includes contributions from both polymers and surfactants associated in solution. Since we have obtained independently the scattering profile for 0.5 wt % of PEO in water and that for 30 mM hydrogenous SDS in water, we have added these two profiles and compare their sum in Figure 8 with the scattering profile that we obtained from the aqueous solution containing both 0.5 wt % PEO and 30 mM SDS. The scattering profile from the PEO+SDS solution is quite different than that obtained by summation of scattering contributions from the individual components. In particular, at low q values, the PEO + SDS solution exhibits lower scattering intensity compared to the summed profile. Further, the correlation peak maximum in the PEO + SDS case falls at a lower q value compared to the summed profile. This comparison suggests alteration following polymer + surfactant association in the conformation of polymer chains and/or the structure of micelles from their original states in plain water.

Conformation of Polymers Present in Polymer + Surfactant Complexes. In order to decouple the individual scattering contributions from polymers and from surfactants present in these complexes we have utilized contrast matching.

More specifically, changes in the conformation of the hydrogenated polymer because of possible surfactant binding can be directly realized by the use of deuterated surfactants that present negligible scattering contrast with the deuterated solvent. The scattering contribution from surfactants bound to polymer can then be obtained by subtracting (a) the polymer scattering with deuterated surfactant from (b) the overall scattering from polymer with hydrogenous surfactants as discussed below.

Figure 9 shows SANS data from 0.5 wt % PEO D₂O solution in the presence of 30 mM deuterated SDS which are “invisible”

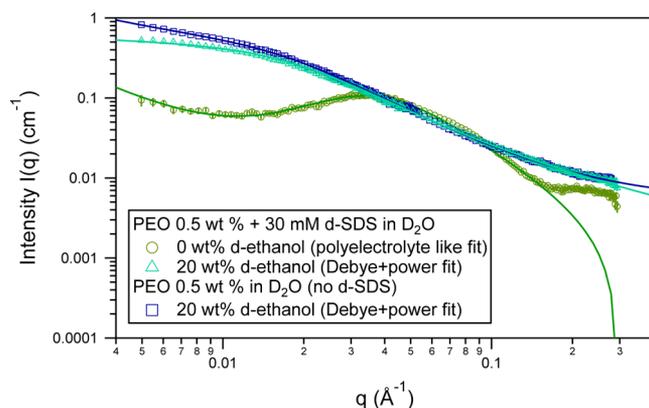


Figure 9. SANS profiles of 0.5 wt % PEO solutions containing 30 mM deuterated SDS in D₂O without (O) or with 20 wt % deuterated ethanol (Δ). The profile (\square) for PEO dissolved in deuterated water + ethanol (no SDS added) is shown for comparison. Markers represent experimental data and solid lines represent the corresponding fits to models denoted in the inset.

with respect to scattering. The interaction peak clearly suggests a polyelectrolyte-like behavior of the PEO chains owing to the repulsive interactions between the bound micelles on their strands. The peak location (q_{peak}) in the present case coincides with the one found in the case of hydrogenated surfactants (no polymer) (see Figure 5).

These data were fitted using the polyelectrolyte + power law type model. The polyelectrolyte model can capture well the interaction peak at intermediate q , while the power law fits the data well in the low q range. The power law exponent of 1.68 and power-law intensity I_p of $1.06 \times 10^{-5} \text{ cm}^{-1} \text{ \AA}^{-1.68}$ indicate the presence of small amounts of association networks possibly due to polymer–polymer and/or polymer–micelle–polymer entanglements.

The degree of ionization of the polymer and the effective monomer length extracted from the polyelectrolyte model are 0.033 and 6.35 Å, respectively. These can be used, together with the contour length of a surfactant-bound PEO chain (estimated to 1.34 μm for PEO degree of polymerization 2043 and monomer length 6.6 Å) to assess the amount of surfactant bound per polymer chain. The resulting number of effective surfactant molecules per chain would be ~ 2108 , out of which ~ 69 molecules would be charged (given a degree of ionization of ~ 0.033). Since the charge on a polymer chain arises only because of the charges of the bound micelles, the number of micelles bound per polymer chain would be ~ 6.35 , considering ~ 10.8 charges per micelle (obtained from fits to SANS data of 30 mM SDS in the absence of alcohol). The number of surfactant molecules bound per polymer molecule would be ~ 482.5 , considering ~ 76 SDS molecules per micelle.

Accordingly, the concentration of bound SDS would be ~ 29.5 mM, which indicates that almost all SDS initially added to solution is bound to PEO. For 0.5 wt % PEO ($M_w = 85\,000$), Chari et al.²⁹ reported the maximum amount of SDS bound to PEO at saturation to be about 75 mM on the basis of self-diffusion NMR and SANS measurements.

