Effect of Cosolvents on the Binding Interaction between Poly(ethylene oxide) and Sodium Dodecyl Sulfate

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The micellization of sodium dodecyl sulfate (SDS) in different glycol−water solvent mixtures was studied using the isothermal titration calorimetric (ITC) technique. At the same time, microcalorimetric titrations were also carried out to monitor the binding interaction of SDS and poly(ethylene oxide) (PEO) in the presence of different cosolvents. The demicellization of SDS in mixtures of water and cosolvents is different from that in water due to the reduction in solvent polarity and charge interaction of surfactants. The critical micelle concentration (cmc) first decreases with the addition of a small amount of cosolvents and then increases at higher cosolvent concentrations. The thermodynamics of surfactant micellization can be analyzed using the solubility parameters of solvent mixtures. For the binding interaction between SDS and PEO in different solvent mixtures, the dehydration process at low SDS concentrations is replaced by the chain solubilization process with decreasing solvent polarity. With further reduction in the solvent polarity, the binding interaction between SDS and PEO becomes weak and no aggregates can be formed beyond a certain glycol concentration. The binding interaction between SDS and PEO in different solvent mixtures was analyzed and ascribed to the effects of PEO solubility and hydrophobicity of SDS.

Introduction

Surfactant micellization and polymer chain conformation in solution are strongly dependent on the characteristics of the solvent. As a result, the solvent property can significantly alter the surfactant−polymer interaction. Addition of a cosolvent into the aqueous system not only affects the solvent polarity but also changes the solvent microenvironment. Polyhydric alcohols (also known as glycols), such as ethylene glycol (EG), propylene glycol (PG), and glycerol (GR), comprises a series of environmentally friendly nonaqueous polar solvent with applications in personal care and pharmaceutical product formulations.[1] They have many characteristics similar to water and can form a hydrogen-bonded network by themselves or with water, and thus are miscible with water. These polyhydric alcohols and their mixtures with water are typical examples of H-bond networks that can be used to study the cooperative dynamics, glass transition, and scaling properties.[2,3] In addition, they also possess higher cohesive energies and have fairly high dielectric constants.[4,5] The addition of glycol into water not only decreases the polarity of the solvent but also affects the transport properties.[6] The physical properties of the three most common glycols are summarized in Table 1.[1,7]

Studies on the aggregation behaviors of amphiphilic molecules in glycol−water mixtures have been reported by several research groups.[4,5,8−10] Such studies provided a better understanding on the effects of the structure and polarity of solvents on the micellization or aggregation process of amphiphiles. Several studies on the micellization behavior of different surfactants in glycol−water mixtures have been reported.[4,10−14] The critical micelle concentration (cmc) shifted to a higher value with the addition of glycols to nonionic surfactant solutions, while the aggregation number and the size of the micelles decreased. The micellization of nonionic surfactant in glycol−water mixtures is controlled by the structure-breaking ability of glycols and the interaction of cosolvents with the surfactant headgroups. The monomer concentration continues to increase, and finally micelles cannot be formed in alcohol-rich solvents.

Since the solubility of poly(ethylene oxide) (PEO) in water is due to the formation of hydrogen bonding with water molecules, the solution behavior of PEO in glycol solution should be very interesting. Not only are glycols less polar solvents than water, but they are also strong hydrogen-bonding agents. Both glycols and water can act as hydrogen donor in the H-bond, while PEO, glycols, and water can act as the hydrogen acceptor.[8] Competition for the establishment of hydrogen bonds with PEO occurs when glycols are added to water. Glycerol is a poorer solvent than water for PEO at 25 °C. Although PEO can dissolve into water at room temperature, it is almost insoluble in pure glycols. The aggregation behavior of hydrophobically modified end-capped PEO was examined by rheological and light scattering studies.[8] It was found that the aggregation is enhanced with increasing solvent polarity, and the polymers precipitate from solution when the molar ratio exceeds 1.0. Alexandridis and co-workers conducted a comprehensive investigation on aggregation of Pluronic PEO−PPO−PEO (PPO = poly(propylene oxide)) block copolymers in mixtures of water and glycols.[1,9,15,16] The micelle and core radii, micelle aggregation number, and polymer volume fraction in the micellar core and corona decreased with increasing ethanol−water ratio. Addition of glycerol to water led to a larger aggregation number and higher volume fraction of the corona of the micelle. On the basis of the relative polarity of glycol, a

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TABLE 1: Physicochemical Parameters of Water and Three Used Glycols at 298 K

solvent	molar mass	density[a] (g/mL)	dielectric constant[a]	δ^b (MPa$^{1/2}$)	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)
Water	18	1.000	78.5	47.8	15.5	16.0	42.4
glycerol	92	1.257	40.1	36.2	17.4	12.1	29.3
ethylene glycol	62	1.110	37.7	33.0	17.0	11.0	26.0
propylene glycol	76	1.033	32.0	30.2	16.8	9.4	23.3

[a] The density and dielectric constant of the solvent are given at 25 °C. [b] δ = solubility parameter.

hypothesis on the phase behavior was proposed, where the structure transformed from a cubic to hexagonal, to bicontinuous cubic, and then to lamellar structures as the solvent progresses from a polar to one that is less polar.

