INTERACTION BETWEEN CATIONIC AND CONVENTIONAL NONIONIC SURFACTANTS IN THE MIXED MICELLE AND MONOLAYER FORMED IN AQUEOUS MEDIUM

Nabel A. Negm* and Ahmad M. El Sabagh
Egyptian Petroleum Research Institute, Nasr city, Cairo, Egypt

Artigo

Mixed micellization and surface properties of cationic and nonionic surfactants dimethyl decyl-, tetradecyl- and hexadecyl phosphineoxide mixtures are studied using conductivity and surface tension measurements. The models of Rubingh, Rosen, and Clint, are used to obtain the interaction parameter, minimum area per molecule, mixed micelle composition, free energies of mixing and activity coefficients. The micellar mole fractions were always higher than ideal values indicating high contributions of cationics in mixed micelles. Activity coefficients were less than unity indicating synergism in micelles. The negative free energies of mixing showed the stability of the surfactants in the mixed micelles.

Keywords: mixed micelles; regular solution theory; interaction parameter.

INTRODUCTION

Surfactant mixtures have been studied from the viewpoints of molecular interaction as well as of practical applications. It is generally accepted that the interaction between ionic and nonionic surfactants in an adsorbed film and micelle is larger than that between anionic and anionic surfactants or cationic and cationic surfactants and that between nonionic surfactants.[1-7] Industrial surfactant systems are typically mixtures of different chemical species such as ionic and nonionic surfactants, electrolytes, dyes and fillers. Some of these species are added to obtain beneficial synergistic effects and others to control ionic strength, pH, viscosity and other physicochemical properties of the system.[8,9] Thus, desirable surface properties for specific applications can be obtained by adjusting the compositions of these systems. However, choosing an appropriate surfactant system requires an understanding of the adsorption phenomena in these systems as well as the interactions between molecules adsorbed at the interface. In other words, a theoretical model of the adsorption process in mixed systems is required. Previously, ionic-nonionic surfactant mixtures have been analyzed first by using an ideal solution model[10] and the micelle or the surface layer is treated explicitly as a separate phase with a composition distinct from that of the bulk. Then, nonideality of mixing has been taken into consideration by applying regular solution theory. Recently, several molecular thermodynamic theories have been developed for predicting the properties and interactions in binary surfactant systems[11-13] and analyzed in terms of different formalisms like that of Clint, Rubingh, Rosen, Motomura, Lange, and Clint,[14-20] to understand their behavior in aqueous solutions which based on phase separation model and assumes ideal mixing of the surfactants in the micellar phase. Rubingh proposed a treatment based on regular solution theory (RST) for nonideal mixed systems which have been extensively used. Apart from this, the study of Singh *et al*.[21] and Maeda *et al*.[22] used the treatment of Rosen *et al*.[23] who improved the nonideal solution treatment of Rubingh[17] for mixed micelle formation by binary surfactant systems to estimate,

the surfactant molecular interaction and also the composition in the adsorbed monolayer at the air/water interface. The molecular thermodynamic approach,[24-26] on the other hand, suggests that electrostatic interactions among the ionic and polar head groups cause nonideality of the surfactant mixing. The types of molecular interactions in surfactant systems include: electrostatic interaction between ionic hydrophilic groups; ion-dipole interaction between ionic and nonionic hydrophilic groups; steric interactions between bulky groups; van der Waals interactions between hydrophobic groups, and hydrogen bonding among surfactant molecules.

The origin of the interaction between ionic and nonionic surfactants in adsorbed films and micelles was investigated by applying the thermodynamic treatment of surfactant mixtures to the mixtures of inorganic salt and nonionic surfactant[27,28] and to those of nonionic and ionic surfactants with different ionic head groups and counter ions.[29] It is concluded from those studies that: the polar head group of nonionic surfactant attracts inorganic cations in adsorbed films and micelles and a large difference in the size of head group between ionic and nonionic surfactants is favorable for the packing of the surfactants in adsorbed films and micelles, and a counter ion with a large hydration radius is less effective than that with a small hydration radius for the shielding of the charge on the ionic head group of surfactant in adsorbed films and micelles and causes large interaction between the head groups of ionic and nonionic surfactants.[30-32]

The main objective of the work is to investigate mixed micellization and adsorption properties of cationic-nonionic mixed systems consist of: cetyltrimethyl ammonium bromide (CTAB) and three conventional nonionic surfactants namely: decyldimethyl phosphine oxide (DDPO), tetradecyldimethyl phosphine oxide (DTPO) and hexadecyldimethyl phosphine oxide (DHPO). The selection of these surfactants due to: various hydrophobic chain lengths, as a factor expected to screen the ideality of mixing, and a large difference in their cmc values. Such an investigation is expected to lead to describe the contribution of the individual components in the mixed aggregates and mixed adsorbed monolayer. Also, realize the applicability of thermodynamic molecular model to binary systems. The analysis of data has been made in the light of various theoretical models, including those of Rubingh, and Clint.