In the aforementioned fits to Figure 9, the contrast factor K was fixed at ~ 12.4 barns which was calculated using $b_p = 4.13 \times 10^{-13}$ cm, $b_s = 1.92 \times 10^{-12}$ cm, $v_p = 38.9$ cm³/mol,⁶¹ and $v_s = 18.1$ cm³/mol. The scattering lengths were calculated using additive contributions of scattering lengths from the atoms constituting monomer or solvent. The polymer monomer concentration C used was 0.11 M, obtained from the monomer molecular weight of 44.05 g/mol and 0.5 wt % polymer concentration. The Bjerrum length for aqueous solution used was 7.1 Å.

Structure of Micelles Present in Polymer + Surfactant Complexes. As mentioned earlier, the overall scattering originating from a solution that contains hydrogenated PEO and hydrogenated SDS includes contributions from both the polymer and surfactant. Hence, the scattering from the surfactants incorporated in these complexes can be estimated by subtracting the scattering due to polymers present in these complexes (obtained by using deuterated surfactant that is contrast-matched to the deuterated solvent) from the overall scattering. Figure 10 shows the subtracted ($I_{\text{Subtract}} = I_{\text{PEO+h-SDS}}$

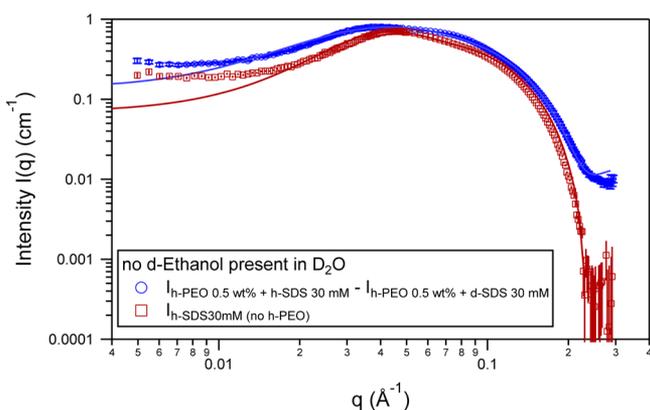


Figure 10. SANS intensity profile (○), reflecting surfactant bound on 0.5 wt % PEO in D₂O, that has been obtained by subtracting SANS data for PEO with 30 mM deuterated SDS from corresponding data of PEO with hydrogenous SDS. The experimentally obtained SANS profile (□) for 30 mM SDS in D₂O (in the absence of PEO) is shown for comparison. Solid lines represent fits using the core–shell prolate form factor and Hayter–Penfold-type structure factor.

– $I_{\text{PEO+d-SDS}}$) scattering profile of surfactants in the presence of polymers. The interaction peak in the scattering profile is located at a slightly higher q value (0.038 Å⁻¹) indicating slightly lower intermicelle distances (163 Å) for the polymer-bound micelles as compared to the free micelles (170 Å).

To obtain quantitative information on the structure and interactions of PEO-bound micelles, the scattering profile of surfactants in the presence of PEO (I_{Subtract}) was fitted using the same form and structure factors as for SDS in water in the absence of PEO. Compared to the free SDS micelles (Table 6), polymer-bound micelles are slightly larger in size with aggregation number of 79 (76 for free SDS micelles). The volume fraction of the micelles in the presence of PEO is higher than that found in its absence, since in the presence of polymer

the onset of micellization commences at a surfactant concentration lower than the CMC in the absence of polymer. On the other hand, the fractional charge of a surfactant in a polymer-bound micelle is lower as compared to the plain surfactant case. The lower value of the coupling constant $\Gamma_k \sim 0.30$ for polymer-bound SDS as compared to that (~ 0.45) for SDS in water indicates lower electrostatic repulsions between head groups, which may explain the slightly higher aggregation number observed. It emerges from the above that the structure of SDS micelles bound to the polymer is not very different from the structure of free micelles in aqueous solution. Similar findings have been reported for SDS in water in the presence of poly(vinylpyrrolidone).⁵

Effect of Ethanol on Polymer–Surfactant Association. From the analysis of the polymer conformation and the properties of bound micelles presented in the previous two sections, it becomes evident for aqueous solutions without added alcohol that, when SDS is added to dilute PEO solutions above a certain concentration, micelles form on the polymer chain and alter the polymer conformation from Gaussian coil (typical of a neutral polymer in a good solvent) to that of a polyelectrolyte (charged polymer) due to electrostatic repulsion between polymer-bound micelles. The surfactant micelles associated with the polymer have almost similar composition as micelles free in solution. These polymer-bound micelles can reinforce entanglements between multiple polymer chains, leading to the enhanced extension thickening behavior that has been observed for PEO–SDS aqueous solutions.⁸ Having established the structure of polymer and surfactant associated in aqueous solution, we proceed next to examine the changes in this structure that can be affected upon addition of alcohol.

