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## Adsorption Properties for Aqueous Solution of Binary Mixture of Cocamidopropyl betaine- Sodiumdodecyl sulfate Surfactants on Air-Liquid Interface

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### Abstract

The Critical micelle concentration (CMC) of aqueous solution of Zwitterion surfactant Cocamidopropyl betaine (CAPB), anionic surfactants sodium dodecyl sulfate (SDS) and their binary mixture solutions have been determined by tensiometer techniques at temperature 298 K. The interfacial parameters  $\Gamma_{\max}$ ,  $A_{\min}$ ,  $\Pi_{\text{cmc}}$ ,  $pC_{20}$  and  $\Delta G^{\circ}_{\text{ads}}$  for the individual and the binary mixture systems were calculated. The deviation from the ideal of the mixed micelles has been discussed on the basis of Clint theory. The results of the mixed systems were analyzed in the light of the regular solution theory (Rubingh) and Rosen's theory to evaluate the composition of the mixed micelle and the activity coefficient. The negative values of interaction parameters ( $\beta^m$ ) for mixed micelle formation indicate the attractive interaction for certain systems.

**Keywords:** Amphoteric surfactants; Anionic surfactants; Binary mixture; Thermodynamic micellization; Surface tension.

### 1. Introduction:

Binary mixture of surfactants always used in practical applications to enhance the properties of individual surfactant.

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Therefore, the investigations of the mixed surfactant systems have received great interest in research, such as the mixed surfactant systems of anionic – cationic [1], anionic – nonionic [2], anionic – anionic [3], cationic – nonionic [4] and cationic- cationic [5]. However, studies carried out on a mixture of amphoteric surfactant with other types of surfactant were few. The mixed micelle formation of N,N- dimethyl N- Lauryl lysine-Sodium dodecyl Sulfate (SDS) was reported [6], and the effect of inorganic electrolytes on the dissolution behavior to the system was studied in term of surface tension, pH, and relative viscosity [7]. The behavior of the binary system of 2-(N-2-hydroxytetradecyl-N-methylamino) ethyl hydrogen phosphate and sodium dodecyl sulfate in aqueous solution was studied. They found that C14-HMP reduced the ability of SDS to denature protein, to inhibit enzyme activity and to decrease trans epidermal water loss [8].

The mixed micelle formation of N, N- dimethyl N- isotherms, adsorption and relaxation kinetics of mixed solutions of anionic and zwitterion surfactant (Betaine) were measured by means of the Wilhelm plate method. The results indicate that the critical micellization concentration (CMC) increases monotonically with the rise of the mole fraction of SDS in the surfactant blend. The experimental surface tension isotherms are fitted by means of the two-component van der Waals model, and an excellent agreement between theory and experiment was achieved [9]. A various combinations of zwitterion with cationic Gemini surfactants were studied using pyrene fluorescence and Kraft temperature measurements [10]. The mixtures of these surfactants indicate the presence of synergistic interactions which largely decrease at higher hydrophobicity of both components. The synergistic interactions of binary cationic Gemini and Zwitterion (N-dodecyl-N,N-dimethyl glycine) surfactants was investigated by measuring the surface tension as a function of total concentration at various pH, under 298 K, and atmospheric pressure. The results were analyzed by applying regular solution theory and Motomura's theory [11]. The phase behavior of mixtures of the zwitterion tetradecyldimethylamine oxide and the anionic lithium perfluorooctanoate has been studied [12]. They show an extended range of formation of unilamellar vesicles. A tensiometric study of micellization behavior of the mixtures of amino sulfate amphoteric surfactant and octadecyltrimethyl ammonium bromide in aqueous solution at 40 °C has been investigated [13]. The mixed micelle formation and synergistic or antagonism effect are explained by the electrostatic interaction between ionic head groups of surfactants and the steric effect of surfactant.

Therefore, the aim of our study was to determine experimentally and on the basis of the regular solution model the mixed CMC and the interaction parameter of SDS –CABP system. These measurements were performed in aqueous solution using tensiometric measurements. The interfacial properties of the individual and mixed system have also been studied.

## **2. Experimental**

### **2.1. Materials**

Cocamidopropyl betaine (CABP) and sodium dodecyl sulfate (SDS) were obtained from the state company of vegetable oils – Iraq. For CAMP and after water evaporation, several recrystallizations from dry ethanol were performed to eliminate sodium chloride, while SDS was used without further purification. All solutions used for conductivity measurements were prepared with deionised water (conductivity < 3  $\mu\text{S cm}^{-1}$ , at 25 °C).