Mixtures of water-soluble polymers and surfactants are commonly found in pharmaceutical formulations, personal care products, household and industrial detergents, paints and coatings, and drilling and enhanced oil recovery fluids. Hence, they are of fundamental interest to researchers, and the elucidation of their physical properties, intermolecular interaction, and hydrophobic aggregation phenomena is of vital importance.[17−19] The interaction and aggregation behaviors of polymer−surfactant systems are controlled by the balance of hydrophobic attraction and repulsive interactions arising from either electrostatic or excluded volume effect. Addition of glycols to polymer−surfactant systems not only affects the hydrophobic but also these repulsive interactions. Hence, the aggregation behavior changes with the amount of cosolvent present. Studies on polymer−surfactant interaction in aqueous system have been extensively reported, but there is a lack of detailed studies on the interaction of surfactants and polymers in glycol−water solvent mixtures. In this paper, the effects of cosolvent on the micellization behavior of sodium dodecyl sulfate (SDS) are examined using the isothermal titration calorimetric (ITC) technique, which directly provides the enthalpy changes associated with the surfactant demicellization process. The surfactant demicellization is discussed on the basis of their solvent solubility parameters, and the effect of different glycols and mixture compositions on the binding interaction of SDS and PEO is examined.

Experimental Section

Materials. PEO of molecular weight 300 000 Da (designated as PEO300K) was donated by Dow Chemicals. SDS was purchased from BDH and used as received without further purification. The deionized water was from Alpha-Q Millipore water purification system. Cosolvents, such as ethylene glycol, propylene glycol, and glycerol were purchased from Merck. First, different weight ratios of glycol−water mixtures were prepared. Then, 1 wt % PEO and 0.2 M SDS in aqueous solution and different solvent mixtures were prepared and used as stock solutions. The sample solutions were diluted from these stock solutions using deionized water or various solvent mixtures. All PEO solutions were stored in the dark, away from light, and allowed to equilibrate at room temperature for at least 24 h before the measurement was carried out. Before ITC experiments, both solutions in either titration cell or syringe were degassed.

Isothermal Titration Calorimetry. The enthalpy changes of PEO and SDS interactions in the presence of cosolvents were measured by a Microcal isothermal titration calorimeter. A detailed description of this power compensated differential instrument could be found elsewhere.[20] The microcalorimeter consists of a reference cell and a sample cell of 1.35 mL in volume, with both cells insulated by an adiabatic shield. The titration was carried out by step-by-step injections of concen-
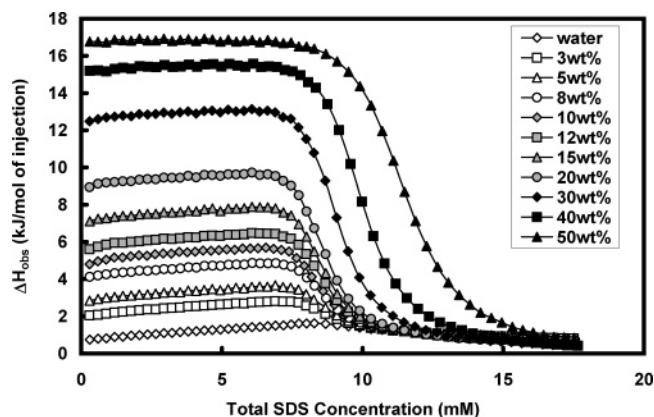

Figure 1. ITC thermograms for 0.1 M SDS dilution in glycerol−water mixed solvents with different ratios of glycerol and water at 298 K and 1 atm.

trated titrant solution from a 250 μL injection syringe into the sample cell filled with dilute titrate solutions. The syringe is tailored-made such that the tip acts as a blade-type stirrer to ensure continuous mixing efficiency at 400 rpm. Using interactive software, an injection schedule was automatically carried out after setting up the number of injections, the volume of each injection, and the time interval between each injection. The ITC measurements were performed at a constant temperature of 25.0 ± 0.02 °C controlled by a Poly-Science water bath.

Results and Discussion

1. Effects of Cosolvents on the Micellization of SDS. In aqueous solution, SDS monomers associate into micelles to minimize the system's Gibbs free energy at a concentration exceeding the cmc. At 25 °C, the cmc of SDS was found to be ∼8 mM in aqueous solution with an averaged aggregation number of ∼70.[21] The addition of cosolvent such as glycols (glycerol, ethylene glycol, and propylene glycol) into water decreases the solvent polarity. Thus, the presence of cosolvent alters the properties of both the head and tail groups of an ionic surfactant and its corresponding micellization behavior. To understand the micellization of SDS in less polar solvents, ITC experiments were carried out to monitor the demicellization behaviors of SDS in the glycol−water solvent mixtures. Figure 1 shows the typical dilution thermograms of 0.1 M SDS into different weight ratios of glycerol−water mixtures. It is evident that the ITC thermograms exhibit an "S"- shape at high glycerol contents, which is different from that in aqueous medium. In addition, the observed enthalpy for the demicellization of SDS increases with increasing amounts of glycerol.