The effect on the scattering profile of adding 20 wt % deuterated ethanol to a D₂O solution containing 0.5 wt % PEO and 30 mM hydrogenous SDS is presented in Figure 11.

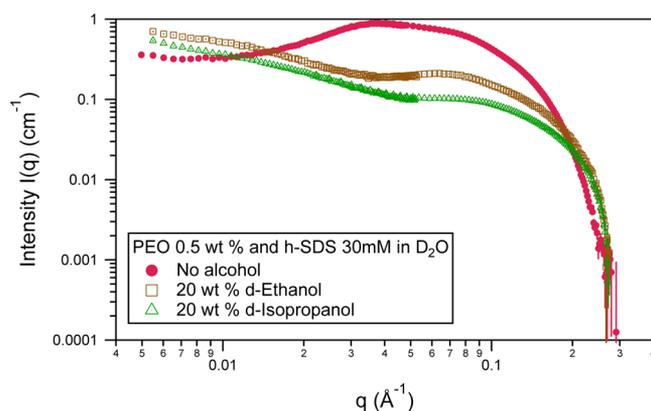


Figure 11. SANS profiles of 0.5 wt % PEO aqueous (D₂O) solutions in the presence of 30 mM hydrogenated SDS, and in the absence of added alcohol or in the presence of 20 wt % deuterated ethanol or deuterated 2-propanol.

Ethanol causes a pronounced decrease in the overall scattering intensity. The low q region of the scattering profile shows behavior similar to that from PEO aqueous solution in the absence of added surfactant. The intermediate q region, however, shows a peak similar to one found for aqueous SDS solutions with 20 wt % of ethanol present (see Figure 5). The peak maximum shifts toward higher q , indicating higher micelle number density and shorter interaction distances.

In order to focus on the effect of ethanol on the conformation of polymers that associate with surfactants, we employed deuterated surfactants to match their scattering contrast with the deuterated solvent. Figure 9 shows the SANS profile of an aqueous solution containing 0.5 wt % PEO and 30 mM deuterated SDS without and with ethanol (20 wt %) present. It is clear that the polyelectrolyte-like conformation of PEO (emanating from the bound SDS) is lost upon addition of 20 wt % ethanol, which intimates a complete dissociation of SDS micelles from the polymer chain. Instead, the scattering profile from PEO + SDS in water + ethanol appears similar to the one obtained from PEO in water + ethanol system with no surfactant present, where the polymer conformation is that of a Gaussian coil. A similar observation has been reported⁵ regarding the loss of polyelectrolyte-like nature of the nonionic polymer poly(vinylpyrrolidone) (PVP) in the presence of 30 mM SDS by addition of 5 wt % ethanol in water. The radius of gyration of PEO chains in the presence of 30 mM SDS in water with 20 wt % ethanol was found 84.6 Å by fitting the Debye + power law model to the scattering data of Figure 9; this value of the radius is slightly lower than that found for PEO in water–ethanol (no surfactant).

In order to decouple the structure of SDS micelles associated with PEO in aqueous ethanol solutions, we subtract the scattering due to polymers present in these complexes (obtained with the aid of contrast-matched surfactant) from the overall scattering: ($I_{\text{Subtract}} = I_{\text{PEO+h-SDS}} - I_{\text{PEO+d-SDS}}$). The scattering profile for micelles in this case (Figure 12a) shows similarity to that of surfactant solution with no polymers present. The interaction peak is located at exactly the same q value (0.069 \AA^{-1}), indicating the same intermicelle distances. This scattering profile was fitted using the same model as that used for SDS–water–alcohol system, and parameters related to micelle structure and intermicelle interaction were obtained (see Table 6). In the presence of 20 wt % ethanol, PEO-bound SDS micelles have a higher aggregation number (26) and lower fractional charge (0.28) compared to the corresponding values (21 and 0.36) found for SDS micelles in aqueous solutions in the absence of PEO (Table 6). Minor variation in SDS aggregation numbers because of binding with PVP in the presence of ethanol has been reported by Griffiths et al.⁵ The structure of SDS micelles in the presence of PEO in aqueous ethanol solutions has not been previously reported in the literature.

Effect of 2-Propanol on Polymer–Surfactant Association. Figure 11 shows the effect of 20 wt % deuterated 2-propanol on the scattering from D_2O solution containing 0.5 wt % PEO and 30 mM hydrogenous SDS. Isopropanol decreases the intensity of the interaction peak, and shifts it toward higher q values compared to ethanol. Similar to ethanol, addition of 2-propanol appears to cause the complete disassociation of micelles from the polymer, allowing the PEO chains to recover their Gaussian conformation.

