Adsorption and Micellar Properties of Binary Ionic/Nonionic Surfactant Mixtures in Ethylene Glycol + Water

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The adsorption behavior and micellar properties of the mixed binary ionic/nonionic surfactants containing cetyltrimethylammonium bromide (CTAB) and *p*-(1,1,3,3-tetramethylbutyl)polyoxyethylene Triton X-100 (TX-100) in aqueous mixture of ethylene glycol (EG) have been studied through surface tension and conductometry techniques. The Gibbs energy of the mixed micellization ($\Delta G^{\circ}_{\text{mic}}$) was obtained from the critical micelle concentration (CMC) and counterion degree dissociation (α_{diss}) values. The differences in the Gibbs energies of mixed micellization of TX-100/CTAB between water and water + EG mixtures were calculated to monitor the influence of cosolvent on the micellization process. The role of the structure-breaking ability of EG (g_{sb}) and electrostatic interaction in the process of micellization are surveyed in this article. The cosolvent effect on the interaction between two surfactants, CTAB and TX-100, in a mixed monolayer at the air−liquid interface (β^{δ}) and mixed micelle (β^{M}) was analyzed on the basis of regular solution theory. Furthermore, considering nonrandom mixing and headgroup size effects on the basis of the Gibbs−Duhem relation, proposed by Hall, β^{M} was calculated. It was observed that, as the amount of EG in the aqueous medium increased, the intermolecular interactions decreased for both the planar air/aqueous interface and the micellar systems. However, at higher volume fractions of EG, β^{M} increased because of reduction in electrostatic self-repulsion interaction between ionic headgroups through mixing. Finally, the analysis of the variations of surface tension as a function of solution composition and total surfactant concentration suggests that the surface activity of CTAB or TX-100 and their mixtures decreases with the increase in the amount of EG in aqueous media.

Introduction

Surfactants are widely used in both industry and everyday life, and the properties of aqueous solutions have received considerable attention. The formation of micelles and their dependence on environmental factors (temperature, additives, etc.), thermodynamics of formation, counterion binding, aggregation numbers, catalyzing functions, and so forth, are important physicochemical aspects that need detailed and intensive attention for both fundamental understanding and application prospects. Changing solvent quality provides the opportunity to study the role of the so-called cosolvent or solvophobic effect[1] and the increasing use of surfactants in applications which require water-free or water-poor media which in turn makes this type of research more interesting.[2]

In recent years, however, many authors have turned their attention to micelle formation and the aggregation process of micelles in solvent systems constituted by a mixture of water with some polar organic solvents.[3−18] The polar organic solvents with properties similar to water, such as ethylene glycol (EG), formamide, formic acid, and glycerol, have been widely studied. All of these solvents are characterized by a high dielectric constant, high cohesive energy, and considerable hydrogen bonding abilities.[19] Evans proposed that the ability of a solvent to form hydrogen bonds is a prerequisite for micellization.[20] However, the ability of water to form unique hydrogen bonded networks is not a necessary condition for the aggregation process. The gradual re-establishment of water with other polar solvents allows one to explore a wide bulk phase polarity range and its influence on micellization. A lot of studies have been carried out to concern the aggregation behavior of both ionic and nonionic surfactants in different solvent systems.[3−18] However, we could find few studies on the aggregation and interaction of mixed surfactants in mixed solvents. Moore et al. found that the mixed system of alkyltriphenyl phosphonium bromide in water and aqueous EG mixtures exhibited synergism in the formation of mixed micelles. The synergistic effects are decreased with EG increase because of the solvation of the polar headgroups by the solvent and the decrease of headgroup−headgroup repulsions.[21] The mixed aggregation tetradecyltrimethylammonium bromide (TTAB) and Triton (X-100) has been studied in water + ethanol mixtures by Rafati and Maleki. They found that the stability of mixed micelles decreases when the participation of the cosurfactant increases.[22] The study of mixed micelle formation by cetylpyridinium chloride and TTAB in pure water independently, water along with varying amounts of EG, and with diethylene glycol (DEG) has proved that mixed micelle formation between them is quite non-ideal in pure water and that nonideality decreases with increasing amounts of EG or DEG.[23] Soni et al. have investigated the effect of nonelectrolyte additives, such as 2-butoxy ethanol, on the phase, thermodynamic, and association properties of two silicone surfactants based on poly(dimethyl siloxane)−graft−polyethers in aqueous solutions.[24] But, more detailed investigations are needed to understand the solvophobic effect due to added cosolvents on the colloidal behaviors such as micellization

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and surface adsorption of binary surfactant mixtures. To our knowledge, no study has examined the increase of EG to mixed surfactants on the nature of the nonrandom mixing of surfactants. It would be of interest and importance, from both practical and academic viewpoints, to investigate this phenomenon in systems containing multiple surfactants. Hence, in the present study, we have investigated the mixed micelle and adsorption properties of binary surfactant systems containing the cationic surfactant cetyltrimethylammonium bromide (CTAB) and the nonionic surfactant *p*-(1,1,3,3-tetramethylbutyl)polyoxyethylene Triton X-100 (TX-100) in aqueous mixtures of EG. The surface excess (Γ_{max}) and minimum area per molecule were also evaluated from surface tension plots. Calculating the values of parameters such as the interaction parameter (β^{*M}), the packing parameter (P*), and the size parameter (ρ), the nature and strength of the interactions between the surfactant mixtures were obtained. Finally, the stability of mixed micelles was examined as a function of the permittivity of medium. In addition, we have modified molecular thermodynamic theory and added a new term as g_{sb} that is attributed to the structure breaking of water. The solvophobic effects due to the change in the solvent composition were discussed in various interaction terms such as headgroup−headgroup or chain−chain interactions and hydrogen bonding.