Generally, for the demicellization of nonionic surfactant solutions in aqueous medium, an S-shape ITC curve is always observed since the dilution heat of monomer is much less than the heat of demicellization, where ΔH_{obs} is independent of surfactant concentration at the premicellization region ($C <$ cmc). For example, nonionic surfactants such as polyoxyethylenated alcohols ($C_{12}E_9$) and polyoxyethylenated alkylphenols (Triton-X) display a well-defined S-shape dilution curve in
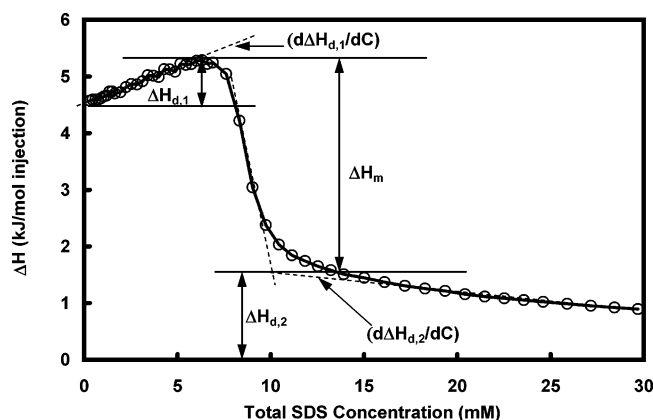
Figure 2. ITC thermogram of the SDS−water system (31 °C and 1 atm), demonstrating the determination of thermodynamic parameters.

Figure 3. Cmc for SDS in different glycol−water solvent mixtures at 298 K and 1 atm.

Figure 4. Micellization enthalpies for SDS in different glycol−water solvent mixtures at 298 K and 1 atm.

water.[22,23] However, due to the higher cmc and the charge character of SDS solution in water at 298 K, an S-shape titration curve is not observed.[24−26] For SDS dilution thermogram in water at 31 °C (Figure 2), it is evident that ΔH_{obs} is linearly dependent on surfactant concentration at the premicellization region, where the slope is designated as $k_1 = (d\Delta H_{d,1}/dC)$. A similar result at SDS concentration below the cmc has been reported.[27] They attributed this nonideal behavior to the probable reason of pairwise interaction between the alkyl groups since the slope is much larger than that expected for the dilution of a simple 1:1 electrolyte. Although the enthalpy associated with SDS demicellization varies with changes in temperatures, k_1 values do not change with temperature.[28] By adding glycerol into water, the solvent polarity decreases, and this alters the SDS demicellization as shown in Figure 1. The dielectric constants for water and glycerol are 78.5 and 40.1, while the dipole moments are 3.11 and 2.68 for water and glycerol, respectively.[9,15,16] Hence, increasing glycerol content will result in the reduction in the polarity of solvent mixtures. Since the micellization of ionic surfactant is controlled by the balance of hydrophobic and charge interaction of the tail and head groups, respectively, the change in the dielectric properties and solvent polarity will alter the solvation character of ionic surfactants. Experimental results indicate the decrease of slope k_1 in the premicellar region resulted in an ideal S-shape titration curve at glycerol content of ∼50 wt %. The nonideal behavior is possibly attributed to the pairwise hydrophobic interaction, which was also observed for some nonionic surfactants at the premicellar region.[29] A reduction in the polarity minimizes the hydrophobic interaction of SDS tail groups in the solvent mixtures. At C = cmc, surfactant micelles with n anionic monomers and m counterions coexist with free $n − m$ counterions. The effective micellar charge fraction β $(=m/n)$ is related to the counterion binding associated with the surfactant micellization.[28] Beyond the cmc, only surfactant and monomer dilution heats were observed. In aqueous system, the ΔH measured after the cmc also includes the small contribution arising from the decrease in surfactant monomer concentration beyond the cmc. The dilution enthalpy is also proportional to the SDS concentration as evident from Figure 2 and the slope $d\Delta H_{d,2}/dC$ (denoted by k_2) is a constant of ∼ −0.041 kJ/mol mM for SDS in both aqueous and mixed solvents.