Figure 12b shows the subtracted ($I_{\text{Subtract}} = I_{\text{PEO+h-SDS}} - I_{\text{PEO+d-SDS}}$) scattering profile of SDS in the presence of PEO in aqueous 20 wt % 2-propanol- d solution. The scattering profile for micelles in this case is similar to that from surfactant solution with no polymers present (Figure 6). The maximum in the peak in the scattering profile is located at exactly the same q value (0.079 \AA^{-1}) indicating the same intermicelle distance (93 Å) for micelles in the presence of PEO compared to micelles in its absence (at 20 wt % 2-propanol). Parameters related to micelle structure and intermicelle interactions were obtained

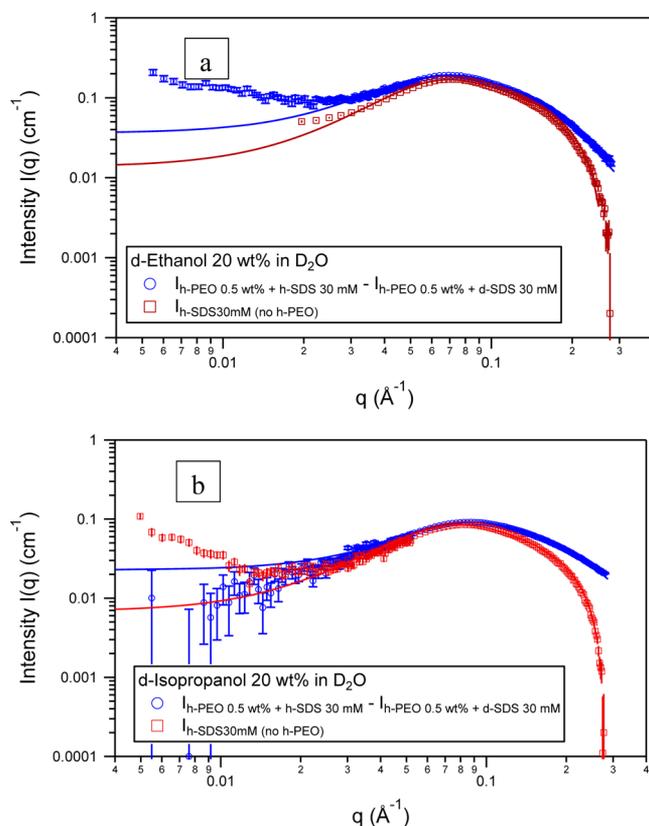


Figure 12. SANS intensity profiles (O) reflecting surfactant bound on 0.5 wt % PEO in D_2O with 20 wt % (a) ethanol- d or (b) 2-propanol- d , obtained by subtracting SANS data for PEO + d-SDS from corresponding data of PEO + h-SDS. The experimentally obtained SANS profiles (\square) for 30 mM SDS in D_2O with 20 wt % d-alcohol (in the absence of PEO) are shown for comparison. Solid lines represent fits to the core–shell prolate form factor and Hayter–Penfold structure factor.

from fits to the same model used for SDS aqueous solutions. Micelles have aggregation number ~ 11 , fractional charge of 0.62, and around 15 2-propanol molecules in each micelle (see Table 8). The surfactant aggregation number is much smaller and the fractional charge much higher in the case of 2-propanol compared to the corresponding PEO–SDS–ethanol–water system (26 and 0.28, respectively, as shown in Table 6). The above results establish that 2-propanol can affect SDS micelles to a greater extent compared to ethanol, irrespective of whether PEO is present in the aqueous solution or not.

5. CONCLUSIONS

This study addresses the conformation of a “model” nonionic polymer, poly(ethylene oxide), in aqueous solutions as affected by the presence of a common ionic surfactant, sodium dodecyl sulfate, and subsequent addition of short-chain alcohol (ethanol or 2-propanol). Structural information has been obtained by judicious analysis of small-angle neutron scattering data. The structure and interactions of the SDS micelles in water in the absence or presence of PEO and in the absence or presence of alcohol have also been resolved utilizing SANS.

PEO chains of $M_w = 90\,000$ adopt nearly Gaussian conformation in dilute aqueous solutions below the overlap polymer concentration ~ 2 wt % at 25°C . The presence of up to 20 wt % ethanol does not affect much the PEO

conformation, however, addition of 20 wt % 2-propanol leads to great reduction (31%) in the polymer radius of gyration.