*e-mail: nabelnegm@hotmail.com

EXPERIMENTAL

Materials and methods

Materials

The nonionic surfactants (DDPO, DTPO, DHPO) were all Aldrich products and used as received. The cationic surfactant (CTAB) was purified by recrystallization three times from dry ethanol to obtain the pure surfactant (ascertained using elemental and ^{1}H NMR data), Scheme 1.

n = 10 (DDPO), 12 (DTPO) and 14 (DHPO).

(CTAB)
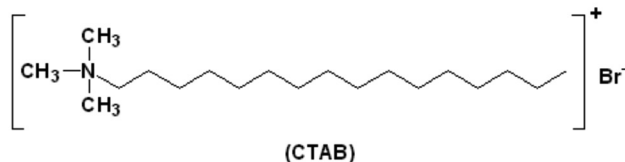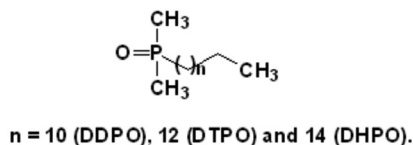
Scheme 1. *Chemical structures of the used surfactants*

Surface tension measurements

The surface tension (γ) measurements were made with a Krüss K6 tensiometer by the platinum ring detachment method. Surfactant concentration was varied by adding concentrated surfactant solution in small installments, and the readings were noted after thorough mixing at 25 ± 0.5 °C. The γ values were mean average of three readings. The accuracy of γ measurements was within ± 0.5 mNm^{-1}. The cmc values were determined by extrapolating the pre- and post micellar regions and determine the concentration corresponds to this point in the γ vs. logarithm of surfactant concentration plots.

Conductivity measurements

The conductivity of solutions was recorded at 25 ± 0.5 °C by a digital conductivity meter (Cyber Scan 350) from Eutech Instruments, having a sensitivity of 1 µScm^{-1} and an accuracy of 0.5%. The solutions were prepared in deionised double distilled water having conductivity in the range of 2-3 µS cm^{-1}. The electrode was washed after each reading several times with deionised water.

RESULTS AND DISCUSSION

Micellar mole fraction (X_1, X_{ideal})

In aqueous medium, the surfactant solutions of low concentration behave as simple electrolyte solutions and most of the surfactant molecules exist as free monomers. However, above a certain concentration, known as critical micelle concentration (*cmc*), micelles start to form. In a homogeneous series, the *cmc* of surfactants is related to the number of carbon atoms in the hydrophobic chain. The surfactant chain length is a major driving factor for micellization[33] and hydrophobic interactions a major driving force. Entropy increases when water molecules in hydration shell around the hydrophobic parts of monomeric amphiphiles are released during micelle formation. As the length of hydrophobic chain increases, more water molecules are released resulting in more entropy increase, hence micellization occurs at lower concentration, i.e., *cmc* value decreases. Addition of one methylene group (-CH$_2$) in the hydrophobic chain halves the

cmc value. However, effect of head group and counter ion on *cmc* is comparatively lesser. It is reported that replacement of methyl group of dodecyl trimethyl ammonium bromide by an ethyl group decreases the *cmc* from 15.13 to 13.97 mM.[33] As the technique of surface tension measurements is more accurate (own to be able to detect small micellar aggregates), conductivity data are used in confirming the data obtained from surface tension measurements.

Figure 1 represents the variation of surface tension vs. log *C* of the different surfactants used at 25 °C. It is clear that increasing the hydrophobic chain length of the dimethyl alkyl phosphine oxide surfactants considerably decreases their *cmc* values. Comparing the obtained data of the pure components (surface tension at equilibrium, surface excess and critical micelle concentration values) with the published data[33] showed good agreement with some deviation which can be attributed to the need of further purification for the components used.
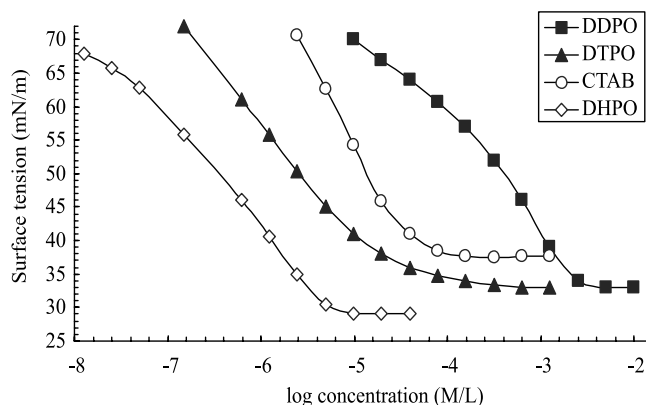

Figure 1. *Surface tension vs. log concentration of pure surfactants at 25 °C.* ■:*DDPO,* ▲:*DTPO,* ○:*CTAB,* ◇:*DHPO*

Figure 2 represents the variation of surface tension vs. log concentration of different binary mixed systems under consideration. The *cmc* values of the different solutions were extracted from Figure 2 and listed in Table 1. The ideality of the mixing process can be evaluated to determine the ideal value of the critical micelle concentration (*cmc$_{ideal}$*) at certain bulk mole fractions using Clint equation based on the pseudophase thermodynamic model[17] as follows:

$$(1/cmc_{ideal}) = \alpha_1/cmc_1 + (\alpha_2/cmc_2) \tag{1}$$

where, α_1, α_2: are the mole fractions of components 1 and 2 in the mixed system, cmc_1, cmc_2 are the critical micelle concentrations of pure component 1 and 2, respectively. This equation makes difference between ideal and nonideal surfactant mixtures.