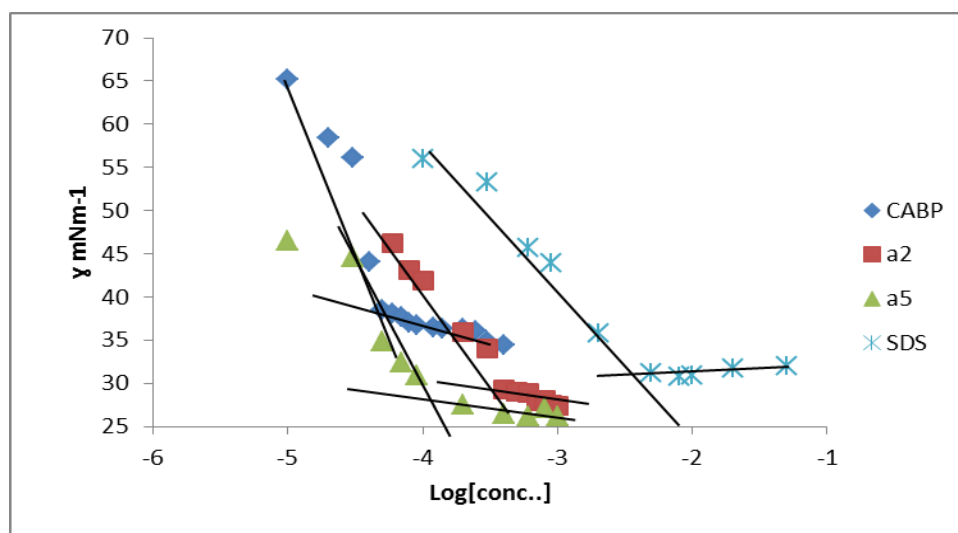
## 2.2. Measurements

Surface tension measurements were carried out on S.E.O. Co. Ltd, tension meter (Korea) using a du Nouy ring method. All measurements were repeated three times. Conductivity measurements were performed using WTW Conductivity Meter (Germany). The conductivity meter was calibrated with a KCl standard solution of known conductivity.

## 3. Results and discussion

### 3.1 Critical Micelle Concentration

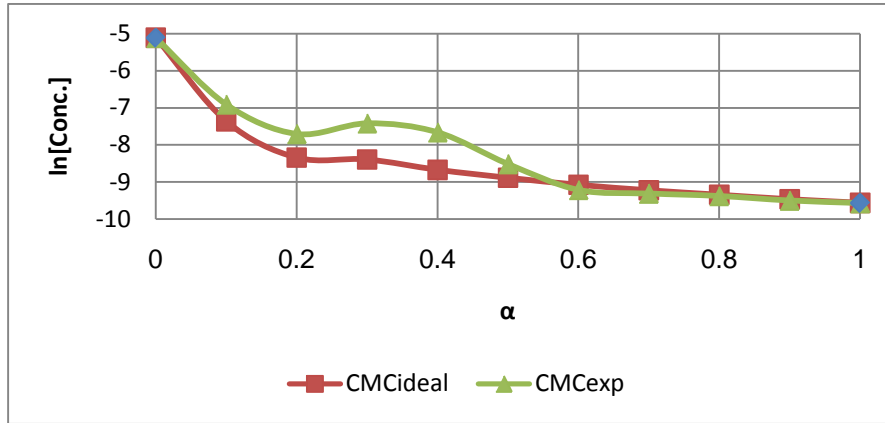
For CMC determination, tension meter experiments were performed for single and for mixed surfactant systems CAPB/SDS. The surface tensions ( $\gamma$ ) versus natural logarithm of surfactant concentration ( $\ln[C]$ ) plots for individual and typical mixed surfactant systems at 293K are shown in Figure -1.



**Figure 1:** Surface tensions ( $\gamma$ ) versus ( $\ln[C]$ ) for mixed surfactant systems CAPB/SDS.

The concentration at which the intersection of the tangent lines drawn before and after the break in curve is obtained is the CMC of that substance. Conductivity measurements are also used in the determination of individual ionic surfactant solutions, and the breaks observed on the curves of conductivity against the surfactant concentration plots (not shown) indicate the CMC points, their actual values being taken as the intersection of the tangent lines drawn before and after the break. The results obtained for CMC are listed in Table (1).

It should be noted that the present results are in the range of the results previously obtained at 298 K by P.A.Kralchevsky et al. [14]. Figure 2 shows the variation of mixed CMC values with mixture composition at 298 K.



