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Interfacial and micellar properties of binary mixture (tetraethylene glycol dodecylether / hexadecylpyridinium chloride) in aqueous solution

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ABSTRACT

The interfacial/micellar behaviour of a mixture of tetraethylene glycol mono-n-dodecyl ether and hexadecylpyridinium chloride has been investigated. The critical micellar concentration (cmc) values of mixed surfactants have been estimated from surface tension measurements. The cmc values are lower than cmc values for an ideal mixture indicating attractive interactions between both surfactants. Interfacial properties have been analysed by means of the surface excess, the minimum surface Gibbs energy (G_{Smin}), the negative logarithm of the surfactant concentration in the bulk (C_{20}) required to produce a 20 mN·m-1 reduction in the surface tension of water (pC_{20}) and ratio CMC/C_{20}. Theoretical models of Rubingh and Rodenas, which was developed and previously reported by our research group, have been used to estimate composition of mixed micelles. The predicted values are similar. The negative values of excess Gibbs energy in aqueous solution indicate that the non-ideal mixed micellar systems are more stable than the corresponding ideal systems.

Keywords: *mixed micelles, surface tension, critical micellar concentration.*

1. INTRODUCTION

The activity of surfactant is to reduce drastically the surface tension of the aqueous layer, which has a great biological impact because it is involved in processes such as thin aqueous layer lining the respiratory epithelium of lungs; interfacial properties of surfactant proteins; or interactions between surfactants and DNA. The toxicity of cationic, anionic and non-ionic surfactant on aquatic organisms has been also shown to be highly correlated with interfacial activity [1]. The general nature of the relationship between interfacial activity of surfactants and their biological or technical effects indicates that adsorption is a critical parameter for predicting and understanding the effects.

In most practical applications, such as the control of emulsion properties, mixtures of surfactants, rather than individual surfactants, are used. Especially when the mixture shows synergism and the properties of the mixture are better than those attainable with the individual components by themselves. Synergistic properties in mixtures of surfactants produce a higher decrease in the surface tension and a lower critical micelle concentration (cmc) value than each individual surfactant does.

The investigation of synergism in terms of molecular interaction between two different surfactants adsorbed in different interfaces are measured by the parameter β. The β value is related to the free energy change upon mixing of the two surfactants [2]. Rubingh's model [3] is based on the regular solution theory. It considers $\beta = (E_{11} + E_{22} - 2E_{12})/ RT$, where E_{11}, E_{22} and E_{12} are the molecular interaction energy between two monomers of surfactant 1, two monomers of surfactant 2 and monomers of surfactants 1 and 2 in the mixed system, respectively. A negative value of β indicates that, upon mixing, the two surfactants show a greater attraction than before mixing and the mixture of the surfactants so that, the mixture produces a synergetic effect. β near to zero reveals little interaction between surfactants and the ideal mixing, whereas the positive value denotes the antagonism between surfactants. Mixtures of an ionic and a nonionic surfactant normally yield a deviation from ideal behavior with a β value between -5 to -1. Synergistic effects in mixtures of two nonionic surfactants are usually less while for mixtures of anionic and cationic surfactants are usually several magnitudes larger. For examples, β value for sodium dodecyl sulfate ($C_{12}SO_4^-Na^+$)/ dodecyltrimethylammonium bromide ($C_{12}TA^+Br^-$ mixtures has been found to be -25.5 [4].

We have herein attempted a thorough physicochemical study on different aspects of binary mixtures of non-ionic (tetraethylene glycol mono-n-dodecyl ether, $C_{12}E_4$) and cationic (hexadecylpyridinium chloride, CPyCl) in aqueous medium. The composition dependent adsorption behavior of the mixed components at the air/solution interface in the light of thermodynamics has been explored, together with the understanding of energetics of mixed micelle formation and mutual interaction of the monomers in the micelle.

2. EXPERIMENTAL SECTION

Tetraethylene glycol mono-n-dode cylether (Nikkochemical, 99+%) and hexadecylpyridinium chloride (Sigma) were used as supplied. In addition, the CPyCl was also used after recrystallization from ethanol/ether mixtures. Both solvents were supplied by Merck.