Figure 3 shows the graphical presentation of *cmc* values of various binary mixtures of CTAB-DDPO/DTPO/DHPO surfactants, respectively. All the figures show that the *cmc* values of each mixture vary nonlinearly with respect to the regular change in bulk mole fraction. Due to the presence of cationic head groups in combination with those of bulky nonionic phosphine oxide head groups in the stern layer of the mixed micelle, a nonideal behaviour is expected in the mixed state.

It is clear from data represented in Table 1 that the experimental *cmc* values (*cmc$_{exp}$*) of different mole fraction combinations of CTAB-dimethylalkyl phosphineoxide, determined from the surface tension-log *C* plots, are always lower than the theoretical *cmc* values of each individual component and also from the ideal values (*cmc$_{ideal}$*). The lower *cmc$_{exp}$* values compared to *cmc$_{ideal}$* is attributed to the attractive interactions between the two mixed components. This attraction mo-
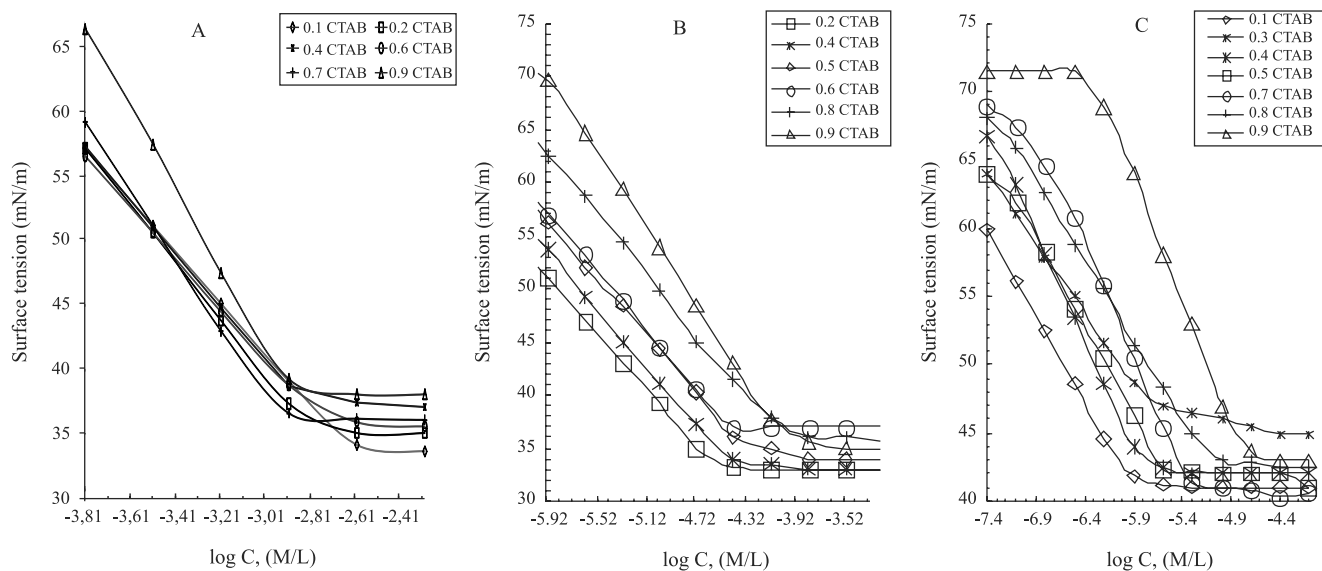
Figure 2. *Variation of surface tension vs. log concentration of A. CTAB-DDPO, B. CTAB-DTPO, C. CTAB-DHPO binary systems at 25 ºC.* ◇:*0.1 CTAB,* □:*0.2 CTAB,* ✳:*0.4 CTAB,* ○:*0.6 CTAB,* +:*0.7 CTAB,* △: *0.9 CTAB*