Materials and Methods

Materials. CTAB (Merck), TX-100, *p*-(1,1,3,3-tetramethylbutyl) phenoxypoly(ethylene glycol) (Merck), and EG (Merck) were used for preparation of stock solutions in pure water and EG−water mixed solvents. Samples were prepared by mixing the appropriate volumes of CTAB and TX-100 stock solutions. Doubly distilled deionized water was used for all sample preparation and dilution.

a. Surface Tension Measurements. Surface tension measurements were made at 298 K with a Krüss K12 tensiometer under atmospheric pressure by the ring method.[25] The platinum ring was thoroughly cleaned and then flame-dried before each measurement. Measurements of the surface tension of pure water at 298 K were performed to calibrate the tensiometer and check the cleanliness of the glassware. The uncertainty of the measurements was $\pm$ 0.1 $mN \cdot m^{-1}$. In all cases more than three successive measurements were carried out, and the standard deviation did not exceed 0.08 $mN \cdot m^{-1}$. The temperature was controlled to within ± 0.1 K.

b. Electrical Conductivity Measurements. Conductivity measurements of surfactant solution were made by a conductometer model, Jenway 4510. After investigating the conductivity of the solvent, three successive conductivity measurements of the surfactant solutions were carried out under controlled constant temperature. The uncertainty of the measurements was $\pm$ 0.01 μs.

Results and Discussion

a. Critical Micelle Concentration and Thermodynamic of Micellization. Figure 1 shows typical plots of the surface tension (γ) and conductivity (κ) measurements of mixed surfactant (CTAB/TX-100) in the volume fraction = 0.1 EG solutions, since the mole fraction of CTAB is equal to 0.5. As it is shown, the surface tension curve has a clear break at which micelles start to form. That is, the concentration corresponding to the break in the curve represents the critical micelle concentration (CMC) in all of the systems (Figure 2). The observed CMC values for pure surfactants CTAB ($1 \cdot 10^{-3}$ $mol \cdot L^{-1}$) and TX-100 ($0.25 \cdot 10^{-3}$ $mol \cdot L^{-1}$) in aqueous solution are in good agreement with the reported values.[26,27] A comparison of surface tension at CMC, γ_{CMC}, of pure components also indicates a higher surface activity of TX-100 ($\gamma_{CMC} = 29$ $mN \cdot m^{-1}$) compared with CTAB (γ_{CMC} = 34 $mN \cdot m^{-1}$).

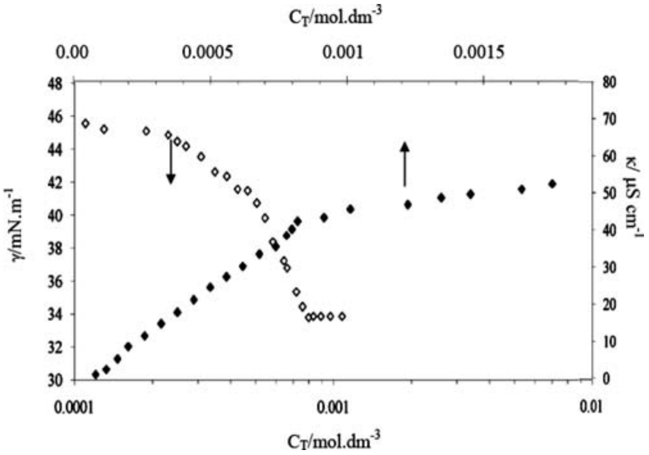

Figure 1. Effect of the total concentration on the specific conductivity and surface tension in water + EG solutions (χ_{EG} = 0.1) at 298 K: ◆, conductivity; ◇, surface tension. A solution molar relation of CTAB/TX-100 of 1:1 is considered.

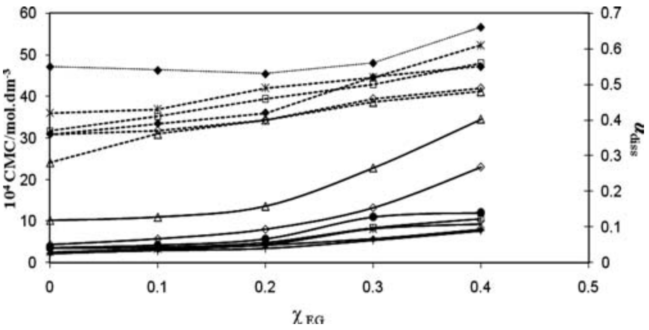

Figure 2. Effect of the EG content on the CMC and a_{diss} in solution for different composition of CTAB/TX-100 at 298.0 K: Δ, pure CTAB; ◇, CTAB/TX-100 (α_{CTAB} = 0.8); ●, CTAB/TX-100 (α_{CTAB} = 0.6); □, CTAB/TX-100 (α_{CTAB} = 0.5); ∗, CTAB/TX-100 (α_{CTAB} = 0.4); ◆, CTAB/TX-100 (α_{CTAB} = 0.2); +, pure TX-100. The solid lines indicate the CMC values taken from surface tension, and the dashed lines indicate the a_{diss} values obtained conductometry technique.

The specific conductivity, κ, versus concentration plots produced breaks that corresponded to the CMCs of both ionic and ionic−nonionic mixed surfactant systems (Figure 1). The values of CMC estimated from the electrical conductivity plot are given in Supporting Information. It can be seen in the Figure 1 that the slopes of the linear region above CMC are smaller than those below CMC. This is a consequence of counterion binding at the surface of micellar aggregates. In other words, there is an effective loss of ionic changes since a number of counterions are confined to the micelle surface. The degree of counterion dissociation, α_{diss}, corresponds to the average number counterions/surfactant ion that dissociates from the micelle, and this parameter can be estimated from the ratio between the slopes of the curves above and below the CMC (William's method).[28−30] The value of α_{diss} is more in the CTAB/TX-100 mixture than in pure CTAB systems (Figure 2). This suggests the reduction of the charge density at the micellar surface due to the presence of TX-100 in the micelle. Furthermore, Figure 2 shows that, for all the compositions of CTAB/TX-100 studied, an increase in volume fraction of EG in the solution results in an increase

Table 1. Values of ΔG°_M for CTAB/TX-100 in Water + EG Solutions at $T = 298.0$ K