Profound changes to the PEO chain conformation are caused from the addition of SDS to dilute (0.5%) PEO solutions. These changes are attributed to the association of surfactant micelles with the polymer. The SDS-induced polyelectrolyte-like scattering behavior of PEO emerged from SANS experiments carried out with contrast-matched deuterated surfactant and solvent, and was analyzed using the polyelectrolyte + power law model. The results indicate that almost all surfactant micelles associate to polymer, with approximately 6–7 SDS micelles bound to each PEO chain. Micelles associated with polymer are similar in structure and interactions compared to micelles that formed in aqueous solutions in the absence of polymer. The parameters that support this conclusion came from analysis using the core–shell prolate ellipsoid form factor and Hayter–Penfold-type structure factor of scattering data from surfactants associated with polymer, data calculated by subtracting the scattering from polymer with deuterated surfactants from the overall scattering from polymer with hydrogenous surfactants.

Addition of alcohol affects both the polymer and the surfactant present in these polymer–surfactant complexes, and alters the polymer–surfactant association. Alcohol localizes at the micelle surface and thus interacts closely with polymers that bind with micelles. At high (20 wt %) alcohol concentrations, PEO chains regain their Gaussian conformation following the dissociation of micelles bound to them. Such a dissociation offers a molecular-level explanation to the observed decrease in extension thickening of PEO-SDS solutions at high alcohol concentrations.⁸ The effect of alcohol on polymer-associated micelles is analogous to the effect on micelles free in solution. In the absence of polymer, addition of alcohol in SDS aqueous solutions leads to a decrease in the aggregation number (by 19% per mole of ethanol), micelle size and intermicelle interaction, and to an increase in the micelle degree of ionization (by 41% per mole of ethanol). For the PEO-bound micelles the surfactant aggregation number shows a 17% reduction and the fractional charge a 41% of increase per mole of ethanol-*d* added.

Isopropanol is more effective than ethanol in influencing the properties of SDS micelles in aqueous solutions, either in the presence or in the absence of PEO. For free micelles, the surfactant aggregation number decreases by 28% per mole of 2-propanol-*d* added (compared to 19% per mole of ethanol-*d*), while the fractional charge rises by 78% per mole of 2-propanol-*d* (41% per mole of ethanol-*d*). The effect of 2-propanol-*d* on PEO-bound micelles is the same in terms of the surfactant aggregation number of (29% decrease per mole of 2-propanol-*d*), but the micelles degree of ionization increases to a lesser extent (24% per mole of 2-propanol-*d*).

To the best of our knowledge, this is the first SANS study on PEO-SDS in water + alcohol solutions, and one of very few reports that provide structural information for polymer–surfactant–water–alcohol systems. Further, SANS analysis results on PEO with $M_w = 90\,000$ and on SDS–water–2-propanol solutions have not been previously reported. The present study provides a case study of charging a nonionic polymer in solution and subsequently uncharging it by means of external additives. It quantifies the effects of alcohol on polymer+surfactant structure in aqueous solutions, and allows for direct comparison between ethanol and 2-propanol in terms of their ability to modulate polymer conformation and micelle

structure and interactions. The fundamental insights provided here on polymer and surfactant organization in solution, as well as the specific information on systems that are widely used in practice, should prove beneficial to applications of complex fluids in formulations and nanomaterials synthesis.

AUTHOR INFORMATION

Corresponding Author

*(M.T.) Telephone: (716) 645-1191. E-mail: mtsianou@buffalo.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work. We also acknowledge funding from the Donors of the Petroleum Research Fund (#50534-DNI7), administered by the American Chemical Society. We appreciate stimulating discussions with Professor P. Alexandridis at our department.