Table 1. Ideal and nonideal micellar mole fractions (X_{ideal}, $X_{nonideal}$), interaction parameters (β), activity coefficients (f_1, f_2), free energy of mixing (ΔG_{ex}), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) of the different binary mixed systems of CTAB-DDPO/DTPO/DHPO at 25 ºC

	a_1	X_{ideal}	$X_{nonideal}$	b	f_1	f_2	ΔG_{ex}, kJ mol^{-1}	G_{max}, mol m^{-2}	A_{min}, Å^2
CTAB-DDPO	0.1	0.19	0.21	-0.217	0.872	0.991	-0.09	1.67	99.53
	0.2	0.34	0.37	-0.464	0.884	0.939	-0.27	1.85	89.96
	0.3	0.47	0.48	-0.448	0.884	0.903	-0.28	1.71	96.93
	0.4	0.58	0.57	-0.413	0.925	0.876	-0.25	1.74	95.32
	0.5	0.67	0.64	-0.414	0.950	0.841	-0.24	1.83	90.84
	0.6	0.76	0.72	-0.395	0.970	0.814	-0.19	1.79	92.71
	0.7	0.83	0.78	-0.541	0.974	0.719	-0.23	2.08	79.77
	0.8	0.89	0.71	-0.640	0.984	0.635	-0.21	2.09	79.41
CTAB-DTPO	0.1	0.004	0.151	-5.574	0.018	0.881	-1.77	1.68	98.83
	0.2	0.008	0.170	-4.885	0.035	0.869	-1.71	1.16	145.22
	0.3	0.014	0.167	-4.007	0.062	0.894	-1.38	1.19	139.87
	0.4	0.021	0.173	-3.458	0.094	0.902	-1.23	1.16	142.70
	0.5	0.031	0.186	-3.107	0.128	0.898	-1.17	1.15	143.89
	0.6	0.047	0.216	-3.057	0.153	0.867	-1.28	1.17	141.63
	0.7	0.071	0.240	-2.745	0.205	0.854	-1.24	1.33	124.60
	0.8	0.115	0.247	-2.119	0.301	0.879	-0.98	1.19	139.97
	0.9	0.226	0.302	-0.987	0.618	0.914	-0.52	1.53	108.77
CTAB-DHPO	0.1	0.00158	0.355	-20.150	0.002	0.079	-11.56	1.05	158.61
	0.2	0.00354	0.350	-16.690	0.009	0.130	-9.52	1.32	125.48
	0.3	0.00606	0.359	-16.036	0.014	0.127	-9.25	1.41	117.83
	0.4	0.00940	0.365	-15.177	0.022	0.133	-8.82	0.83	199.83
	0.5	0.01403	0.373	-14.760	0.030	0.128	-8.66	1.12	148.06
	0.6	0.02090	0.383	-14.469	0.041	0.119	-8.58	0.84	197.02
	0.7	0.03213	0.388	-13.118	0.073	0.139	-7.81	1.29	129.18
	0.8	0.05385	0.381	-11.545	0.120	0.187	-6.83	1.00	165.85
	0.9	0.11351	0.419	-10.639	0.275	0.155	-6.49	1.43	115.82

ves the surfactant chains from monomeric phase to micellar phase, which facilitates the formation of the mixed micelles and decreases the free energy of the system.

The ideal contribution of component (i) in the formed mixed micellar system (composed of different components) can be calculated in term of mixed mole fraction in the ideal state (X_{ideal}) as follows:[4]

$$X_{ideal} = \alpha_1 cmc_2 / [(\alpha_1 cmc_2) + (\alpha_2 cmc_1)] \quad (2)$$

A quantitative interpretation of the results can be carried out by considering the regular solution theory (RST) and the treatment proposed by Rubingh.[4] These treatments allow calculating the micellar

mole fractions of the mixed systems using measurable parameters as follows:

$$\frac{(X_1)^2 \ln(\alpha_1 cmc/X_1 cmc_1)}{(1-X_1)^2 \ln[cmc(\alpha_2)cmc_2(1-X_1)]} = 1 \quad (3)$$