**Figure 2:** variation of mixed CMC values

It is observed that the mixed CMC values of various binary compositions decrease with increasing mole fraction of CAPB. Also, the mixed CMC values are intermediate between the CMC values of the two components over the whole range of mixture composition. It is shown that in mixtures have mole fractions from 0.1 to 0.5 of CAPB, the CMC experimental values are greater than the CMC ideal values, while for mixtures have mole fractions from 0.6 to 0.9 the trend was inversed in which the CMC experimental values are less than the CMC ideal values. This deviation indicates a nonideal behavior of solution mixture.

### 3.2 Interfacial Properties

The surface excess ( $\Gamma_{max}$ ) was determined for the individual and mixed surfactant systems by applying Gibbs adsorption isotherm [15] to the relation of surface tension versus  $\ln C$ :

$$\Gamma_{max} = \frac{-\partial\gamma/\partial \ln c}{nRT}$$

The mean surface area per molecule ( $A_{min}$ ) can be calculated from relation

$$A_{min} = \frac{1}{NA \Gamma_{max}}$$

where  $N_A$  denotes the Avogadro's number. Efficiency of adsorption ( $pC_{20}$ ), the negative log of the surfactant molar concentration ( $C_{20}$ ) required to reduced the surface tension of the solvent by 20 mN/m, was determined for each single and mixed system, The free energy of micellization ( $\Delta G_m^\circ$ ) is calculated as follows:

$$\Delta G_m^\circ = RT \ln X_{cmc} \quad \text{for zwitterions surfactant}$$

$$\Delta G_m^\circ = RT(2-n) \ln X_{cmc} \quad \text{for ionic surfactant and the mixtures}$$

Where  $X_{cmc}$  is mole fraction at CMC, and  $n$  is the ionization degrees of micelles of ionic surfactants which were estimated from the ratio of the slopes above and below CMC obtained from plots of conductivity versus concentration [16]. The free energy of adsorption  $\Delta G_{ad}^{\circ}$  at the air/water interface is calculated from the relation:

$$\Delta G_{ad}^{\circ} = \Delta G_m^{\circ} - (\Pi_{cmc} / \Gamma_{max})$$

Where  $(\Pi_{cmc})$  is the surface pressure at CMC which is calculated from the relation:

$$\Pi_{cmc} = \gamma^{\circ} - \gamma_{cmc}$$

Where  $\gamma^{\circ}$  is the surface tension of water without surfactant.

Table (1) include the calculated interfacial and thermodynamic parameters  $pC_{20}$ ,  $\Gamma_{max}$ ,  $A_{min}$ ,  $\pi_{cmc}$ ,  $\Delta G_m^{\circ}$  and  $\Delta G_{ad}^{\circ}$  for the individual and the binary mixtures at 298 K.

**Table 1:** Interfacial and thermodynamic parameters for the individual and the binary mixtures at 298 K.

$\alpha_{CABP}$	( $CMC_{ex}$ ) m M	$\Pi_{cmc}$	$\Gamma_{max}$ mMx10 <sup>3</sup>	$A_{min}$ Å <sup>2</sup>	$-\Delta G_m^{\circ}$ kJ	$-\Delta G_{ad}^{\circ}$ kJ	$PC_{20}$
0	6	34.485	1.407	0.118	44.8	69.3	3.18
0.1	1	36.912	1.945	0.086	39.4	58.5	3.86
0.2	0.45	35.727	1.895	0.088	33.5	52.4	4.17
0.3	0.6	37.588	1.840	0.090	31.4	51.8	4.27
0.4	0.5	38.787	1.606	0.103	28.3	52.5	4.60
0.5	0.2	37.550	1.950	0.851	30.5	49.8	4.83
0.6	0.1	32.109	3.038	0.054	32.2	42.8	4.47
0.7	0.1	32.799	3.596	0.046	32.2	41.4	4.50
0.8	0.1	32.799	3.301	0.055	32.2	43.1	4.60
0.9	0.09	30.754	2.817	0.059	32.5	43.4	4.68
1.0	0.07	25.317	6.705	0.025	33.1	36.4	4.38

It is observed from Table 1 for mole fractions from 0.1 to 0.4 that  $\Gamma_{max}$  values decrease with an increasing mole fraction of CABP in mixed system, indicating gradual lowering of surface activity of those binaries [17], whereas in case of mole fractions from 0.5 to 0.9, the trend is reverse in which surface activity increases with increasing mole fraction of CABP. The trend in  $A_{min}$  values of binaries is the reverse to that of  $\Gamma_{max}$  as expected from the reciprocal interdependence. The  $pC_{20}$  values for the mixtures increases up to  $\alpha=0.5$  and then decreases, suggesting that for extreme compositions of CABP, interfacial adsorption is preferred. The results of  $\Delta G_m^{\circ}$  indicate that the values for the mixture system, decrease (in magnitude) regularly with increasing CABP up to  $\alpha = 0.4$ , indicating low spontaneous micellization and then increased. For  $\Delta G_{ad}^{\circ}$  the values decrease (in

magnitude) regularly with increasing a CABP, indicating that the spontaneous due to hydrophobicity of amphiphiles, which leads them toward air/water interface was decreased.