The dependence of the cmc and ΔH_m on glycerol concentrations for SDS micellization is shown in Figures 3 and 4 and the related thermodynamic parameters are summarized in Table 2. It is evident that the cmc first decreases until 12 wt % glycerol and remains essentially constant up to ∼20 wt % glycerol, where it then increases up to ∼50 wt % glycerol. On the other hand,
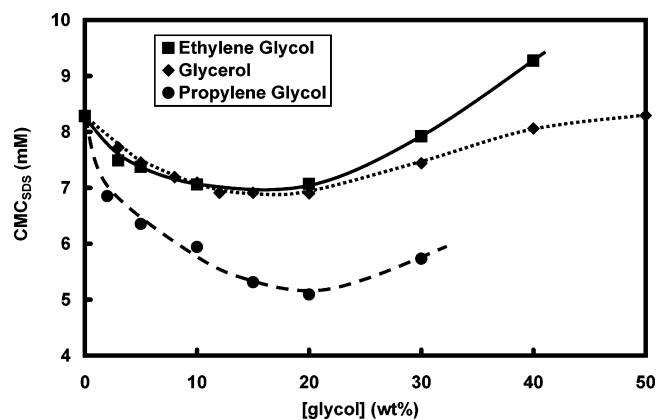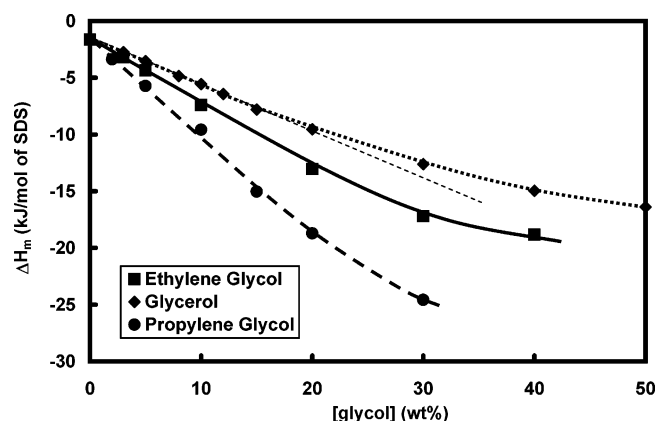
the enthalpy of micellization becomes more negative as the glycerol content is increased. It exhibits a linear relationship up to 20 wt % glycerol; beyond this it deviates from the linear relationship.

From previous studies on the SDS micellization in aqueous medium, it was found that free monomer concentration increases with total SDS concentration in solution and reaches a maximum at the cmc, and then the free monomer concentration decreases slightly.[27] The numerical values of thermodynamic parameters summarized in Table 2 revealed that the micellization is an entropic-driven process when the glycerol content is lower than 20 wt % and becomes a more enthalpy-driven process when the glycerol exceeds 20 wt %. Surfactant micellization in water is an entropic-driven process due to the fact that micellization destroys the water structure and increases the mobility of hydrophobic segments, which gives rise to an increase in solution entropy. The addition of large amounts of glycerol into water not only decreases the solvent polarity but significantly changes the water structure. Glycerol has three −OH groups per molecule, and it has similar properties to water. Glycerol can act as either donor or acceptor in forming hydrogen bonds; thus, glycerol molecules can form a hydrogen bond by themselves or with water molecules. Addition of small amounts of glycerol (up to 20 wt % glycerol or 4.7 mol %) does not significantly alter the solvent polarity. However, these glycerol molecules will reduce the electrostatic interaction from these SDS head groups, which decrease the cmc values. Within this concentration range, the water structure prevails and the micellization is driven by an increase in entropy. The ΔH_m of surfactant micellization increases linearly with glycerol concentration. Beyond 20 wt % glycerol content, an increasing

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TABLE 2: Thermodynamics of SDS Micellization in Different Glycol−Water Mixed Solvents at 298 K and 1 atm

[cosolvent] (wt %)	cmc (mM)	ΔH_m (kJ/mol)	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)	δ (MPa$^{1/2}$)
			Ethylene Glycol			
0	8.28	−1.63	15.5	16.0	42.4	47.0
3	7.49	−3.19	15.5	15.9	42.0	47.5
5	7.37	−4.35	15.6	15.8	41.7	47.2
10	7.06	−7.39	15.6	15.5	40.9	46.5
20	7.07	−13.04	15.8	15.1	39.4	45.1
30	7.92	−17.21	15.9	14.6	37.8	43.7
40	9.27	−18.83	16.1	14.1	36.2	42.3
			Glycerol			
0	8.28	−1.63	15.5	16.0	42.4	47.9
3	7.72	−2.74	15.5	15.9	42.1	47.6
5	7.45	−3.53	15.6	15.8	41.9	47.4
8	7.19	−4.85	15.6	15.7	41.6	47.1
10	7.09	−5.56	15.7	15.7	41.3	46.9
12	6.91	−6.43	15.7	15.6	41.1	46.8
15	6.91	−7.80	15.7	15.5	40.8	46.5
20	6.90	−9.54	15.8	15.4	40.2	46.0
30	7.44	−12.62	16.0	15.0	39.1	44.9
40	8.06	−14.96	16.2	14.6	37.9	43.8
50	8.29	−16.39	16.3	14.3	36.6	42.7
			Propylene Glycol			
0	8.28	−1.63	15.5	16.0	42.4	47.9
2	6.85	−3.38	15.5	15.9	42.0	47.6
5	6.35	−5.73	15.6	15.7	41.5	47.0
10	5.94	−9.58	15.6	15.4	40.5	46.2
15	5.31	−15.04	15.7	15.0	39.6	45.3
20	5.09	−18.71	15.8	14.7	38.7	44.5
30	5.73	−24.58	15.9	14.1	36.8	42.7