The values of X_1 were obtained by solving Equation 3 iteratively. Values of X_{ideal} and X_i were recorded in Table 1 and plotted in Figure 4 for the different mixed systems. It is clear from Figure 4 that the values of X_1 deviate positively and negatively from the ideal values (X_{ideal}) depending on the bulk mole fraction (α_1) and the hydrophobic chain length of the different components participated in the mixed micelles.
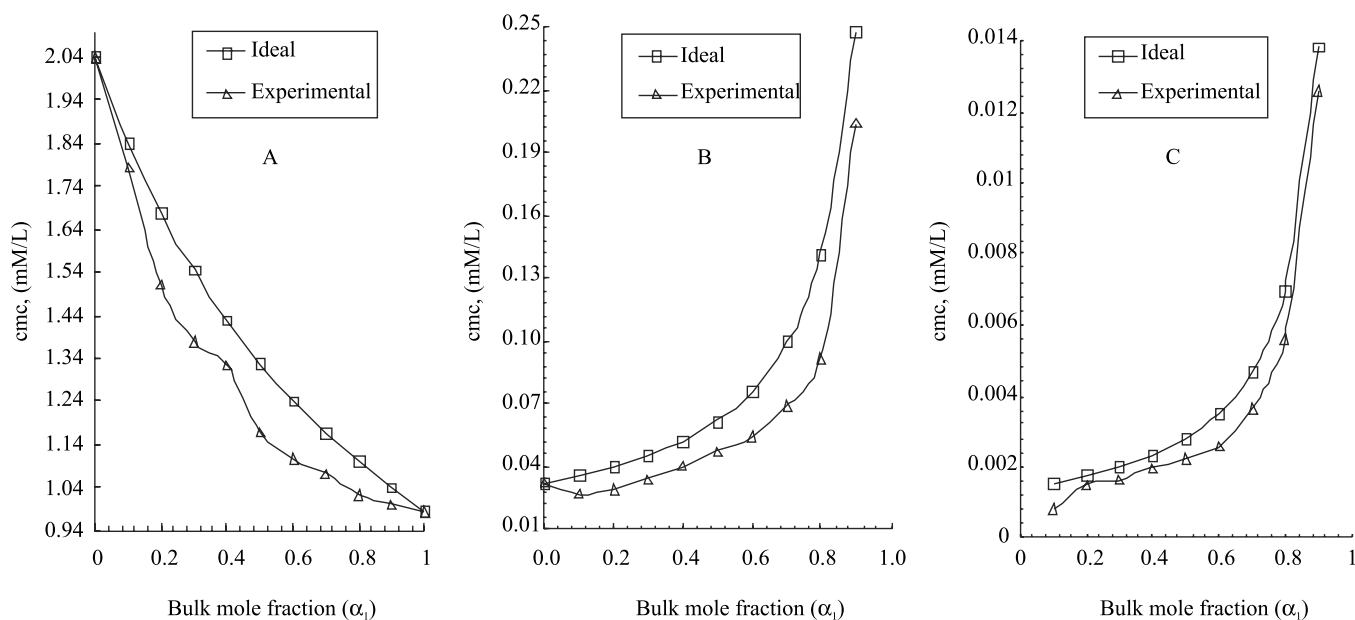
Figure 3. *Dependence of ideal and experimental cmc values on the bulk mole fractions of A. CTAB-DDPO, B. CTAB-DTPO, C. CTAB-DHPO binary systems at 25 °C. □: Ideal, △: Experimental*
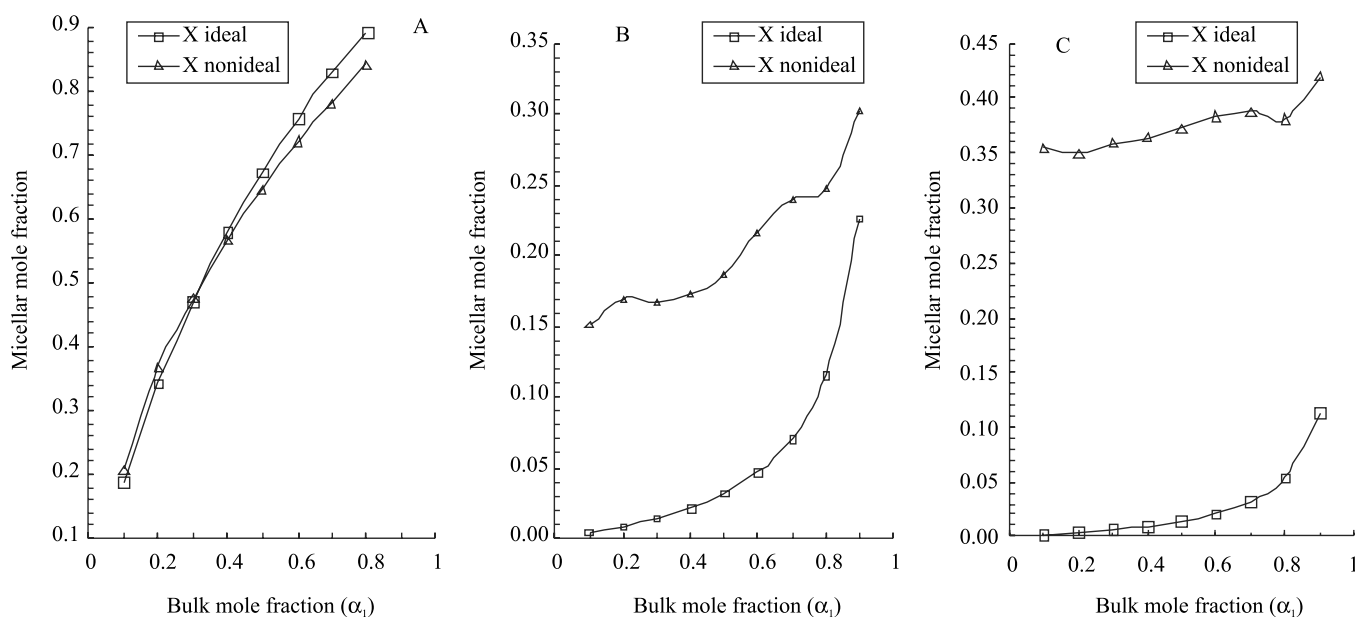