	ΔG°_M/kJ·mol^{-1}			
α_{CTAB}	$\chi_{EG} = 0.1$	$\chi_{EG} = 0.2$	$\chi_{EG} = 0.3$	$\chi_{EG} = 0.4$
0	0.6	1.0	2.1	3.0
0.2	0.9	1.7	3.7	7.6
0.4	1.3	4.1	7.2	10.1
0.5	1.5	3.9	7.1	9.6
0.6	1.5	3.6	8.8	9.9
0.8	1.4	3.6	7.2	10.1
1	2.5	4.5	7.8	10.1

in the CMC and α_{diss} values. The influence of the increase of EG in the solution on CMC and α_{diss} can be analyzed by considering the Gibbs energy of micellization, ΔG°_{mic}, which was calculated for nonionic surfactants and ionic surfactants or a mixture of ionic/nonionic surfactants by using eqs 1 and 2, respectively.[31,32]

$$\Delta G^\circ_{mic} = RT \ln \chi_{CMC} \tag{1}$$

$$\Delta G^\circ_{mic} = RT(2 - \alpha_{diss})\ln \chi_{CMC} \tag{2}$$

where χ_{CMC} and α_{diss} present the CMC values on the mole fraction scale and degree of counterion dissociation, respectively. According to molecular thermodynamics, ΔG°_{mic} is evaluated as the sum of the Gibbs energy contributions:[33,34]

$$\Delta G_{mic} = g_{tr} + g_{int} + g_{pack} + g_{ele} + g_{st} \tag{3}$$

where (1) g_{tr} is the surfactant tail transfer Gibbs energy which accounts for transforming the surfactant tails of surfactant types from the aqueous solution to the core of mixed micelle; (2) g_{int} is the interfacial Gibbs energy which accounts for forming the interface between the micelle core and the aqueous solution; (3) g_{pack} is the packing Gibbs energy which accounts for packing the surfactant tails in the micelle core; (4) g_{st} is the steric Gibbs energy which accounts for steric interactions between the surfactant headgroups; and (5) g_{ele} is the electrostatic Gibbs energy which accounts for the electrostatic interaction between the surfactant headgroups.

The studies show that the ability of a solvent, such as water, to form hydrogen bonds is a necessary condition for the formation of micelles.[19] Structural research on water has shown that liquid water is mostly best-described as a rather broken-down and slightly expanded form of the ice lattice. Thus, liquid water partly retains the tetrahedral bonding and consequent network structure characteristic of crystalline ice.[35] Regarding the water structure break-down, we have added a new term in the eq 3 to calculate ΔG°_{mic} which is represented by g_{sb}. So,

$$\Delta G_{mic} = g_{tr} + g_{int} + g_{pack} + g_{ele} + g_{st} + g_{sb} \tag{4}$$

where g_{sb} is the difference between the chemical potentials of the more structured and less structured forms of the solvent (Supporting Information).[36,37]

The magnitude of the surfactant tail transfer energy is considerably smaller in EG than in water, and it is a major contributor for the increase in CMC of ionic, nonionic, and ionic/nonionic surfactant mixtures as the amount of EG in the mixture increases. The interfacial energy is smaller in EG solutions than in water because of the considerably smaller EG + hydrocarbon interfacial tension compared with the water + hydrocarbon interfacial tension. The steric energy and the packing energy are decreased because of the decrease in the micellar aggregation number of ionic, nonionic, and ionic/nonionic mixed micelles upon the increasing volume fraction of EG (χ_{EG}) in the solution. There is a dependence of the CMC on these energy contributions, g_{int}, g_{pack}, and g_{st}, but their contributions are much lower than that of the surfactant tail transfer energy.[38] The variation of CMCs of CTAB, TX-100, and their mixture with the volume fraction of EG shows that the electrostatic energy has an important contribution in the EG + water solution (Figure 2). In a higher mole fraction of CTAB in the CTAB/TX-100 mixture, particularly in pure CTAB, the CMC values varied sharply upon the increase of the volume fraction of EG in solution because of the increase of the electrostatic repulsions between the charged headgroups located at the aggregate surface. The dielectric constant of EG is lower than that of water (37.7 as compared with 78.39 at 298 K).[37] An increase in the volume fraction of EG from 0 to 0.4 results in a decrease in the dielectric constant from 78.39 to 56.7 at 298 K.[37] This decrease should lead to an increase in the magnitude of electrostatic repulsion interaction energy in water + EG solution compared with the pure water. The g_{sb} is increased with the addition amount of EG in solution. It is generally accepted that the disruption of the structured water around the hydrophobic group favors demicellization. The effect of EG on the micellization can be estimated by using eq 5 as follows:[15]

$$\Delta G^\circ_M = \Delta G^\circ_{mic}(\text{water} - \text{EG}) - \Delta G^\circ_{mic}(\text{water}) \tag{5}$$

The values of ΔG°_M are summarized in Table 1. It can be seen that the presence of EG in the bulk phase affects the micellization process of CTAB, TX-100, and CTAB/TX-100 mixtures and leads less spontaneously. The positive values of ΔG°_M can be understood as the basis of a reduction in the solvophobic interactions caused by the improved solvation, which leads to an increase in the solubility of the hydrocarbon tails and electrostatic repulsion between headgroups (in ionic systems) in the presence of EG and consequently in an increase in the CMC. Then, it can be suggested that the structure-breaking ability of EG (g_{sb}) and increase in the repulsion interaction (g_{elec}) between headgroups, due to decrease dielectric constant (ε), are dominating factors in the variation of ΔG°_M. Also, g_{sb} can be calculated by analyzing the g_{elec} contribution to ΔG°_M. g_{elec} can be calculated by using an approximate analytical solution to the Poisson−Boltzmann equation.[38] It is remarkable that the ability of a solvent to bring about the self-association of surfactants can be related to its cohesive energy density, which can be characterized by the Gordon parameter,[39] $G = \gamma/\bar{\nu}^{1/3}$, where γ is the solvent surface tension and $\bar{\nu}$ is the average volume. The average molar volumes of the mixtures were estimated from eq 6:

$$\bar{\nu} = \bar{\nu}_{EG}\chi_{EG} + \bar{\nu}_{water}\chi_{water} \tag{6}$$

Table 2a shows the solvent surface tension, γ, the molar volume, $\bar{\nu}$, the dielectric constant, ε, and the Gordon parameter, G, for the EG + water mixtures used as bulk phases in the micellar solutions. The G values show that the presence of EG in the solvent induces a decrease in the solvent cohesiveness by increasing the solubility of the hydrocarbon tails and decreasing the solvophobic effect. Table 2b shows the values of ε which were calculated by using different theories such as Onsager,[37] Guggenheim,[37] and Kirkwood theories[40] (Supporting Information). The dielectric constants of EG/water mixtures which have been predicted on the basis of Kirkwood theory are in agreement with experimental data (Table 2b).