fraction of water structure is destroyed by glycerol molecules since they form hydrogen bonds with water molecules. The solvent polarity is decreased dramatically, and thus the solubility of the surfactant tails increases, as evident by the reduction in k_1 values. Correspondingly, the electrostatic interactions of the charge groups are also shielded with further addition of glycerol. Both effects lead to an increase in cmc values due to changes in the solvent−surfactant interaction. Similar behavior had also been observed previously for nonionic surfactants or amphiphiles in glycol−water mixtures.[8] Under this condition, the surfactant micellization is driven by enthalpy instead of entropy, as depicted by the deviation from the linear relationship at glycerol content exceeding ∼20 wt %.

To verify the above interpretation, SDS micellization behaviors in other glycol−water solvent mixtures, which have lower solubility parameters and dielectric constants, such as ethylene glycol and propylene glycol, were examined. Similar ITC thermograms for SDS in ethylene glycol−water and propylene glycol−water solvent mixtures at 298 K and 1 atm were observed. Since ethylene glycol and propylene glycol have similar chemical structure but possesses a lower polarity compared to glycerol,[16] trends identical to the glycerol−water mixtures should be expected, where an S-shape titration curves were reported for excess amounts of ethylene glycol or propylene glycol in water. The micellization enthalpy increases with the content of ethylene glycol or propylene glycol, where the cmc first decreases until a critical ethylene glycol or propylene glycol concentration. The cmc then increases with the solvent compositions. The comparisons on the SDS micellization in different glycol and water mixtures are shown in Figures 3 and 4 with thermodynamic parameters summarized in Table 2.

Although the SDS micellization behaviors in mixtures of water and different glycols are similar, different glycols give rise to changes in micellization properties due to different solubilities, as evident from Figures 3 and 4. The main reason for the difference is attributed to the different polarity or different solubility parameters. Although all these glycols can form a strong hydrogen bond with water, the polarity has the following trend: water > glycerol > ethylene glycol > propylene glycol.[16] However, the hydrophobicity of the three glycols has the following trend: propylene glycol > ethylene glycol ≅ glycerol. From Figure 3, it is evident that the dependence of the cmc on the solvent composition of ethylene glycol and glycerol is identical up to ∼20 wt % since their hydrophobic character is fairly identical. However, propylene glycol is much more hydrophobic, which produces much lower cmc values, as evident in Figure 3. In addition, the lowest cmc occurs at ∼15 wt % glycerol or ethylene glycol but occurs at ∼20 wt % for propylene glycol, which also reinforces that propylene glycol has a stronger effect on the surfactant micellization. Beyond this critical concentration, the cmc increases with glycol content in the following trend: ethylene glycol > glycerol > propylene glycol, which is directly correlated to their capability to destroy water structure. The effect of different glycol contents on the micellization enthalpy is shown in Figure 4, where the micellization enthalpy increases linearly with glycol composition and deviates from this linear relationship at higher concentrations.

The solvent solubility parameter is commonly used to describe the cohesion energy of a solvent since it was derived from the energy required to convert a liquid to a gas. The energy of vaporization is a direct measure of the total cohesive energy between the molecules in liquid state. The term solubility parameter was first used by Hildebrand and Scott,[30,31] where the Hildebrand solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = \left(\frac{E}{V}\right)^{1/2} \tag{1}$$

where V is the molar volume of pure solvent and E is the energy of vaporization. The square of the Hildebrand solubility parameter can be described as the sum of the square of the Hansen's D, P, and H three-dimensional solubility parameters,
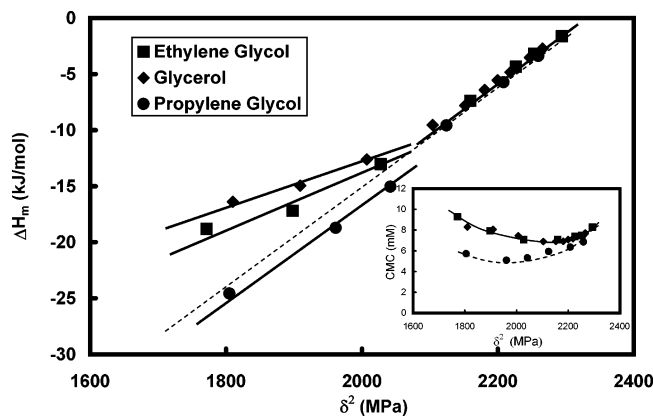
Figure 5. Solubility parameter dependence of the SDS micellization enthalpy and cmc in different glycol–water solvent mixtures at 298 K and 1 atm.

which are related to the contributions arising from dispersive interaction, dipole–dipole interaction, and hydrogen binding:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad (2)$$

For the solvent mixture, δ, δ_D, δ_P, and δ_H were calculated as volume average:[7,32]

$$\delta_x = \sum (\delta_x)_i \phi_i \qquad (3)$$

where x stands for D, P, or H, i referring to cosolvent or water and ϕ_i referring to the volume fraction of component i in the solvent mixture. The numerical values of calculated solubility parameters of solvent mixtures are listed in Table 2.