Figure 4. *Variation of ideal and nonideal micellar mole fractions of: A. CTAB-DDPO, B. CTAB-DTPO, C. CTAB-DHPO binary systems at 25 °C at different bulk mole fractions. □: Ideal, △: Experimental*

Analyzing X_1 data of CTAB-DDPO binary system at different mole fractions (Table 1) reveals that X_i values of CATB are higher than X_{ideal} in the poor regions of CTAB ($\alpha_1 = 0.1$, 0.2 and 0.3). While in the rich regions of CTAB (0.4, 0.5, 0.6, 0.7 and 0.8), X_1 decreases gradually to reach the ideal values then to be lower than X_{ideal}. A higher X_1 than that of corresponding X_{ideal} value indicates that the mixed micelles have high contribution of the cationic component than the nonionic component, while a lower X_1 than X_{ideal} value suggests the poor cationic content in the mixed micelles. Therefore, CTAB molecules are rich in the mixed micelles at lower α_1 region. That suggests the nonideality of the mixed systems at the lower mole fractions. Decreasing the difference between X_1 and X_{ideal} indicates the increase of ideality extent in the behaviour of the mixed system. at $X_1=X_{ideal}$ ($\alpha_1 = 0.35$), the system exhibits complete ideal behaviour ($cmc_{exp} = cmc_{ideal}$). Ideal system has not any type of interaction between the different components, and also low free energy. Increasing X_{ideal} than X_1 indicates the nonideality of the mixed system (antagonism), which is attributed to the hydrophilic repulsion of head groups or dipole-dipole repulsive interaction between the surfactant head groups, either identical or different head groups (N$^+$, P=O).[33]

That was explained from the regular solution theory point of view. In the regular solution theory, the molecules in the mixed system are assumed to be of comparable volume, completely interchangeable. That occurs only when the chemical structures of the different surfactants are similar or in the range, which did not exist in CTAB-DDPO mixed system. CTAB has high hydrophobicity than DDPO as shown from the surface tension-log C profiles of the individual components; DDPO and CTAB, Figure 1.

In case of X_1 higher than X_{ideal}, the system shows nonideal behaviour (synergism). The synergistic effect occurs due to the difference

in hydrophobicity of the mixed surfactant. At lower mole fractions of CTAB, the mixed solution interface is excessively covered by DDPO molecules than CTAB molecules, as shown from the surface tension values of the mixed systems. Then, preferential penetration of CTAB molecules occurs into the interface and displaces DDPO molecules to the bulk. The micellization occurs at lower cmc than cmc_1 and cmc_2; thus due to the richness of CTAB in the bulk of the solution, a high participation of CTAB molecules in the formed mixed micelles occurs. While, at higher bulk concentration of CTAB, the preferential adsorption occurs faster, that replaces DDPO molecules effectively to the solution bulk. Due to the hydrophobicity factor and the incompatibility between the decyl and hexadecyl hydrophobic chains and the repulsion between head groups. DDPO molecules participate in the mixed micelles increases which decrease X_1 than X_{ideal}.

For CTAB-DTPO and CTAB-DHPO binary systems, it is clear that X_1 are always higher than X_{ideal} values, which indicates that the cationic-nonionic mixed micelles are rich in cationic component even in cationic poor region of the mixtures, Table 1. That indicates the synergistic behaviour of the CTAB-DTPO and CTAB DHPO mixed systems. Increasing the difference between the hydrophobic chain length of the cationic and nonionic components, i.e., increasing the dissimilarity, increases the repulsion between the chains, and the opposite is true. That is called the hydrophobic effect. The synergistic behaviour of CTAB-DTPO and CTAB-DHPO systems occurs due to the hydrophobic effect and the low attraction between the head groups. The attraction between head groups occurs due to the relatively high partial negative charge on phosphine groups (P=O) and the positively charged ammonium group (N$^+$). The partially high negative charged head group is due to the high inductive effect of the tetradecyl and hexadecyl chains. That does not occur in case of DDPO and CTAB head groups due to the minor inductive effect of decyl chain on the phosphine group of DDPO. The richness of CTAB molecules in the mixed micellar phase is attributed to the higher hydrophobicity of DTPO and DHPO nonionic components than the cationic component. The more hydrophobic component is preferentially adsorbed at the interface and consequently pumps the less hydrophobic components to the bulk. Hence, its contribution in the formed mixed micelles increased consequently. On the other hand, lower cmc value of DHPO (0.014 mM) increases its tendency towards adsorption at the interface and consequently decreases its contribution in the formed mixed micelles and increases the contribution of the cationic one. That can be suggested from the large deviation between X_1 and X_{ideal} of the CTAB-DHPO mixed system at all mole fractions, Figure 4. While, this deviation decreased in case of CTAB-DDPO mixed system due to the less hydrophobicity of DDPO than DTPO and DHPO. It is obvious from Figure 4c that the difference between the X_{ideal} and X_1 values decreases by increasing the mole fraction of CTAB. That suggests the continuous adsorption of CTAB molecules to the interface by increasing its mole fraction.