Figure 3 shows the plot of ΔG°_{mic} versus $1/\varepsilon$ for different mixtures of CTAB/TX-100. For a given binary mixture, ΔG°_{mic} increases steadily upon increasing $1/\varepsilon$, this increase being nearly linear at a low volume fraction of EG. At a high volume fraction of EG, the increase in ΔG°_{mic} with increasing $1/\varepsilon$ deviates from

Table 2

(a) Solvent Surface Tension, γ, Solvent Molar Volume, ν, Dielectric Constant, ε, and Gordon Parameter, G, for Some EG−Water Mixtures ($T = 298.0$ K)

χ_{EG}	γ/mN·m^{-1}	$\bar{\nu}$/mL	ε	G/mN·m^{-2}
0	71.06	18.07	78.74	27.12
0.1	62.43	21.85	70.80	22.38
0.2	59.30	25.64	65.60	20.11
0.3	57.25	29.42	60.9	18.58
0.4	56.50	33.47	56.70	17.54
1	48.00	55.90	37.70	12.56

(b) Calculated Values of ε for Some EG + Water Mixtures by Different Methods

χ_{EG}	ε_{exp}	$\varepsilon_{Kirkwood}$	$\varepsilon_{Onsager}$	$\varepsilon_{Guggenheim}$
0	78.74	78.74	78.74	78.74
0.1	70.80	68.29	78.12	77.51
0.2	65.60	60.85	77.51	75.18
0.3	60.90	55.36	76.33	74.07
0.4	56.7	51.08	73.00	71.42
1	37.70	37.70	37.70	37.70

linearity. In addition, for all mole fractions, the plots fit approximately with the straight line (correlation coefficient ≈ 0.93 to 0.98). The slope of the straight lines was found to be ≈ 12 for the pure CTAB as well as the binary mixtures at all composition, but for pure TX-100, the slope was found to be ≈ 5, indicating the importance of electrostatic interaction. In addition, Figure 4 shows the plots of ΔG°_{mic} against the Gordon parameter for all composition of CTAB/TX-100 mixtures. According to Figure 4, a decrease in the Gordon parameter of the bulk phase causes the micellization process less spontaneously.

b. Surfactant−Surfactant Interaction in the Micellar Phase and Monolayer at the Liquid−Air Interface. The nature and the strength of the interaction between two surfactants in a binary system can be determined in terms of the Clint equation[41] for an ideal (non-interacting) mixed system

$$\frac{1}{\mathrm{CMC}} = \frac{\alpha_1}{\mathrm{CMC}_1} + \frac{1 - \alpha_1}{\mathrm{CMC}_2} \tag{7}$$

where CMC denotes that of the mixed micelle, α_1 is the mole fraction of the surfactant 1, and CMC$_1$ and CMC$_2$ are the CMC of the components 1 and 2, respectively. In Figure 5 the CMC values have been plotted versus α_{CTAB} in water + EG solutions. One can see in Figure 5 that all curves show deviation from ideality and suggest non-ideality with synergism; however, it is observed that the non-ideality decreases with an increase in the amount of EG.

The non-ideality in mixed micelle formation can be illustrated by using the regular solution theory, proposed by Rubingh, based on the phase separation method of micellization,[42−44] with

$$\left[\frac{X_1^M \ln\left(\frac{\mathrm{CMC}\alpha_1}{\mathrm{CMC}_1 X_1^M}\right)}{(1 - X_1^M)^2 \ln\left(\frac{\mathrm{CMC}(1 - \alpha_1)}{(1 - X_1^M)\mathrm{CMC}_2}\right)}\right] = 1 \tag{8}$$

where X_1^M is the mole fraction of surfactant 1 in the mixed micelle. Equation 8 can be solved iteratively to obtain the value of X_1^M. The interaction parameter for mixed micelle formation in solution, β^M, is calculated by using the following equations:

$$\beta^M = \frac{\ln\left(\frac{\mathrm{CMC}\alpha_1}{\mathrm{CMC}_1 X_1^M}\right)}{(1 - X_1^M)^2} \tag{9}$$

The interaction parameter for mixed micelles was also analyzed by using a modified version of Rubingh method, suggested by our group,[45] which is based on the following equations for the excess Gibbs energy for the formation of mixed micelles, G^{ex}:

$$G^{ex}/RT = \beta^{*M}\left(\frac{X_1^M}{X_1^M + \rho X_2^M}\right)\left(\frac{\rho X_2^M}{X_1^M + \rho X_2^M}\right) \times \left(1 - \frac{X_1^M}{(X_1^M + \rho X_2^M)P^*}\right) \tag{10}$$

which is arranged as:

$$G^{ex}/RT = A(X_1^M)(1 - X_1^M)(BX_1^M + 1)\left(\frac{1}{(1 + CX_1^M)^3}\right) \tag{11}$$

$$A = \frac{\beta^{*M}}{\rho} \qquad B = \frac{P^* - \rho P^* - 1}{\rho P^*} \qquad C = \frac{1 - \rho}{\rho}$$

where β^{*M} is the interaction parameter in the micelle; X_1^M is the mole fraction of surfactant 1 (ionic surfactant) in the mixed micelle; ρ is the size parameter; and P^* is the packing parameter. For binary surfactant mixtures, P^* can be employed to represent the constraints on the packing of surfactant 1 in micelles rich in surfactant 2. The packing constraint is directly related to the nonrandom mixing in the system.[46]

