

Surface Properties of Mixed Adsorbed Surfactants Film of Tween 20 and Tween 80 on Liquid – Air Interfacial

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Abstracts: The surface properties of mixed adsorbed surfactants film of Tween 20 and Tween 80 on water – Air have been investigated by surface tension measurements at 298 K. The critical micelle concentration (CMC), Γ_{max} (maximum surface excess), A_{min} (minimum surface area per molecule), γ_{cmc} (surface tension at the CMC), $P^{C_{20}}$ (the negative log C_{20} where C_{20} is the surfactant molar concentration required to reduce the surface tension of the solvent by 20 mN/m), and CMC/C_{20} have been determined. The results show that the surface activity by $P^{C_{20}}$ values is in the order of TW-80 > TW-20 while the CMC/C_{20} values indicate the mixtures of $\alpha_1 = 0.3$ and 0.5 prefer adsorption at interface but other mixture preferred micelle formation. The results of the mixed systems were analyzed in the light of Rosen's theory to evaluate the composition of the mixed adsorbed film and the corresponding interaction parameters (X_1° and β°). The negative values of interaction parameters β° indicate the attractive interaction for certain systems. The existence of synergism in surfactant mixtures at the adsorbed film was examined.

Keywords: surface properties, mixed surfactants, synergism in surface tension reduction, surface excess, minimum molecular area

1. Introduction

In many industrial fields, surfactant mixtures are used because the commercial surfactants contain mixtures of different hydrophobic chain lengths. Also, they are used because the surfactants are deliberately mixed to optimize some aspect of their performance [1]-[2]. So that, studies to obtain superior properties of mixed surfactants as compared to single surfactant have been performed in several cases.

Mixed micellization of binary and ternary mixtures lithium dodecylsulfate, polyoxyethylene(23)laurylether, and polyoxyethylene-tertoctylphenylether, is studied in aqueous solution using tensiometric, conductometric, and spectrophotometric methods. Several parameters, e.g., critical micelle concentration (CMC), degree of counterion binding, free energies of micellization, and interfacial adsorption, have been evaluated. Established theories of Clint, Rosen, Rubingh, Motomura, Georgiev, Maeda, and Blankshtein were applied to evaluate the mole fraction of different components in the self-aggregated phase, interaction parameter, free energy contributions, and expected CMC [3].

The effect of adding alkylamines ($C_4-C_8NH_2$) on the aggregation properties of two cationic gemini surfactants has been studied using tensiometry method at 303 K. Data on (CMC), the surface properties C_{20} (the surfactant concentration required to reduce the surface tension by 20 mN/m), Γ_{max} (maximum surface excess), A_{min} (minimum surface area per molecule) evaluated from surface tension versus surfactant concentration plot, the interaction parameters β° (for mixed monolayer formation at the aqueous solution/air interface), and β^m (for mixed micelle formation in aqueous medium) are reported. A synergistic interaction was observed both in the micelle as well as at interface, as evident from interaction parameters. CMC values decreased with increasing amine concentrations and the extent of the effect followed the sequence:

octylamine > heptylamine > hexylamine > entylamine > butylamine [4].

The mixed surfactant systems of sodium dodecyl trioxyethylene sulfate and gemini surfactants of the series N,N'-bis-(dimethyldodecyl)- α,ω -di alkanediammonium dibromide, at different molar ratios were studied by surface tension measurements of aqueous solution. Various parameters like CMC, Γ_{max} , A_{min} , interaction parameter of mixed micelle and adsorption monolayer (β^m , β°) as well as thermodynamic and micellar properties have been determined using Clint, Rubingh, Maeda and Rosen approach. The strong interaction showing very low CMC and large negative interaction parameter β° were due to weakening of the electrostatic head group repulsion which favors the mixed micelle formation. Thermodynamic parameters for all three cationic-anionic mixed systems were evaluated. From excess free energy of micellization, they conclude that thermodynamically stable micelles are formed with strong synergistic interaction [5]. The surface properties and adsorption behavior of mixed binary surfactants containing alkylpyridinium chloride and triton X-100 (TX-100) have been studied at 298K. The values of β° and the mole fraction of components (X_1°) at the air-water interface in the pre-micellar region were calculated on the basis of Rosen's model. In the new approach, they proposed to estimate surface parameters in a pre-micellar region, using different fixed values of the surface tension instead of a single-value of the surface tension. The β° values is negative at all compositions showing a synergistic effect between the components. β° was found to considerably decrease with decreasing surface tension due to more migration of TX-100 to the surface layer and reduction in electrostatic self-repulsion between head groups in the ionic surfactant [6].