The surface tension (σ) of surfactant solutions were measured at different concentrations with a LAUDA Tensiometer TE 1C using a Pt ring. All measurements were carried out at 25.0±0.1 ºC. Each experiment was repeated several times and a good reproducibility was achieved. The CMC values were obtained as the sharp break point in the surface tension against the logarithm of concentration curves at different mole fractions of non-ionic surfactant.

3. RESULTS SECTION

Some of the surface tension data in aqueous solution of mixtures of $C_{12}E_4$/CPyCl at different composition at 25 ºC are represented in Fig. 1. The surface tensions of individuals $C_{12}E_4$ and CPyCl surfactants show some remarkable decreases with the surfactant content until a clear break in the curve. The critical micelle concentration at the individual surfactants and at different mole fractions of nonionic surfactant (noted by sub index 1) in the mixture (α_1) were obtained as the break point of both straight lines of Figure 1.

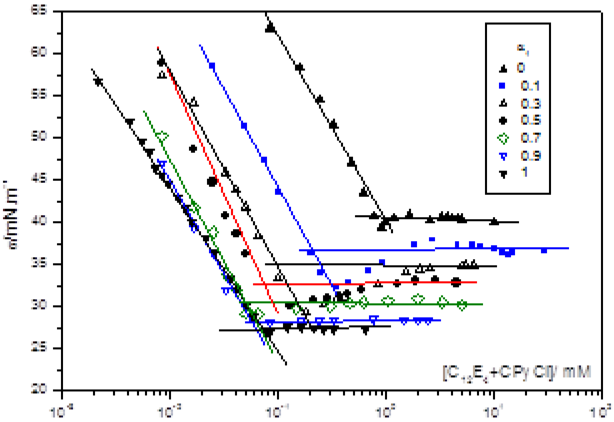

Fig. 1. Surface tension against the total surfactant concentration for the mixed micelles at different non-ionic molar ratio (α_1) given in the legend.

The surface tension shows a minimum with the concentration for some $C_{12}E_4$/CPyCl ratios but not for individual components. The individual surfactants are pure compounds and no impurity is present as the surface tension measurements endorse. The same effect has been also described for mixed systems of monovalent ionic surfactant and with zwitterionic surfactants [5] with MEGA-n's. The minima have been explained [6] by considering that one surfactant acts as an impurity against the others. Other authors suggest that the surfactant having a higher surface activity has a trend of the quicker (in dynamics) or the more preferential adsorption (in energetics) compared to the other, having a lower surface activity. In the initial (early) stage after a fresh surface is made, the more active surfactant molecules may have a larger gain in Gibbs free energy upon adsorption and thus the larger gain may cause the faster translation from bulk phase to interface than in the lower active surfactants, even if the molecular sizes are comparable to each other [7]. For the system $C_{12}E_6$/CTAB (in presence of sufficient electrolyte) has been also reported that adsorption of surfactant in the interphase is diffusion controlled at short times, by dynamic surface tension studies [8]. The adsorption models commonly predict the time-dependent surface concentration, while experimentally the time-dependent interfacial tension is measured instead. Thus, we consider the latter hypothesis as the most consistent for this mixed system, and the difference of one order of magnitude of the cmc values for each pure surfactant could be related cause.

In order to evaluate the surface activity and synergism concerned in terms of adsorption, we can examine the slope of γ versus log c curve below CMC to obtain the maximum interfacial excess concentration surface excess.

$$\Gamma = \frac{1}{2.303RT}\left(-\frac{\partial\sigma}{\partial \log c}\right)_T$$

The efficiency of adsorption of the surfactant at the interface water/air can be estimated by the negative logarithm of the surfactant concentration in the bulk required to produce a 20 mN.m^{-1} reduction in the surface tension of water (pC_{20}). This concentration is close to the minimum concentration needed to produce saturation adsorption at the interface. The ability of surface tension reduction can be described in terms of surface tension at cmc (σ_{CMC}). All of these parameters together with the critical micelle concentrations (cmc) are reported in Table 1.