Figure 5 shows the dependence of the enthalpy for SDS micellization on the solubility parameter for various glycol–water mixtures. With increasing solubility parameter, the micellization enthalpies become less negative, suggesting that the micellization process is increasingly driven by an entropic rather than an enthalpic process. However, it is interesting that the general profile can be divided into two regimes with the boundary of $\delta^2 \sim 2100$ MPa. We observed that ΔH is independent of glycol types at $\delta^2 > 2100$ MPa, while it depends on glycol types for $\delta^2 < 2100$ MPa. For the former (high δ^2 value), the addition of glycol resulted in the decrease in the charge interaction of micelles; thus, the effect of solvent polarity is negligible. At $\delta^2 < 2100$ MPa, due to the different polarity of these three glycols, the reduction in the solvent polarity varies and this will directly impact the solvent–surfactant interactions.

The cmc of SDS in different glycol–water mixtures is shown as an inset in Figure 5. It is evident that the cmcs of SDS are almost independent of the types of glycols for $\delta^2 > 2100$ MPa, where the cmc increases with δ^2. However, the cmc becomes dependent on the glycol types for $\delta^2 < 2100$ MPa, where cmc decreases with increasing δ^2. In the presence of small amounts of glycol, the glycol induces the shielding of charge interaction, which will have negligible impact on the solvent properties. However, at higher glycol content, the effect of solvent properties becomes more significant, where the reduction in the solvent polarity and the enhanced shielding of the charged SDS head groups produce a higher cmc. The thermodynamic parameters strongly indicate that the addition of glycols reduces the micellization of SDS.

From the relationship between thermodynamic parameters and solvent solubility parameters, we can conclude that the effect of glycol addition on the micellization of SDS can be normalized using the solubility parameters. As the solubility of the mixed
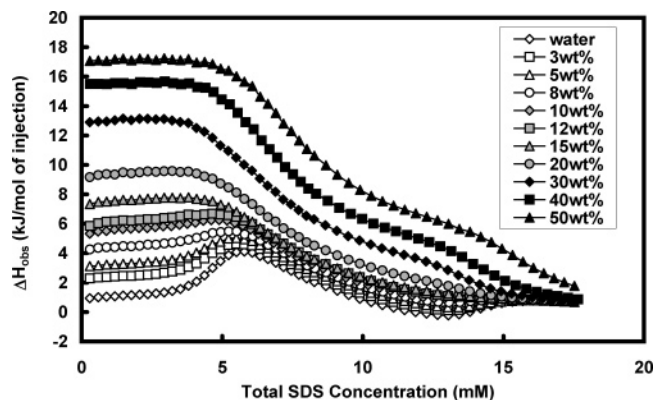

Figure 6. ITC thermograms for titrating 0.1 M SDS into 0.1 wt % PEO solutions in glycerol–water solvent mixtures at 298 K and 1 atm.

solvent is greater than 46 (MPa)$^{1/2}$ ($\delta^2 = 2100$ MPa), addition of glycol only alters the effect of charged surfactant head groups. With further reduction in the solvent solubility parameter, glycol molecules will have an impact on the solvent–surfactant interactions, where not only charge groups but also tail groups are affected. From Table 2, it is evident that the contribution from the dispersion Hansen solubility parameter is negligible, and the main contribution to the solvent solubility parameter is attributed to the H-bond Hansen solubility parameter, which is related to the destruction of water structure.

2. Interaction of SDS and PEO in Water–Glycol Mixed Solvents. The solubility of PEO in water is attributed to the formation of H-bond between PEO and water molecules. In the presence of glycols, it reduces the solubility of PEO in the solvent mixture due to the formation of H-bond between water and glycol molecules. Although the binding interactions between SDS and PEO in aqueous solution have been studied previously, the interaction between SDS and PEO in various glycol–water mixtures is scarce. The ITC thermograms for the binding interaction between SDS and PEO300K in various glycerol–water mixtures are shown in Figure 6. It is obvious that the titration curves are different when the glycerol content was varied, where the observed enthalpy increases with increasing amounts of glycerol, especially for glycerol concentration greater than 20 wt %. In addition, the decrease in the charge interaction with increasing glycerol concentration is also evident. Since the addition of glycerol into water not only alters the SDS micellization but also PEO conformation in solution, the physics of such a system is rather complex. The goal of this study is to provide some insights into the characteristic of the interactions between SDS and PEO in the presence of various glycol systems.