Interaction parameter (β) and activity coefficient (f_i)

The interaction parameter in the mixed micelles, β, is a magnitude of the degree of interaction operating between the unlike components in the mixed micellar state relative to their self interaction before mixing under similar conditions. The values of β can account for deviation of the mixed system from ideality, and can be calculated from the following equation:[23,27]

$$\beta = [\ln(\alpha_1 cmc / X_1 cmc_1)]/(1-X_1)^2 \qquad (4)$$

The calculated values of β are listed in Table 1. It is clear that β values are always negative for all the studied mixed systems indicating

that the interactions between the two components in the mixed micellar phase are less repulsive than the interactions occurred between the individual components. Higher negative values of β indicate strong attraction between the different components in the mixed micelles while, values close to zero indicate approximately ideal mixing.[21,34] The results show that β, although not constant, is negative throughout the concentration range and over the different mole fractions in the three studied binary systems, suggesting strong synergism in the mixed micelles formation. The existence of synergism in mixtures of surfactants depends not only on the strength of interaction occurs between the different molecules, but also on the associated properties of each surfactant in the mixture.[35] In the studied binary systems, comparing the β values reveals that the least synergism is observed in CTAB-DDPO, due to the low β values, while the most synergistic effect occurs in CTAB-DHPO binary system. The highest synergistic effect in the latest system is attributed to the homogeneity between the hydrophobic chains of the different surfactants participated in the formed mixed micelles. Consideration of tail-tail interaction was neglected by Rubingh in the treatment and explanation of the synergistic mechanism.[36] Later on, several investigators[22,37-39] proved that the synergistic effect is a result of both head group-head group and tail-tail interactions (hydrophobic interaction). The synergism extent decreases by decreasing the similarity between the hydrophobic chains, as indicated from the variation of β values by changing the hydrophobic chain from hexadecyl chain in DHPO (-10.64) to decyl chain in case of DDPO (-0.640).

The most effective parameter explains the extent of interaction between the different surfactants incorporated in the mixed micelles is the activity coefficient f_1, f_2, which relates to the interaction parameter throughout Equations 5-6:

$$f_1 = \exp[\beta(1-X_1)^2] \qquad (5)$$

$$f_2 = \exp[\beta(X_1)^2] \qquad (6)$$

The obtained values of f_1, f_2 are less than unity showing the nonideality of the systems. Decreasing the values of f_1, f_2 from unity indicates the low interaction between the different components incorporated in the mixed system. The β values of the different systems showed a gradual decrease of the interaction occur between the cationic and different nonionic components by increasing the hydrophobic chain lengths. This supported by the gradual decrease in f_1, f_2 values by the same trend.

A close inspection of Table 1 demonstrates that β values decrease gradually by increasing α_1. That could be explained by plotting the relation between β and f_1 values, Figure 5. It is clear that the gradual increase of f_1 decreases β values gradually. The increase of f_1 values indicates the presence of some sort of repulsion between the different molecules. That decreases the stability of the formed mixed system than the maximum values. The gradual decrease of f_1 values indicates the increase of the system stability, which assists the mixed micelles formation.

The activity coefficients used to calculate excess free energy of mixing (ΔG_{ex}) by the relation:

$$\Delta G_{ex} = RT[(X_1 \ln f_1) + (1-X_1)\ln f_2] \qquad (7)$$

where, R is universal gas constant, and T is absolute temperature.