Table 1. Mole fraction of non-ionic surfactant (α_1), surface tension at the cmc (σ_{CMC}), critical micelle concentration (cmc), concentration surface excess (Γ), negative logarithm of the surfactant concentration in the bulk that produces a 20 mN.m^{-1} reduction in the surface tension (pC_{20}), ratio between cmc and C_{20} (cmc/C_{20}) and the minimum free surface energy (G^S_{min}).

α_1	σ_{CMC} / mN m^{-1}	cmc /mM	Γ / µmol m^{-2}	pC_{20}	cmc/C_{20}	G^S_{min} / kJ mol^{-1}
0	40.4	0.90	4.58	3.52	3.0	8.82
0.1	36.4	0.18	4.34	4.33	3.9	8.39
0.3	34.8	0.090	3.93	4.77	5.3	8.84
0.5	33.0	0.065	3.70	4.98	6.2	8.92
0.7	30.5	0.039	4.33	5.17	5.8	7.04
0.9	28.4	0.044	4.23	5.29	8.6	6.71
1	27.4	0.065	3.41	5.40	16	7.94

As shown in Table 1, the larger the mole fraction of non-ionic surfactant in the mixed system, the larger the value of pC20, the more efficiently the mixed surfactants are adsorbed at the surface and the more efficiently they reduce surface tension.

Gibbs energy of the given air/water interface G^S_{min} defined by [6]:

$$G^S_{min} = \sigma_{CMC} / \Gamma \qquad (2)$$

is the Gibbs energy change accompanied by the transition from the bulk phase to the surface phase of the solution components. So that, the lower the value of the free energy, the more thermodynamically stable surface is formed, or the greater surface activity is attained. The G^S_{min} is higher for $\alpha_1 \leq 0.5$ that for

$\alpha_1 > 0.5$. The cationic surfactant makes less stable the surface. The highest mole fraction of non-ionic surfactant stabilizes the water surface.

The experimental cmc values for all mixed systems are lower than the corresponding ideal cmc values given by Lange equation [9] based on the pseudophase model.

$$\frac{1}{cmc^*} = \frac{\alpha_1}{cmc_1} + \frac{(1-\alpha_1)}{cmc_2} \qquad (3)$$

where cmc_1 and cmc_2 denote the cmc of individual surfactants 1 (non-ionic) and 2 (cationic), respectively and α_1 the mole fraction of surfactant 1. The experimental cmc are lower than the corresponding to the ideal mixture (Fig. 2). The cmc values show negative deviation from the ideal behaviour indicating attractive interactions between the two surfactants.

For nonideal mixtures of surfactants in the micelles there is to introduce the activity coefficients. In such way, the critical micelle concentration is given by

$$cmc\ (\chi_1) = \chi_1 f_1(\chi_1) cmc_1 + (1-\chi_1) f_2\, \chi_1 cmc_2 \qquad (4)$$

where χ_1 is the mole fraction of the 1 surfactant in the mixed micelle and f_1 is its activity coefficient.

Rubingh's model [3] considers the activity coefficients f_i given by the regular solution theory:

$$\ln f_i = \exp\left[\beta\left(1-\chi_i\right)^2\right] \qquad (5)$$

where χ_i is the mole fraction of the i surfactant in the mixed micelle. The β parameter takes into account the interaction energy between the monomers of surfactant 1, surfactant 2 and monomers of surfactants 1 and 2 in the mixed system. This model has the restriction that the activity coefficients given by the regular theory of real solution must be considered. The mole fraction and coefficient activity of each surfactant in mixed micelles together cmc values predicted by Rubingh's model are collected in table 2.

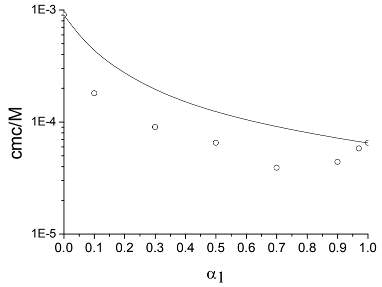

Figure 2. cmc values against different mole fraction α of the non-ionic surfactant. Dots represent experimental cmc values and the fits to ideal mixture.