During the course of titrating concentrated SDS into PEO in the solvent mixture, ITC measures the total enthalpy changes during the titration process, i.e.,

$$\Delta H_{obs} = \Delta H_{dil} + \Delta H_{demicel} + \Delta H_{binding} \qquad (4)$$

Comparing with the enthalpy for titrating SDS into water

$$\Delta H_{obs} = \Delta H_{dil} + \Delta H_{demicel} \qquad (5)$$

It is evident that the difference in the enthalpy between titrating SDS into PEO solution and that into the solvent mixture is attributed to SDS–PEO interaction.[33] The difference curves for titrating SDS into PEO and SDS dilution in various solvent mixtures are shown in Figure 7. All the difference curves display similar trends (the shape is identical to SDS–PEO in aqueous solution) for glycerol content lower than 8 wt %, which displays
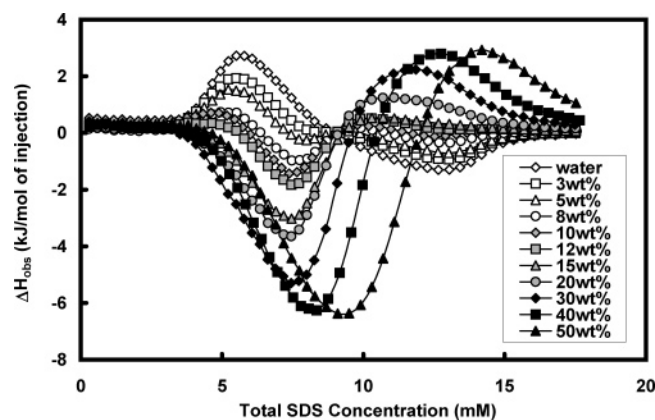
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Figure 7. Difference curves for titrating 0.1 M SDS into 0.1 wt % PEO solutions in glycerol−water solvent mixtures at 298 K and 1 atm.

Figure 8. Difference curves for titrating 0.1 M SDS into 0.1 wt % PEO solutions in different ethylene glycol−water solvent mixtures and water at 298 K and 1 atm.

an endothermic peak at low SDS concentrations followed by an exothermic peak at high SDS concentrations. However, the areas of both peaks decrease when the glycerol was increased from 0 to 5 wt %. On the basis of previous study on the SDS−PEO system in water,[34] the endothermic peaks at low SDS concentrations are attributed to the polymer-induced SDS micellization, where PEOs are dehydrated and solubilized into the core of mixed micelles, while the exothermic peaks at high SDS concentrations are associated with the dehydration of previously solubilized PEO from the micellar core and bind to the surface of SDS micelles. Within this glycerol concentration range, the critical aggregation concentration (cac) values determined from the thermogram increase and the saturation concentration C_2 decrease with glycerol concentration, which suggest a reduction in the binding capacity of SDS to PEO. Addition of small amounts of glycerol not only decreases the charge interaction among SDS molecules but also reduces the solubility of PEO segments. The positive enthalpy corresponds to the formation of SDS mixed micelles at low SDS concentrations through the dehydration/desolvation of PEO chains, and the negative enthalpy at high SDS concentrations is associated with the rehydration/resolvation of PEO chains. The lower proportion of PEO dehydration/desolvation gives rise to an overall reduction in the total enthalpy change indicated by the peak areas of the titration curves.

At glycerol concentrations ranging from 8 to 15 wt %, the titration curves exhibit a different trend from those at low glycerol contents, where only one exothermic peak is evident at low glycerol concentrations. The different titration curves suggest the presence of different binding mechanisms. As the amounts of glycerol increase, the solvent quality will be further altered; i.e., the solvent polarity decreases, where the solvent for PEO changes from a good to a poor solvent due to the disruption of hydrogen bonds between PEO and water by glycerol molecules.[8] Hence, the solubility and the flexibility of PEO chains in the solvent mixtures decrease. As a result, both the desolvation and resolvation processes are minimized, and PEO could be directly solubilized into the core of SDS mixed micelles through the exothermic hydrophobic interaction. Compared with the temperature dependence of the binding interaction between SDS and PEO,[35] similar trends were observed at temperatures above the LCST of poly(propylene glycol) (PPG). For the formation of SDS/PEO mixed micelles at the cac, the observed enthalpy change is the result of the dehydration/desolvation (positive enthalpy) of PEO segments and hydrophobic attraction (negative enthalpy). Within this glycerol concentration range, the decrease in cac values and the increase in the exothermal peak area strongly indicate the continuous
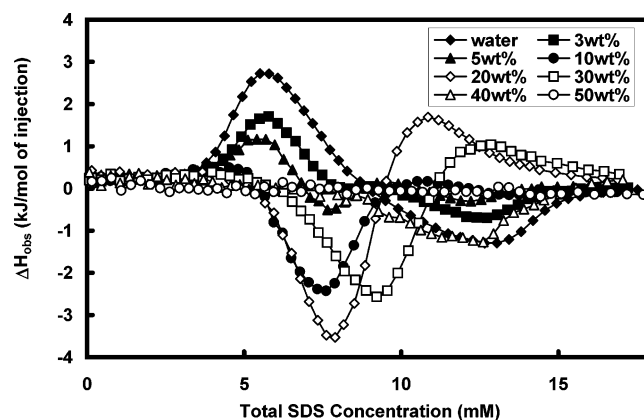
reduction in the solubility of PEO in the solvent mixture. However, C_2 was found to remain constant.