REFERENCES

- (1) Holmberg, K.; Jönsson, B.; Kronberg, B.; Lindman, B. *Surfactants and Polymers in Aqueous Solution*; Wiley: New York, 2002.
- (2) Fukui, H.; Satake, I.; Hayakawa, K. Thermodynamic Effects of Alcohol Additives on the Cooperative Binding of Sodium Dodecyl Sulfate to a Cationic Polymer. *Langmuir* **2002**, *18* (11), 4465–4470.
- (3) Mukherjee, S.; Dan, A.; Bhattacharya, S. C.; Panda, A. K.; Moulik, S. P. Physicochemistry of Interaction between the Cationic Polymer Poly(diallyldimethylammonium chloride) and the Anionic Surfactants Sodium Dodecyl Sulfate, Sodium Dodecylbenzenesulfonate, and Sodium N-Dodecanoylsarcosinate in Water and Isopropyl Alcohol-Water Media. *Langmuir* **2011**, *27* (9), 5222–5233.
- (4) Nilsson, S.; Blokhuis, A. M.; Hellebust, S.; Glomm, W. R. Influence of Hydrophobic Cosolutes on the Associative/Segregative Phase Separation of Aqueous Cationic Surfactant-Polymer Systems. *Langmuir* **2002**, *18* (17), 6504–6506.
- (5) Griffiths, P. C.; Hirst, N.; Paul, A.; King, S. M.; Heenan, R. K.; Farley, R. Effect of Ethanol on the Interaction between Poly(vinylpyrrolidone) and Sodium Dodecyl Sulfate. *Langmuir* **2004**, *20* (16), 6904–6913.
- (6) Francisco, K. R.; da Silva, M. A.; Sabadini, E.; Karlsson, G.; Dreiss, C. A. Effect of Monomeric and Polymeric Co-Solutes on Cetyltrimethylammonium Bromide Wormlike Micelles: Rheology, Cryo-TEM and Small-Angle Neutron Scattering. *J. Colloid Interface Sci.* **2010**, *345* (2), 351–359.
- (7) Dai, S.; Tam, K. C. Effect of Cosolvents on the Binding Interaction between Poly(ethylene oxide) and Sodium Dodecyl Sulfate. *J. Phys. Chem. B* **2006**, *110* (42), 20794–20800.
- (8) Smither, L. M.; Torres, M. E.; Muller, A. J.; Saez, A. E. Elongational Flow of Solutions Containing Poly(ethylene oxide)/Sodium Dodecyl Sulfate Complexes in the Presence of N-Alkanols. *J. Colloid Interface Sci.* **2001**, *244* (1), 164–172.
- (9) Antoniou, E.; Alexandridis, P. Polymer Conformation in Mixed Aqueous-Polar Organic Solvents. *Eur. Polym. J.* **2010**, *46* (2), 324–335.
- (10) Bernardes, J. S.; Piculell, L.; Loh, W. Self-Assembly of Polyion-Surfactant Ion Complex Salts in Mixtures with Water and N-Alcohols. *J. Phys. Chem. B* **2011**, *115* (29), 9050–9058.
- (11) Lin, Y. N.; Alexandridis, P. Cosolvent Effects on the Micellization of an Amphiphilic Siloxane Graft Copolymer in Aqueous Solutions. *Langmuir* **2002**, *18* (11), 4220–4231.
- (12) Chronakis, I. S.; Alexandridis, P. Rheological Properties of Oppositely Charged Polyelectrolyte-Surfactant Mixtures: Effect of

Polymer Molecular Weight and Surfactant Architecture. *Macromolecules* **2001**, *34* (14), 5005–5018.

(13) Hansson, P.; Lindman, B. Surfactant-Polymer Interactions. *Curr. Opin. Colloid Interface Sci.* **1996**, *1* (5), 604–613.

(14) Piculell, L. Understanding and Exploiting the Phase Behavior of Mixtures of Oppositely Charged Polymers and Surfactants in Water. *Langmuir* **2013**, *29* (33), 10313–10329.

(15) Tam, K. C.; Wyn-Jones, E. Insights on Polymer Surfactant Complex Structures During the Binding of Surfactants to Polymers as Measured by Equilibrium and Structural Techniques. *Chem. Soc. Rev.* **2006**, *35* (8), 693–709.

(16) Tsianou, M.; Alexandridis, P. Surfactant-Polymer Interactions. *Surf. Sci. Ser.* **2005**, *124*, 657–708.

(17) Goddard, E. D. Polymer-Surfactant Interaction: Part 1. Uncharged Water-Soluble Polymers and Charged Surfactants. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; pp 123–170.

(18) Ivanova, R.; Lindman, B.; Alexandridis, P. Modification of the Lyotropic Liquid Crystalline Microstructure of Amphiphilic Block Copolymers in the Presence of Cosolvents. *Adv. Colloid Interface Sci.* **2001**, *89*, 351–382.

(19) Rhein, L. D.; Schlossman, M.; O'Lenick, A.; Somasundaran, P. *Surfactants in Personal Care Products and Decorative Cosmetics*. CRC Press: Boca Raton, FL, 2006.

(20) Scharnagl, C.; Reif, M.; Friedrich, J. Stability of Proteins: Temperature, Pressure and the Role of the Solvent. *Biochim. Biophys. Acta: Proteins Proteomics* **2005**, *1749* (2), 187–213.

(21) Shukla, D.; Schneider, C. P.; Trout, B. L. Molecular Level Insight into Intra-Solvent Interaction Effects on Protein Stability and Aggregation. *Adv. Drug Delivery Rev.* **2011**, *63* (13), 1074–1085.

(22) Wicks Jr, Z. W.; Jones, F. N.; Pappas, S. P. *Organic Coatings: Science and Technology*. Wiley-Interscience: New York, 1999.

(23) Hoff, E.; Nyström, B.; Lindman, B. Polymer-Surfactant Interactions in Dilute Mixtures of a Nonionic Cellulose Derivative and an Anionic Surfactant. *Langmuir* **2001**, *17* (1), 28–34.