Table 2. Mole fraction of non-ionic surfactant in mixed micelles (χ_1), β parameter, activity coefficients of surfactants (f_1 and f_2) and cmc obtained from the Rubingh's treatment ($\mathbf{cmc^R}$) at different mole fraction of non-ionic surfactant (α_1)

α_1	χ_1	β	f_1	f_2	cmc^R/ mM
0.1	0.541	-3.30	0.496	0.381	0.17
0.3	0.653	-3.76	0.636	0.202	0.090
0.5	0.707	-4.22	0.696	0.122	0.064
0.7	0.709	-6.18	0.592	0.047	0.039
0.9	0.793	-5.96	0.774	0.0237	0.044
0.97	0.910	-4.75	0.962	0.0195	0.058

Rubingh's model predicts cmc values very close to experimental cmc values. In order to reach these cmc values it is necessary to introduce different β values with the composition of the mixtures. Similar results have been obtained with other surfactant mixtures [10, 11]. It decreases with the amount of non-ionic surfactant in the mixture until $\alpha_1 = 0.7$ and, then, it increases. The negative values of β indicate synergism between the two surfactants in the mixed micelle formation. By comparing with the mixed micelles of analogous system $C_{12}E_4$/CTAB [10], the mixed micelles with CPyCl exhibit a stronger synergist effect, probably due to the attractive interaction between the pyridinium groups and the oxyethylene oxide groups [12]. These interactions are more important than the counterion effect, because Br^- counterions show stronger interactions than Cl^- counterions.

Instead of considering the activity coefficients given by eq. (4), it can be considered the Gibbs-Duhem equation to relate the activity coefficients such as we described for mixed micelles of $C_{12}E_4$/CTAB [10]. From this treatment, the mole fractions of surfactant i in the mixed micelles are given by

$$\chi_1 = -\left(1-\alpha_1\right)\alpha_1 \frac{d\ln\left(\mathrm{cmc}\right)}{d\alpha_1} + \alpha_1 \qquad (6)$$

This equation was given by Hoffman et al. [13] as a particular case of Motomura's equation [14]. This equation allows us to calculate the mole fraction of surfactant 1 in the micelle from $d\ \ln cmc/d\alpha_i$ at different α_i. Once the mole fraction of surfactant 1 in the mixed micelles has been obtained, the activity coefficients can be calculated with Eq. 1. This model, called for different authors like Rodenas' treatment [15-21], together with other theoretical models (like Clint's, Rubingh's and Motomura's), explains cmc values of different mixed micelles. The variation of mole fraction of non-ionic surfactant in the mixed micelle (χ_1) as a function of mole fraction in solution (α_1) for the different models is given in Fig. 3. In Fig. 4, the variation of activity coefficients (f_1) with α_1 is plotted.

Once activity coefficients and mole fraction of each surfactant in mixed micelles have been calculate, the cmc of the mixed micelles can be obtained from eq. 4. The cmc calculated from this treatment are collected in Table 3. Excepting at the lowest non-ionic mole fraction in solution, the cmc are similar to the ones calculated from Rubingh's treatment. Thermodynamic parameters predicted by both models are similar. The higher uncertainties obtaining $d \ln cmc / d\alpha_1$ for the α_1 limits explain the differences for $\alpha_1 = 0.1$.

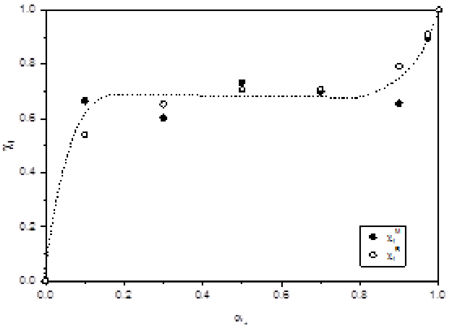

Fig. 3. The χ_1 mole fraction of the surfactant **1** in the micelle against the α_1 mole fraction of the nonionic surfactant (**1**) in the solution. M refers to Rodenas's Model; R refers to Rubingh's Model. Line guides the eyes.