The interaction parameter for mixed monolayer formation at the solution/air interface, β^{σ} is calculated by using the following equations:[26,47,48]

$$\frac{Z_1^2 \ln(\alpha_1 C_{12}^s / Z_1 C_1^s)}{(1 - Z_1)^2 \ln\left[\frac{(1 - \alpha_1)C_{12}^s}{(1 - Z_1)C_2^s}\right]} = 1 \tag{12}$$

$$\beta^{\sigma} = \frac{\ln\left(\frac{\alpha_1 C_{12}^s}{Z_1 C_1^s}\right)}{(1 - Z_1)^2} \tag{13}$$

where Z_1 is the mole fraction of surfactant 1 in the total mixed monolayer (on a surfactant-only basis) and C_1^s, C_2^s, and C_{12}^s are the monolayer concentrations in the solution phases of surfactant 1, surfactant 2, and their mixture, respectively, at the mole fraction α_1 of surfactant 1 required to produce a given γ value. In our experiments, we determined C_1^s, C_2^s, and C_{12}^s, which correspond to a surface tension, of $\gamma = 38.5$ mN·m^{-1}. Equation 12 is solved numerically for Z_1, which is then substituted into eq 13 to calculate β^{σ}. The calculated values of Z_1, β^{σ}, χ_1, and β^M are given in the Supporting Information. A constant γ value of 38.5 mN·m^{-1} was selected for evaluation of Z_1 and β^{σ}, following Zhou and Rosen,[43] as this value is as low as possible and thus ensures that the slopes of the γ versus log (C_t) plots are constant in the region where C_1^s, C_2^s, and C_{12}^s are taken from. However, using different values of constant γ caused slight changes in the evaluated parameters, although the observed trend remained the same. Similar observations have been reported in the literature.[47,48]

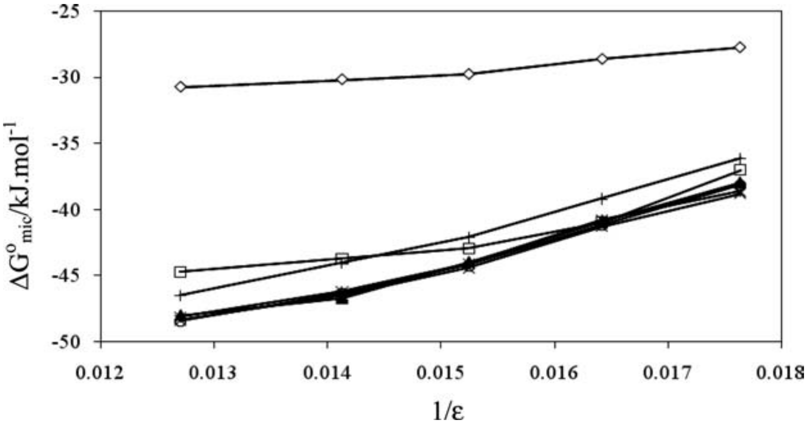

Figure 3. Gibbs energy as a function of the inverse of the dielectric constant for different compositions of CTAB/TX-100 at 298.0 K: +, pure CTAB; ○, CTAB/TX-100 ($\alpha_{CTAB} = 0.8$); ∗, CTAB/TX-100 ($\alpha_{CTAB} = 0.6$); ×, CTAB/TX-100 ($\alpha_{CTAB} = 0.5$); ▲, CTAB/TX-100 ($\alpha_{CTAB} = 0.4$); □, CTAB/TX-100 ($\alpha_{CTAB} = 0.2$); ◇, pure TX-100.

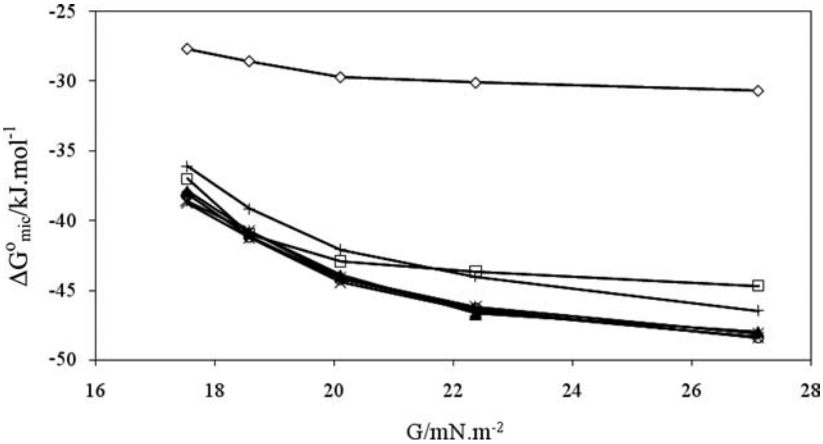

Figure 4. Gibbs energy vs the Gordon parameter for different compositions of CTAB/TX-100 at 298.0 K: +, pure CTAB; ○, CTAB/TX-100 ($\alpha_{CTAB} = 0.8$); ∗, CTAB/TX-100 ($\alpha_{CTAB} = 0.6$); ×, CTAB/TX-100 ($\alpha_{CTAB} = 0.5$); ▲, CTAB/TX-100 ($\alpha_{CTAB} = 0.4$); □, CTAB/TX-100 ($\alpha_{CTAB} = 0.2$); ◇, pure TX-100.