The negative ΔG_{ex} values represented in Table 1 indicate that the mixed micelles formed are more stable than the micelles of individual surfactants. The high negative ΔG_{ex} values of the mixed systems at different bulk mole fractions fall in line with β and f values and can be explained in the light of the above β discussion.
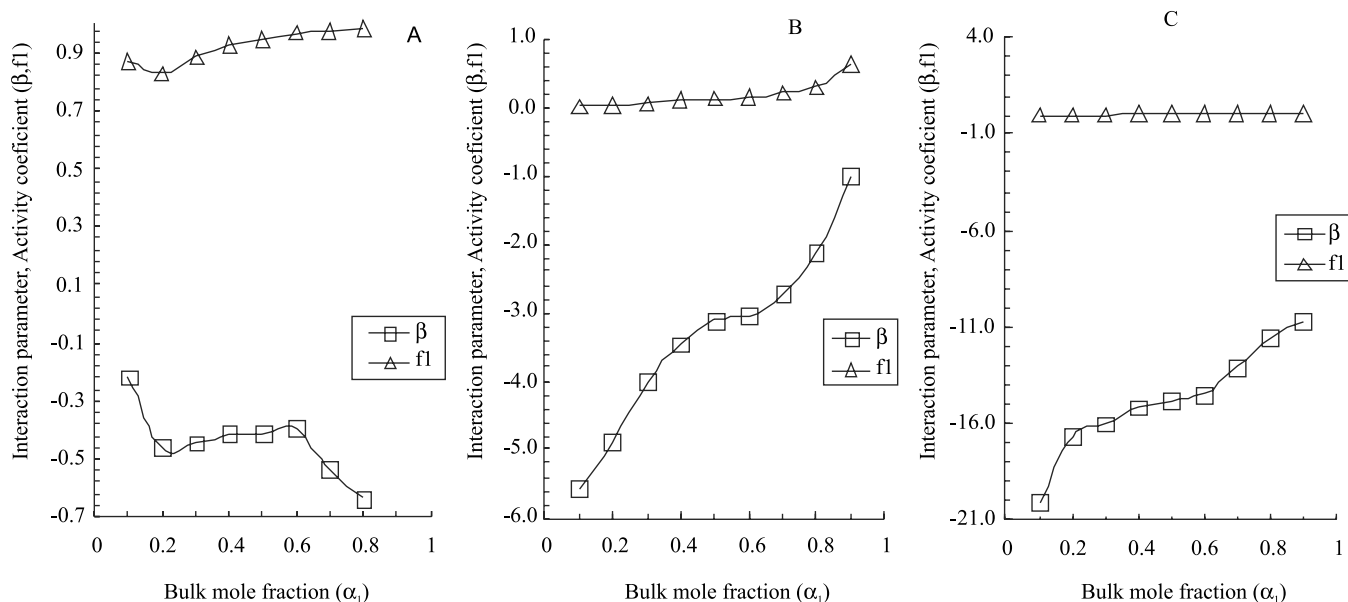
Figure 5. *Dependence of interaction parameter (β) and activity coefficient (f₁) on the bulk mole fractions of: A. CTAB-DDPO, B. CTAB-DTPO, C. CTAB-DHPO binary systems at 25 °C.* □: Ideal, △: Experimental

Properties at the air/water interface

The orientation of adsorbed surfactant molecules at the air-water interface decreases the surface tension of the aqueous phase. The decrease in surface tension occurs due to break down of hydrogen bonds at the surface. Increasing the adsorbed surfactant concentration leads to further decrease in the surface tension values. The amounts of adsorbed surfactants per unit area at various concentrations can be calculated using Gibbs adsorption equation. For surfactant mixtures in water, the Gibbs surface excess is related to surface pressure [π = γ$_o$-γ] by the relation [$d\pi = \sum R T \Gamma_i d \ln a_i$] ($\Gamma_i$ is the surface excess and a_i is the activity of component i at temperature T). The values of surface excess and minimum area per molecule (A_{min} in Å^2) for all the studied mixed systems were calculated using Equations 8-9 [14, 40]

$$\Gamma_{max} = - (1/nRT)(d\gamma/d \ln C) \tag{8}$$

$$A_{min} = 10^{20}/N_A\Gamma_{max} \tag{9}$$

where $d\gamma/d\ln C$ is maximum slope of the surface tension-log C profile at the pre-micellar region, R, T, C and N_A are gas constant, absolute temperature, molar concentration and Avogadro's number, respectively. The number of species at the interface vary with the surfactant bulk concentration (n) were taken as 2.[41] The surface excess concentration (Γ_{max}), determined at surface saturation using the Gibbs isotherm (Equation 8), is a measure of the effectiveness of the surfactant adsorption at the interface, since it is the maximum value which adsorption can attain. The maximum surface adsorption concentration obtained corresponds to the maximum packing and strong tighten surfactant molecules at the interface. The adsorption effectiveness is an important factor in determining properties like foaming, wetting and emulsification, since tightly packed interfacial films have very different interfacial properties as compared to loosely packed noncoherent films. It is clear from the data in Table 1 that, CTAB-DDPO mixed monolayer, the Γ_{max} values increased by increasing the mole fraction of the cationic component, while A_{min} values considerably decrease. That can be attributed to the hydrophobic interaction which pumps the molecules to the interface, which leads to increase the surface concentration and the area occupied at the

interface decreased due to the compactness between the molecules. However, the maximum surface concentration (Γ_{max}) in case of CTAB-DTPO/DHPO mixed monolayer decreases by increasing the cationic mole fractions to reach to the minimum value at 0.83 for DHPO and 1.15 for DTPO. Those values corresponded to the ideality mixing region of the different mixed systems. The decrease of A_{min} by increasing the cationic mole fraction suggests the compactness of the mixed monolayer at the interface, which reveals the homogeneity of different components at the interface.

CONCLUSION

Mixed surfactant systems showed better micellar and interfacial properties than the individual surfactant solutions. The critical micelle concentrations of the different surfactant mixtures were lower than the individual surfactants used. This encourage us to study the behaviors of CTAB-dimethyl alkyl phosphine oxide mixed systems as primer systems used in different biological and industrial applications. The results of the study showed the following topics:

CTAB-dimethylalkyl phosphine oxide mixed micelles are formed due to the attractive interaction between the different components, especially for DTPO and DHPO.

The critical micelle concentration values are lower than both cationic and nonionic components.

The mole fraction of the cationic component is always higher than the ideal values.

The high negative values of mixing free energy showed the stability of the mixed micelles than the individually formed micelles.

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