As proposed by Clint [18] for ideal mixed micelles, the mixed CMC( $C_{12}$ ) for a binary surfactant system is given by the following equation:

$$\frac{1}{CMC_{ideal}} = \frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2}$$

where  $\alpha_1$  is the mole fraction of surfactant 1 in the total mixed solute, and  $C_1$  and  $C_2$  are CMC of surfactants 1 and 2, respectively .

Mixed CMC values obtained experimentally are different from than those obtained by assuming ideal behavior. These deviations could be investigated by calculating  $\beta^m$  parameter values (a measure of the interactions between surfactants in the mixed micellar system) from surface tension ( $\gamma$ )-log concentration (log C) plots of individual surfactants and their mixtures. By considering the phase separation model for micellization, Rubingh [19] derived the relationship shown in Equation below:

$$\frac{[x_1^2 \ln(\frac{cmc \exp \alpha_1}{cmc_1 x_1})]}{(1-x_1)^2 \ln[cmc \exp(1-\alpha_1) cmc_2 (1-x_1)]} = 1$$

where  $X_1$  is the mole fraction of surfactant 1 in the mixed micelle. The equation above was solved iteratively to obtain the value of  $X_1$ , from which the interaction parameter  $\beta^m$  was evaluated using the relationship:

$$\beta^m = \frac{[\ln(\frac{cmc \exp \alpha_1}{cmc_1 x_1})]}{(1-x_1)^2}$$

The interaction parameter is related to the activity coefficients ( $f_1, f_2$ ) and the micellar composition ( $X_1, X_2$ ) as follows:

$$f_1 = \exp[\beta(1-x_1)^2]$$

$$f_2 = [\beta(x_1)^2]$$

The results obtained are listed in Table (2).

For ideal mixing of two components,  $\beta^m$  assumes a value of zero. A positive  $\beta^m$  value means repulsive interaction among mixed species, whereas a negative  $\beta^m$  value implies an attractive interaction; the more negative its value, the greater the interaction. From  $\alpha = 0.6$  to  $\alpha = 0.9$  all mole fractions of the mixed systems,

the  $\beta^m$  values are negative (Table 2) suggesting that the interaction is more attractive between the two components in the mixed micelle than the self-interaction of the two components before mixing[20]. If the values of  $f_1, f_2$  are found to be less than unity non ideal behavior of the mixed systems, was confirmed [21].

**Table 2:** The interaction parameters values for SDS/CAPB mixed surfactant systems at 25C°.

$\alpha_{CABP}$	(CMC <sub>ideal</sub> ) m M	(CMC <sub>ex</sub> ) m M	$X^m$	$\beta^m$	$f_1$	$f_2$
0	6	6	-	-	-	-
0.1	0.633	1	-	-	-	-
0.2	0.238	0.450	-	-	-	-
0.3	0.227	0.600	-	-	-	-
0.4	0.171	0.500	-	-	-	-
0.5	0.138	0.200	-	-	-	-
0.6	0.115	0.100	0.892	-3.431	0.960	0.065
0.7	0.099	0.090	0.9198	-3.383	0.978	0.057
0.8	0.087	0.080	0.930	-3.541	0.982	0.046
0.9	0.077	0.075	0.9675	-3.431	0.996	0.040
1.0	0.070	0.070	-	-	-	-

#### 4. Conclusions

Through investigation of the surface tension, the CMC of CAPB, SDS and their mixture was determined. The experimental CMC values obtained of the mixtures with mole fractions from 0.1 to 0.5 are higher than those predicted from Clint's equation, while the reverse trend is observed in case of the mixtures with mole fractions from 0.6 to 0.9 in which the experimental CMC values are lower than those predicted from Clint's equation. This is indicating the presence of nonideality in the micelles. The interaction parameters in mixed micelle are negative, indicating strong synergistic interaction. From thermodynamic,  $\Delta G_m^\circ$  and  $\Delta G_{ads}^\circ$  values are negative in all systems and show the spontaneity.

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