In previous work, surface properties of mixtures of Nonyl Phenol Ethoxylate (nonionic) and Dehyquarte E-CA (cationic) surfactants were studied using surface tension

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measurements in order to determine synergism in micellization and surface tension reduction at the air/water interface[7]. In the present study the surface properties of Tween 20 and Tween 80 mixed surfactant systems were studied using tensiometry method. The surface parameters, CMC, Γ_{max} , A_{min} , and pC_{20} were estimated. The values of β , X_1 at the air-water interface were also calculated on the basis of Rosen's model.

2. Experimental

The surfactants tween 20 (98%, Fluka, Switzerland), and tween 80 (98.5%, Fluka, Switzerland), were used as received. Deionized water (sp. conductivity = 2×10^{-6} S cm^{-1}) was used throughout this work. Stock solutions (1000 mg/L) of each surfactant were prepared by dissolving 1 g from surfactant in deionized water. The stock solutions were used for the preparation of different concentrations of Tween 20 and Tween 80. The mixed solutions were prepared by mixing two pure solutions and were kept for at least 30 min

for equilibration before measuring the surface tension. The surface tension values were measured by the ring detachment method using tensiometer model DST 30 M, Surface and Electro Optics (SEO) Company- Korea. For each set of experiments, the ring was cleaned by immersed in 5M HCl solution. Each measurement was repeated three times to ensure the reproducibility of the results.

3. Results and Discussions

Figure 1 show the surface tension curves of single and mixed surfactant systems as function of natural logarithm of total surfactant concentration at 293 K. The surface tensions decreased upon increasing the total surfactant concentration and the CMC was taken as the concentration at the intersection of the lines below and up the break point at the curve of surface tension. The values of individual and mixed CMC systems in relation to their mixture compositions are listed in Table 1.

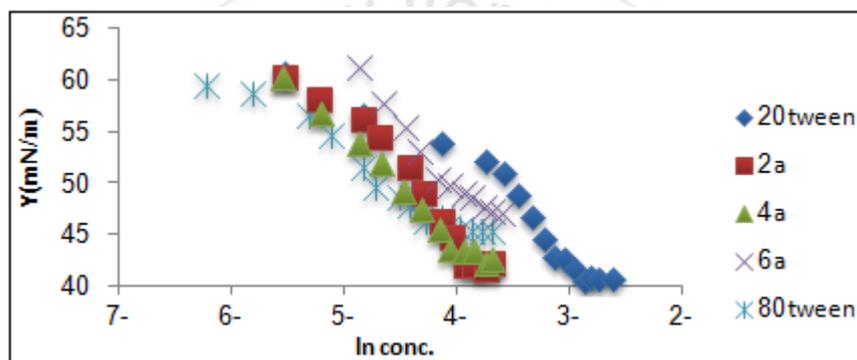


Figure 1: Surface tension versus \ln [surfactant] plots for TW-20 / TW-80 mixed surfactant systems

γ_{CMC} is the surface tension value at the CMC and pC_{20} is the negative $\log C_{20}$, (C_{20} is the surfactant molar concentration required to reduce the surface tension of the solvent by 20 mN/m). The CMC/ C_{20} ratio is the tendency to form micelles relative to adsorb at the air/water interface which measures the efficiency of adsorption. The surface excess (Γ_{max}) is a measure of how much of the interface has been changed by the surfactant; it is expressed by the equation below [8]:

$$\Gamma_{max} = -\frac{1}{nRT} \left[\frac{d\gamma}{d \ln C} \right] \quad (1)$$

Where C is the concentration of the surfactant in solution and n is the number of species constituting surfactant. The

$dy/d \ln C$ factor was obtained from the slopes of the linear plots of γ vs. $\ln C$ (Fig. 1). A_{min} (minimum area occupied by surfactant molecule) is related to the effectiveness of adsorption; in which the smaller A_{min} of the surfactant at interface, the greater is its effectiveness of adsorption. Γ_{max} values were used to calculate A_{min} at the air/water interface using the relationship:

$$A_{min} = 1/N\Gamma_{max}(2)$$

where N is Avogadro's number. The values of γ_{CMC} , pC_{20} , $dy/d \ln C$, Γ_{max} , A_{min} , and CMC/ C_{20} for individual and mixture of TW-20 and TW-80 systems are listed in Table 1.