In the present article, the interaction between the two different surfactants in the mixed micelles was analyzed by the two methods described before. In the Rubingh model, the interaction parameter was calculated through eq 8; the obtained values of β^{M}_{ave} are listed in Table 3. According to the data in Table 3, by increasing EG to the aqueous solution, $|\beta^{M}_{ave}|$ decreases; this can be attributed to the structure-breaking nature of EG in water and the reduction of the hydrophobic interactions which are the main driving forces for mixed micellization. On the other hand, $|\beta^{M}_{ave}|$ increases at a higher volume fraction of EG. The increase in the $|\beta^{M}_{ave}|$ values at a higher volume fraction of EG can be mainly attributed to the decrease in electrostatic repulsion between ionic headgroups upon the mixing of CTAB and TX-100. All of the reports of researchers about the determination of the interaction parameters are in low volume fraction of EG (up to $\chi_{EG} = 0.2$) or in low binary cosolvent concentration,[21−23] but in our work as a new evaluation, we determine the interaction parameters at high volume fraction ($\chi_{EG} = 0.4$) of EG. It is very interesting that the obtained $|\beta^{M}_{ave}|$ at a high concentration of EG is completely different in comparison with those results reported by other researchers.[21−23] We observed that the value of $|\beta^{M}_{ave}|$ is decreased up to $\chi_{EG} = 0.3$ but the amount of $|\beta^{M}_{ave}|$ is increased sharply at $\chi_{EG} = 0.4$. However, the application of the Rubingh model yields a composition-dependent interaction parameter, β^{M} (Supporting Information). As we have also discussed previously,[45,49,50] regular solution theory does not adequately describe the behavior of monomers in a surfactant solution nor is it adequate for determining the activity coefficient and excess Gibbs energy in the mixed surfactant systems. Therefore, we proposed the model described before to better treat binary surfactant mixtures in solution. To predict the excess Gibbs energy (G^{ex}) of the nonideal mixtures, we have used the method that Maeda[51] had already proposed on the basis of the Gibbs−Duhem equation, considered by Hall.[52] The excess Gibbs energy was calculated as follows:

$$G^{ex} = RT[X_1^{M} \ln f_1 + (1 - X_1^{M}) \ln f_2] \tag{14}$$

where X_1^{M} is the mole fraction of CTAB in the mixed micelle. It is calculated from the ln(CMC) versus α_1 plot in the following equation:

$$X_1^{M} = \frac{\alpha_1[1 - (1 - \alpha_1)(\mathrm{d}\ln(\mathrm{CMC})/\mathrm{d}\alpha_1)]}{[1 + \nu(1 - \alpha_1)\{\alpha_1(\mathrm{d}\ln(\mathrm{CMC})/\mathrm{d}\alpha_1) + 1\}]} \tag{15}$$

where $\nu = 1 - \alpha_{diss}$ is the degree of counterion binding. The activity coefficients f_1 and f_2 were calculated according to the phase separation model (Supporting Information).

Figure 6 shows the variation of G^{ex} (determined using eq 14) as a function of the mole fraction of CTAB in the mixed micelle (X_1^{M}) for the systems with different EG + water compositions. Obviously, in the plot, the excess Gibbs energy is not symmetric with respect to the mole fraction, unlike the regular solution

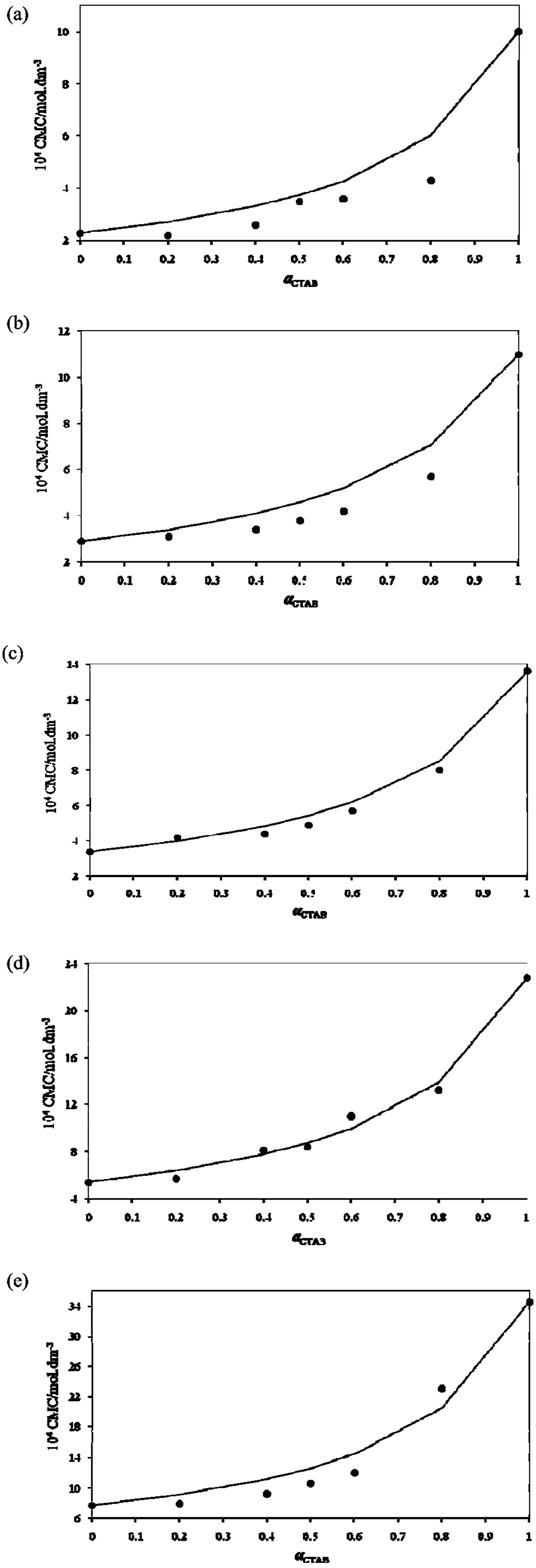

Figure 5. Experimental (symbols) and calculated (solid curves) CMC of mixed CTAB/TX-100 solutions, containing different volume fractions of EG: a, $\chi_{EG} = 0$; b, $\chi_{EG} = 0.1$; c, $\chi_{EG} = 0.2$; d, $\chi_{EG} = 0.3$; e, $\chi_{EG} = 0.4$.

Table 3. Cosolvent Effect on $\beta^{M}_{ave}$and β^{σ}_{ave} Values at $T = 298.0$ K

χ_{EG}	β^{M}_{ave}	β^{σ}_{ave}	$\beta^{\sigma}_{ave} - \beta^{M}_{ave}$
0	−1.32	−1.10	0.22
0.1	−1.02	−0.71	0.31
0.2	−0.62	−0.45	0.23
0.3	−0.16	0.68	0.84
0.4	−1.06	0.64	1.70

theory in which the excess Gibbs energy is symmetric and reaches a minimum at a surfactant mole fraction of 0.5.