At glycerol concentration greater than 20 wt %, a different thermogram was observed, where significant exothermic and endothermic peaks at low and high SDS concentrations are observed, respectively and the area of both peaks increases with glycerol concentration. At this glycerol concentration range, the solubility of PEO continues to be low, and such experimental trends should result from the contribution of glycerol effect on SDS aggregation. From previous studies on SDS demicellization process, it is evident that SDS undergoes different behavior at glycerol concentration beyond 20 wt %, where the cmc increases with glycerol content. In the presence of PEO, C_2 increases sharply due to the increase in the CMC of SDS with glycerol content. Further increase in the SDS concentration may lead to the possible structure reorganization, where the endothermic arise from the repulsion of SDS head groups.

To verify the above hypothesis, the SDS−PEO binding interactions in solvent mixtures containing two other glycols and water were also examined. Since propylene glycol and ethylene glycol are less polar than glycerol, hence they should have a more significant effect on the binding interaction between SDS and PEO. Figure 8 shows the difference ITC thermograms for titrating SDS into PEO300K in ethylene glycol−water solvent mixtures, and similar ITC thermograms were observed for propylene glycol−water mixtures. The titration curves are identical to those in glycerol−water mixtures, which indicate that similar binding characteristics must be present. However, the effect of ethylene glycol content on the solvent quality is more significant. At ethylene glycol concentration of 10 wt %, no endothermic peak or no PEO desolvation behavior was detected. At ethylene glycol concentration greater than 20 wt %, it seems that the binding interaction between SDS and PEO decreases, as evident by the increase in the cac and the decrease in the area of both exothermic and endothermic peaks. Beyond the ethylene glycol concentration of 40 wt %, no binding heat can be detected, which indicates that the binding interaction between SDS and PEO is absent. From Figure 9, when the propylene glycol concentration exceeds 30 wt %, no binding interaction between SDS and PEO can be observed. Such a trend is related to the less polar character of ethylene glycol and propylene glycol than that of glycerol since glycerol is more polar and the effect on the PEO solvation and SDS micellization is lower than the other glycols. Due to further decrease in the solvent quality for propylene glycol, the effect on the binding interaction is more significant than for ethylene glycol.
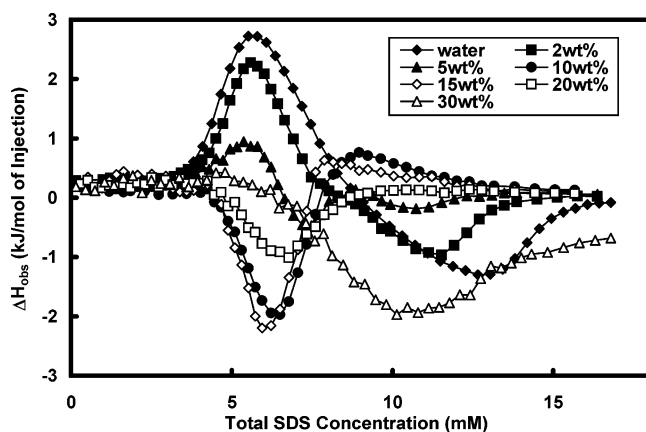
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Figure 9. Difference curves for titrating 0.1 M SDS into 0.1 wt % PEO solutions in different propylene glycol−water solvent mixtures and water at 298 K and 1 atm.

Additional study incorporating other physical techniques, such as NMR, and conductometric and potentiometric titrations, should be explored to elucidate unresolved issues raised in the present study.

Conclusions

Addition of different glycols to aqueous system gives rise to changes in solvent polarity and structure. With increasing content of glycol, the cmc decreases with glycol concentration until 15−20 wt % and then increases. On the basis of the solubility parameters of these glycols, the trend in altering the solvent polarity and water structure is propylene glycol > ethylene glycol > glycerol. For the SDS−PEO binding interaction in the solvent mixtures, the presence of a small amount of glycol reduces the solubility of PEO, which minimizes both the dehydration and rehydration processes. With the increase in glycol concentration, the dehydration process disappears and only the solubilization process dominates. Further increase in glycol concentration not only decreases the solubility of PEO but also decreases the micellization capability of SDS. In such condition, the PEO−SDS aggregation complexes structure may reorganize at higher SDS concentrations. Beyond a critical concentration of the glycols, no interaction between PEO and SDS in solutions was observed, which is attributed to the reduction in polarity and dielectric constant of the solvent mixtures.

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