(24) Jonsson, M.; Skepö, M.; Tjerneld, F.; Linse, P. Effect of Spatially Distributed Hydrophobic Surface Residues on Protein-Polymer Association. *J. Phys. Chem. B* **2003**, *107* (23), 5511–5518.

(25) Liu, Z. H.; Shang, Y. Z.; Feng, J.; Peng, C. J.; Liu, H. L.; Hu, Y. Effect of Hydrophilicity or Hydrophobicity of Polyelectrolyte on the Interaction between Polyelectrolyte and Surfactants: Molecular Dynamics Simulations. *J. Phys. Chem. B* **2012**, *116* (18), 5516–5526.

(26) Davis, J. R.; Panagiotopoulos, A. Z. Micellization and Phase Separation in Binary Amphiphile Mixtures. *Mol. Phys.* **2009**, *107* (22), 2359–2366.

(27) Lindell, K.; Cabane, B. Structures of Physical Gels in the EHEC-SDS-Water System. *Langmuir* **1998**, *14* (22), 6361–6370.

(28) Cabane, B.; Duplessix, R. Decoration of Semidilute Polymer-Solutions with Surfactant Micelles. *J. Phys. (Paris)* **1987**, *48* (4), 651–662.

(29) Chari, K.; Antalek, B.; Lin, M. Y.; Sinha, S. K. The Viscosity of Polymer-Surfactant Mixtures in Water. *J. Chem. Phys.* **1994**, *100* (7), 5294–5300.

(30) Mészáros, R.; Varga, I.; Gilanyi, T. Effect of Polymer Molecular Weight on the Polymer/Surfactant Interaction. *J. Phys. Chem. B* **2005**, *109* (28), 13538–13544.

(31) Philip, J.; Gnanaprakash, G.; Jayakumar, T.; Kalyanasundaram, P.; Raj, B. Three Distinct Scenarios under Polymer, Surfactant, and Colloidal Interaction. *Macromolecules* **2003**, *36* (24), 9230–9236.

(32) Truong, M. T.; Walker, L. M. Controlling the Shear-Induced Structural Transition of Rodlike Micelles Using Nonionic Polymer. *Langmuir* **2000**, *16* (21), 7991–7998.

(33) Wang, G.; Olofsson, G. Titration Calorimetric Study of the Interaction between Ionic Surfactants and Uncharged Polymers in Aqueous Solution. *J. Phys. Chem. B* **1998**, *102* (46), 9276–9283.

(34) Hammouda, B. Solvation Characteristics of a Model Water-Soluble Polymer. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44* (22), 3195–3199.

(35) Almgren, M.; Swarup, S. Size of Sodium Dodecyl-Sulfate Micelles in the Presence of Additives. 3. Multivalent and Hydrophobic Counterions, Cationic and Non-Ionic Surfactants. *J. Phys. Chem.* **1983**, *87* (5), 876–881.

(36) Caponetti, E.; Martino, D. C.; Floriano, M. A.; Triolo, R. Localization of N-Alcohols and Structural Effects in Aqueous Solutions of Sodium Dodecyl Sulfate. *Langmuir* **1997**, *13* (13), 3277–3283.

(37) Førland, G. M.; Samsøth, J.; Gjerde, M. L.; Høiland, H.; Jensen, A. O.; Mortensen, K. Influence of Alcohol on the Behavior of Sodium Dodecylsulfate Micelles. *J. Colloid Interface Sci.* **1998**, *203*, 328–334.

(38) Safarpour, M. A.; Rafati, A. A.; Gharibi, H.; Sameti, M. R. Influence of Short-Chain Alcohols on the Micellization Parameters of Sodium Dodecyl Sulfate (SDS). *J. Chin. Chem. Soc.* **1999**, *46* (6), 983–991.

(39) Zana, R. Aqueous Surfactant-Alcohol Systems - A Review. *Adv. Colloid Interface Sci.* **1995**, *57*, 1–64.

(40) Alexandridis, P.; Yang, L. SANS Investigation of Polyether Block Copolymer Micelle Structure in Mixed Solvents of Water and Formamide, Ethanol, or Glycerol. *Macromolecules* **2000**, *33* (15), 5574–5587.

(41) Sarkar, B.; Lam, S.; Alexandridis, P. Micellization of Alkyl-Propoxy-Ethoxylate Surfactants in Water-Polar Organic Solvent Mixtures. *Langmuir* **2010**, *26* (13), 10532–10540.

(42) Hammouda, B.; Ho, D. L. Insight into Chain Dimensions in PEO/Water Solutions. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45* (16), 2196–2200.