We now consider the capacity of eq 10 to describe the behavior of G^{ex} at different EG concentrations. The values of β^{*M}, ρ, and P^* were obtained by least-squares fitting to obtain the best possible fit of G^{ex} against the mole fraction of surfactant (Figure 6). This model, eq 10, was found to successfully predict the behavior of G^{ex} for CTAB/TX-100 mixtures in water + EG solutions. Even the mole fractions of surfactant in micellar phase are obtained according to the Gibbs−Duhem equation, but the result is very close to our previous result[45,49] since the mole fractions of surfactant in micellar phase are obtained experimentally. In conclusion, we can claim that our proposed model can be used in different systems such as ionic/nonionic in pure solvent,[45] ionic/nonionic in pure solvent with various ionic strengths,[49] anionic/cationic in pure solvent,[50] and finally ionic/nonionic in mixed solvents which is presented in this article. As shown in Table 4, the interaction parameter $|\beta^{*M}|$ goes through a minimum as the volume fraction of EG is increased from $\chi_{EG} = 0$ to $\chi_{EG} = 0.4$ in solution. The initial decrease in $|\beta^{*M}|$, as EG is added to aqueous solution, is attributed to van der Waals interaction decreases between headrophobic groups. The increase in $|\beta^{*M}|$ at a higher volume fraction of EG can be the results from the electrostatic interaction decreases between ionic hydrophilic groups through mixing. Increasing the EG concentration in aqueous solution, the size parameter, ρ, does not change significantly. Increasing the amount of EG in solution, the optimized packing parameter, P^*, decreases (i.e., increasing electrostatic repulsion between headgroups is due to decreasing the dielectric constant (Table 2b)). The initial decrease in G^{ex} can be attributed to synergistic effects between

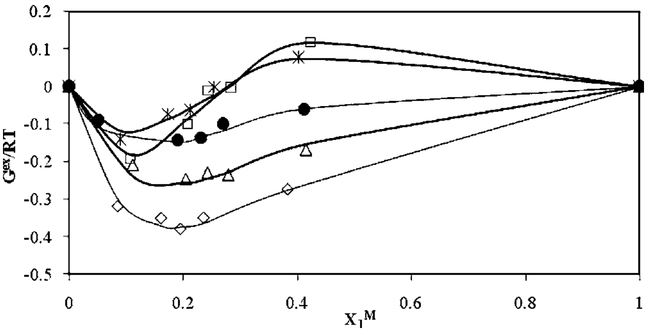

Figure 6. Excess Gibbs energy as a function of mole fraction of CTAB in the mixed micelle (X_1^M) for CTAB/TX-100 mixtures in water−EG solutions at 298 K: ◇, $\chi_{EG} = 0$; Δ, $\chi_{EG} = 0.1$; ●, $\chi_{EG} = 0.2$; ∗, $\chi_{EG} = 0.3$; □, $\chi_{EG} = 0.4$; solid line, fitting.

Table 4. Results of Least-Squares Fitting of the Three-Parameter Asymmetric Regular Solution Model to the Predicted Excess Energy for CTAB/TX-100 in Water + EG Solutions at $T = 298.0$ K

χ_{EG}	β^{*}_{M}	ρ	P^*
0	−2.28	0.38	1.24
0.1	−1.70	0.41	1.02
0.2	−1.16	0.37	0.85
0.3	−1.21	0.39	0.51
0.4	−1.84	0.36	0.52

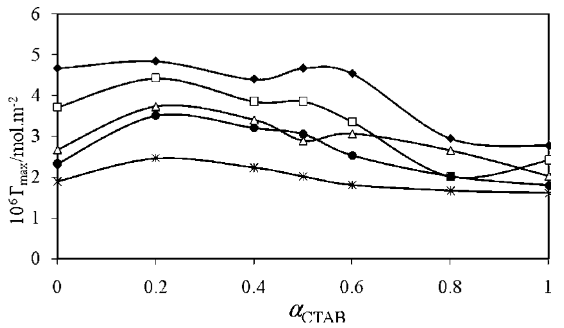

Figure 7. Surface excess concentration as a function of mole fraction of CTAB in the solution for CTAB/TX-100 mixtures in water + EG solutions at 298 K: ♦, $\chi_{EG} = 0$; □, $\chi_{EG} = 0.1$; Δ, $\chi_{EG} = 0.2$; ●, $\chi_{EG} = 0.3$; ∗, $\chi_{EG} = 0.4$.

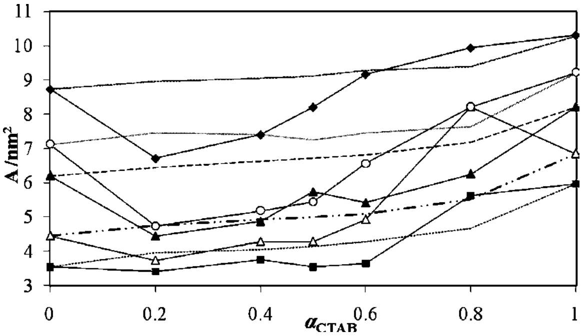

Figure 8. Experimental (solid curves) and calculated (dashed curves) surface area of mixed CTAB/TX-100 solutions, containing different volume fractions of EG: □, $\chi_{EG} = 0$; Δ, $\chi_{EG} = 0.1$; ▲, $\chi_{EG} = 0.2$; ○, $\chi_{EG} = 0.3$; ♦, $\chi_{EG} = 0.4$.

the two surfactants, while the increase in G^{ex} at higher fractions of CTAB can be mainly attributed to a decrease in the stability of the mixed micelles. This behavior is in line with expectations, given that the incorporation of ionic monomers into a micelle leads to an increase in the change density and consequently to greater repulsion between the ionic surfactants. These results are in agreement with previous findings.[53,54]