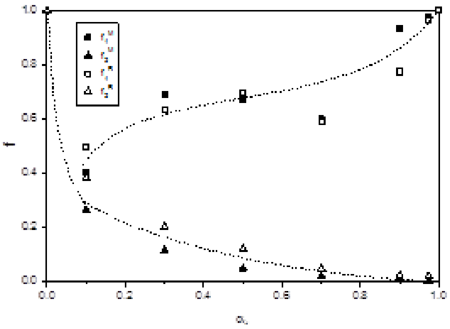

Fig. 4. Activity coefficients against the α_1 mole fraction of the nonionic surfactant (**1**) in the solution. M refers to Rodenas's Model; R refers to Rubingh's Model. Lines guide eyes.

The mole fraction of the nonionic surfactant, in the range $0.1 \leq \alpha_1 \leq 0.9$, has a nearly constant value of $\chi_1 \cong 0.7$. The mole fraction of the cationic surfactant 2 is lower at the interface, and consequently the surfactant distribution is asymmetric [22].

From results we can conclude again that the Rodenas' model, developed in our group, that does not introduce any restrictions on the activity coefficient of the surfactants in the mixed micelle, reaches similar results as the Rubingh's treatment, which considers that micelles behave as a regular solution. Similar conclusion has been recently reported by Ren et al. [19] in mixtures constituted by an amphoteric (sodium n-dodecyl diamine sulfonate) and cationic (octadecyltrimethyl ammonium bromide) surfactants.

The non-ideality in the mixed micelle due to interaction can be assessed by evaluating molar excess standard free energy of micellization and the mixing thermodynamic functions. For these solutions $\Delta S_M = \Delta S^{ideal}$, which means the excess entropy function is $S^E=0$ and $G^E=\Delta H_M$, (because: $\Delta H_M = \Delta H^{ideal} + \Delta H^E$ and $\Delta H^{ideal} = 0$), where:

$$G^E = RT \sum \chi_i \ln f_i \qquad (7)$$

$$\Delta G_M = RT \sum \chi_i \ln \chi_i f_i \qquad (8)$$

The mixing thermodynamic functions have been calculated (Table 3). It is pointed out that small variations in the experimental cmc values produces small changes in all the parameters and in the thermodynamic functions, but this variation does not change the discussion of the results.

Table 3. Mixing thermodynamic functions according to our treatment, Rodenas' model.

α_1	cmc / mM	χ_1	ΔH_M/ kJmol^{-1}	ΔS_M/ JK^{-1}mol^{-1}	ΔG_M/ kJmol^{-1}
0.1	0.097	0.665	-2.60	5.30	-4.18
0.3	0.068	0.603	-2.67	5.58	-4.34
0.5	0.044	0.733	-2.72	4.82	-4.16
0.7	0.032	0.7	-3.85	5.08	-5.36
0.9	0.042	0.657	-4.27	5.34	-5.86

The mixed micelle formation is spontaneous ($\Delta G_M < 0$) for all the compositions. The mixing entropy is positive and nearly constant. The ΔG_M are more favourable to the mixed micelle formation when the mole fraction of nonionic surfactant is the highest. Similar results were reported to the similar system $C_{12}E_4$/CTAB [8]. The same fact occurs with G^S_{min}. So that the mixed monolayer more stable corresponds to the α_1=0.9 so in the water/air surface and as in the micelle/water interface. The negative values of excess Gibbs energy in aqueous solution ($G^E=\Delta H_M$) indicate that the non-ideal mixed micellar systems are more stable than the corresponding ideal systems.

4. CONCLUSIONS

Mixed micelle formation for the $C_{12}E_4$/CPyCl mixed system was studied by surface tension measurements. Regarding to the effect of the mixture in the interface water/air properties, the results show that the larger the mole fraction of non-ionic surfactant, the larger the value of pC_{20}, the more efficiently the mixed surfactants are adsorbed at the surface and the more efficiently they reduce surface tension.

The cmc experimental values of mixed micelles are inferior to the ideal values obtained by the Lange equation. So that, attractive interactions exist between these non-ionic and cationic surfactants. The predicted values of cmc calculated from both the Rubingh's and our treatment are in good agreement with the experimental values, suggesting the validity of both treatments. The interaction parameters between two surfactants always show larger negative values what implies synergistic effect of interaction between two surfactants. Thermodynamic data show that the process of micellization is spontaneous once the cmc has been reached and the micelle formation is more favorable as higher nonionic surfactant mole fraction.

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6. ACKNOWLEDGEMENTS

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