Table 1: Surface properties γ_{CMC} , CMC, Γ_{max} , A_{min} , pC_{20} , and CMC/ C_{20} for TW- 20 and TW- 80 mixture at 293 K

α	γ_{CMC} (mN/m)	pC_{20}	$\Gamma_{max} 10^{-3}$ mmol/m ²	A_{min} Å ² /molecule	CMC (mM)	CMC/ C_{20}
Tween20	41.54	1.444	6.341	26.1	0.0499	1.61
0.1	49.00	1.628	3.985	41.6	0.0233	1.09
0.2	42.00	1.790	5.003	33.1	0.0202	1.45
0.3	43.45	1.879	3.569	46.5	0.0185	1.40
0.4	44.00	1.863	4.357	38.3	0.0166	1.36
0.5	42.45	1.978	3.745	43.4	0.0162	1.54
0.6	50.00	1.804	3.988	41.6	0.0145	0.99
0.7	51.00	1.787	4.119	40.3	0.014	0.97
0.8	46.89	1.869	4.84	34.3	0.0135	1.23
0.9	47.15	1.943	4.729	35.1	0.0115	1.21
Tween80	46.30	1.966	3.469	47.8	0.0125	1.26

The more surface active an amphiphile is, it is more efficient in lowering the surface tension of water and smaller is the amount of surfactant required to lower the surface tension of the solvent by a given amount. If C_{20} is the concentration of a given surfactant to lower the surface tension of the medium by 20 mN m⁻¹, pC_{20} therefore is a measure of propensity of the amphiphile toward interfacial adsorption. Table 1 show that the surface activity by pC_{20} values is in the order of TW-80 > TW-20, which mean TW-20 has a greater tendency to stay in the bulk phase compared to TW-80 and hence exhibits lower surface activity. It may be due to hydrophobicity of the surfactant chain that plays the decisive role. For all the binary mixtures, pC_{20} values increase with an increasing mole fraction of TW-80 indicating low and low surface adsorption [3]. On the other hand, the ease of a particular component toward micellization compared to interfacial adsorption is given qualitatively by CMC/C_{20} . The CMC/C_{20} values for all mixtures studied is noregular but we can say for $\alpha=0.3$ and 0.5 the mixture prefer adsorption at interface while other mixtures preferred micelle formation[1],[9].

The value of Γ_{max} decreases while the A_{min} value obtained increases with an increase in α_1 (Table 1), this indicates that when TW-80 surfactant was added in all mole fractions the mixture have a greater tendency to be adsorbed at the air/water interface, compared to a pure TW-20 surfactant solution. The presence of TW-80 may be increases the repulsion among head groups and low surfactant mixture molecules can be adsorbed at the interface [4].

Rosen model

It is focuses on the adsorbed Langmuirian mixed surfactant film at the air/solution interface and is basically an optimization algorithm. According to this model [10] the mole fraction of the surfactant 1 (X_1) and an interaction parameter at the interface among the components (β°) as the optimization parameters were determined using the two equations below involved in the iteration procedure:

$$\frac{(X^{\circ}1)2 \ln(\alpha 1 C_{12} / X^{\circ}1 C^{\circ}1)}{(1 - X^{\circ}1)2 \ln [(1 - \alpha 1) C_{12} / (1 - X^{\circ}1) C^{\circ}2]} = 1 \quad (3)$$

$$\beta^\circ = \frac{\ln(\alpha 1 C_{12} / X^{\circ}1 C^{\circ}1)}{(1 - X^{\circ}1)2} \quad (4)$$

where C_{12} , C_1° , and C_2° are the molar concentrations of the mixture and pure surfactants 1 and 2, respectively, at a fixed γ value, and α_1 is the stoichiometric mole fraction of surfactant 1 in the solution.

The β° and X_1° values of the binary mixtures studied are represented in Table 2.