Table 3 shows that the average values of $|\beta^{\sigma}_{ave}|$ decrease considerably by increasing EG to the aqueous medium. This is the expected decrease in the values of $|\beta^{\sigma}_{ave}|$ attributed to the reduction of the attractive van der Waals interaction between hydrophobic groups at the planar air/aqueous solution due to the structure-breaking nature of EG in water and the presence of EG in monolayer at the air/aqueous solution interface. Furthermore, it has been shown that the value of $(\beta^{\sigma}_{ave} - \beta^{M}_{ave})$ becomes more positive by increasing the amount of EG (Table 3). This suggests that the reduction of van der Waals interaction caused by the increased amount of EG to the aqueous medium has a greater effect at the planar air/aqueous interface than at the convex micellar surface in an aqueous medium. Shortly, the present results indicate that a greater van der Waals interaction energy reduction is generated at the planar interface than that in the micelle.

c. Interfacial Properties. An effective measure of the adsorption of surfactant in the air−liquid interface is usually obtained by the surface excess concentration, Γ_{max}, which can be determined by the Gibbs equation for dilute solutions.[26]

$$\Gamma_{max} = \frac{-1}{2.303nRT}\left[\frac{d\gamma}{d\log C}\right]_{T,P} \tag{16}$$

where R and T are gas constant and temperature, respectively, γ is the surface tension, C is the concentration of surfactant, and n is the number of species formed in solution considering the dissociation per monomer. The minimum area per headgroup (A_{min}) of surfactant molecules at CMC at the saturated interface was obtained by the following equation:[26]

$$A_{min} = \frac{10^{18}}{N_A\Gamma_{max}}(\mathrm{nm}^2\cdot\mathrm{mol}^{-1}) \tag{17}$$

where N_A is Avogadro's number. The Γ_{max} has been calculated by using the curve-fitting plot of γ versus log C to a polynomial equation (PE) of formula $y = ax^2 + bx + C$ and then calculating the slope of the tangent at the CMC.[55] The R^2 (regression coefficient) value of the fit was between 0.9 and 0.99. According to Figure 7, the pure CTAB produced lower Γ_{max} than pure TX-100, and mutual repulsion between the ionic headgroups of CTAB leads to surface saturation at a comparatively lower concentration than the neutral TX-100 molecules. It can be seen that the values of Γ_{max} of CTAB/TX-100 mixtures decrease considerably by increasing the amount of EG to the medium. This is the expected decrease in the values of Γ_{max} attributed to several factors such as (1) a change in the water structure due to adding EG, (2) the interaction between the EG and the surfactant, and (3) the presence of the EG at the interface.[15] For the binary mixtures, Γ_{max} values were found to be higher than the Γ_{max} of pure CTAB and TX-100 systems because of synergism between them. Also, the Γ_{max} of a binary mixture decreases by adding EG because of the aforementioned factors. As expected, A_{min} demonstrates an inverse trend with respect to Γ_{max} since the amount of EG is increased (Figure 8). Furthermore, the low value of A_{min} in pure water and low fraction of EG in mixed solution suggests that the air/liquid interface is closely packed and therefore the surfactant molecules at the interface are oriented almost perpendicular to the interface. Figure 8 shows the ideal mixing values, A_{ideal}, calculated from the equation $A_{ideal} = Z_1A_1 + (1 - Z_2)A_2$, where Z_1 is the mole fraction of component 1 in the mixed monolayer and A_1 and A_2 designate the minimum area per molecule of CTAB and TX-100, respectively. However, for some cases, the experimental A_{min} values are smaller than A_{ideal}, in spite of the weak synergism between them (Figure 8). In $\chi_{EG} = 0.3$ to 0.4, the larger values of A_{min} in the case of the pure cationic surfactant may be attributed to the greater electrostatic repulsions among CTAB charged headgroups in surface monolayer, compared with dipole−dipole and ion−dipole interactions among TX-100 headgroups and TX-100−CTAB headgroups.

Conclusions

The effect of various amounts of EG as a cosolvent on the adsorption and association properties of two ionic and nonionic surfactants have been investigated. We have obtained the values of CMC and degree of dissociation (α_{diss}) at different volume fractions of EG. It has been observed that the values of CMC increase when the volume fraction of EG is increased in mixed solvents. To consider the effect of cosolvent on surfactant−surfactant interaction in binary ionic/nonionic surfactants, the values of β parameters are calculated. It was shown that adding EG to solution reduces the interaction parameters in both the mixed micelle (β^M) and the mixed monolayer (β^{σ}). At a higher volume fraction of EG, the synergism effect of the mixed micelle is increased significantly, which is a contribution from the decrease in electrostatic interaction between ionic headgroups upon mixing.

Regular solution theory does not adequately describe the behavior of excess Gibbs energy in mixed surfactant systems in water + EG solutions. Therefore, we have determined the micelle interaction parameters, $\beta^{*\mathrm{M}}$, ρ, and P^*, by a modified version of regular solution theory proposed by our group for CTAB/TX-100 mixtures in water + EG solutions. The proposed model on the basis of the Gibbs−Duhem relation provides a good description of the behavior of binary surfactant mixtures in mixed solvents. The interaction parameter, $\beta^{*\mathrm{M}}$, passes through a minimum as the volume fraction of EG in solution is increased from $\chi_{\mathrm{EG}} = 0$ to $\chi_{\mathrm{EG}} = 0.4$. These results agree with those obtained by regular solution theory. The packing parameter, P^*, decreases, whereas the size parameter, ρ, remains constant by increasing the amount of EG to aqueous solutions. The results of the study have illustrated the capability of the modified version of regular solution theory to describe the binary of surfactant mixtures in mixed solvents. Also, the Gibbs−Duhem relation provides a sound basis for the CMC analysis and the micelle composition in solutions.

Supporting Information Available:

Table SM1: values of CMC, a_{diss}, Gibbs energy of micellization, and predicted excess Gibbs energy for CTAB/TX-100 mixtures in water−EG solutions. Table SM2: calculated values of Z_1, β^{σ}, χ_1, and β^{M}. This material is available free of charge via the Internet at http://pubs.acs.org.

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