(43) Almgren, M.; Swarup, S. Size of Sodium Dodecyl-Sulfate Micelles in the Presence of Additives. 1. Alcohols and Other Polar Compounds. *J. Colloid Interface Sci.* **1983**, *91* (1), 256–266.

(44) Borue, V. Y.; Erukhimovich, I. Y. A Statistical Theory of Weakly Charged Polyelectrolytes: Fluctuations, Equation of State, and Microphase Separation. *Macromolecules* **1988**, *21* (11), 3240–3249.

(45) Moussaid, A.; Schosseler, F.; Munch, J. P.; Candau, S. J. Structure of Polyacrylic Acid and Polymethacrylic Acid Solutions: A Small Angle Neutron Scattering Study. *J. Phys. II* **1993**, *3* (4), 573–594.

(46) Sheu, E. Y.; Wu, C.-F.; Chen, S.-H. Effects of Ion Sizes on the Aggregation and Surface Charge of Ionic Micelles in 1:1 Electrolyte Solutions. *J. Phys. Chem.* **1986**, *90* (17), 4179–4187.

(47) Griffiths, P. C.; Paul, A.; Heenan, R. K.; Penfold, J.; Ranganathan, R.; Bales, B. L. Role of Counterion Concentration in Determining Micelle Aggregation: Evaluation of the Combination of Constraints from Small-Angle Neutron Scattering, Electron Paramagnetic Resonance, and Time-Resolved Fluorescence Quenching. *J. Phys. Chem. B* **2004**, *108* (12), 3810–3816.

(48) Kline, S. R. Reduction and Analysis of SANS and USANS Data Using Igor Pro. *J. Appl. Crystallogr.* **2006**, *39*, 895–900.

(49) Cabane, B.; Lindell, K.; Engström, S.; Lindman, B. Microphase Separation in Polymer Plus Surfactant Systems. *Macromolecules* **1996**, *29* (9), 3188–3197.

(50) Kjøniksen, A.-L.; Knudsen, K. D.; Nyström, B. Phase Separation and Structural Properties of Semidilute Aqueous Mixtures of Ethyl(Hydroxyethyl)Cellulose and an Ionic Surfactant. *Eur. Polym. J.* **2005**, *41* (9), 1954–1964.

(51) Debye, P. Molecular-Weight Determination by Light Scattering. *J. Phys. Colloid Chem.* **1947**, *51* (1), 18–32.

(52) Hayter, J. B.; Penfold, J. An Analytic Structure Factor for Macroion Solutions. *Mol. Phys.* **1981**, *42* (1), 109–118.

(53) Tanford, C. Micelle Shape and Size. *J. Phys. Chem.* **1972**, *76* (21), 3020.

(54) Wyman, J. The Dielectric Constant of Mixtures of Ethyl Alcohol and Water from -5 to 40° . *J. Am. Chem. Soc.* **1931**, *53* (9), 3292–3301.

(55) Sears, V. F. Neutron Scattering Lengths and Cross Sections. *Neutron News* **1992**, *3* (3), 26–37.

(56) Caponetti, E.; Martino, D. C.; Floriano, M. A.; Triolo, R. Application of the Small-Angle Neutron Scattering Technique to the Study of Solubilization Mechanisms of Organic Molecules by Micellar Systems. *J. Mol. Struct.* **1996**, *383* (1–3), 133–143.

(57) Shankar, R.; Klossner, R. R.; Weaver, J. T.; Koga, T.; van Zanten, J. H.; Krause, W. E.; Colina, C. M.; Tanaka, F.; Spontak, R. J. Competitive Hydrogen-Bonding in Polymer Solutions with Mixed Solvents. *Soft Matter* **2009**, *5* (2), 304–307.

(58) Hammouda, B.; Ho, D. L.; Kline, S. Insight into Clustering in Poly(ethylene oxide) Solutions. *Macromolecules* **2004**, *37* (18), 6932–6937.

(59) Javadian, S.; Gharibi, H.; Sohrabi, B.; Bijanzadeh, H.; Safarpour, M. A.; Behjatmanesh-Ardakani, R. Determination of the Physico-Chemical Parameters and Aggregation Number of Surfactant in Micelles in Binary Alcohol-Water Mixtures. *J. Mol. Liq.* **2008**, *137* (1–3), 74–79.

(60) Kumar, G.; Chauhan, M. S.; Kumar, A.; Chauhan, S.; Kumar, R. A Study on Solution Behaviour of Sodiumdodecyl Sulphate and Cetyltrimethylammonium Bromide in Water - Alcohol Mixed Media. *Chem. Sin.* **2012**, *3* (3), 628–635.

(61) Hammouda, B.; Ho, D.; Kline, S. SANS from Poly(Ethylene Oxide)/Water Systems. *Macromolecules* **2002**, *35* (22), 8578–8585.