Table 2: Molecular interaction parameters of binary mixtures at 298 K

α	C_{12}	X°	β°	f_1°	f_2°
0.1	0.0217	-	-	-	-
0.2	0.0155	-	-	-	-
0.3	0.0146	0.0564	1.143	2.766	1.003
0.4	0.0140	0.298	-0.809	0.671	0.931

0.5	0.0118	0.387	-1.614	0.545	0.785
0.6	0.0145	0.421	-0.903	0.738	0.852
0.7	0.0136	0.478	-1.250	0.711	0.751
0.8	0.0130	0.531	-1.630	0.698	0.631
0.9	0.0112	0.583	-2.772	0.617	0.389

It was observed from Table (2) that all the systems from $\alpha_1 = 0.4$ to $\alpha_1 = 0.9$ exhibits negative value of interaction parameter which show attractive interaction in mixed monolayer formation, while the system $\alpha_1 = 0.3$ shows positive value which indicate repulsion between components of mixed surfactant system. Table 2 also shows that the mole fraction of TW-80 in the mixed interfacially adsorbed monolayer is always lower than the corresponding stoichiometric proportion and the extent of X_1° increases with an increasing stoichiometric proportion of TX-100 in the mixture reflecting a lower tendency of TW-80 to be adsorbed at the air/solution interface as compared to TW-20[3],[11-13].

The activity coefficients f_1° and f_2° of the surfactant in the mixed adsorption film are related to interaction parameter (β°) as:

$$f_1^\circ = \exp \{ \beta^\circ (1 - X_1^{\circ})^2 \} \quad (5)$$

$$f_2^\circ = \exp \{ \beta^\circ (X_1^{\circ})^2 \} \quad (6)$$

The values of activity coefficients calculated are found to be less than unity for systems α_1 ranged from 0.4 to 0.9 which confirmed the non-ideal behavior of the mixed systems and the value of f_1 is minimum for system $\alpha_1 = 0.5$ [12],[14-15].

Synergism: The existence of synergism in surfactant mixtures has been shown to depend not only on the strength of interaction between them but also on the relevant properties of the individual surfactant components of a mixture. Thus, the conditions for synergism in surface tension reduction efficiency (when the total concentration of the mixed surfactant required to reduce the surface tension of the solvent to a given value is less than that of either individual surfactant) are as follows: (a) β° must be negative, (b) $|\beta^\circ| > |\ln C_1^{\circ} / C_2^{\circ}|$ [4],[16-17]. From the data in Table 2 and the value of $|\ln C_1^{\circ} / C_2^{\circ}| = 1.05$, it is clear that the systems of $\alpha_1 = 0.5, 0.7, 0.8$ and 0.9 show synergism effect, but the systems of $\alpha_1 = 0.4$ and 0.6 show antagonistic effect between the two components of mixed surfactant system TW-20 and TW-80 at air water interface.

4. Conclusions

The following conclusions can be drawn from the investigation of surface properties of interaction of two nonionic surfactants (TW-20 + TW-80):

- 1) From the values of pC_{20} , the surface activity is in the order of TW-80 > TW-20, which means TW-20, has a greater tendency to stay in the bulk phase compared to TW-80 and hence exhibits lower surface activity. For all the binary mixtures, pC_{20} values increase with an increasing mole fraction of TW-80 indicating low and low surface adsorption.
- 2) The CMC/C_{20} values for all mixtures studied is noregular but one can say for $\alpha=0.3$ and 0.5 the mixture prefer

adsorption at interface while other mixtures preferred micelle formation.

- 3) value of Γ_{\max} decreases and A_{\min} value increases with an increase in α_1 , this indicates when TW-80 surfactant was added in all mole fractions the mixture have a greater tendency to be adsorbed at the air/water interface, compared to a pure TW-20 surfactant solution.
- 4) The β° values of systems with the α_1 in the range between 0.4 and 0.9 indicate the attractive interaction and the interaction is more in the case of $\alpha_1 = 0.9$
- 5) The systems of $\alpha_1 = 0.5, 0.7, 0.8$ and 0.9 show synergism effect, but the systems of $\alpha_1 = 0.4$ and 0.6 show antagonistic effect between TW-20 and TW-80 surfactants mixture.

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