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Micelle Formation and Adsorption of Individual and Mixed Nonionic Surfactant (Tween20+ Tween 80) System in Water.

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ABSTRACT

Surface tension of aqueous solutions and critical micelle concentration (CMC) for tween 20, tween 80 and their mixtures have been determined in the temperature range 293-323 K. surface properties, Γ_{\max} (maximum surface excess), A_{\min} (minimum surface area per molecule) and Π_{CMC} (surface pressure at the CMC) for monomeric surfactant have been determined. Thermodynamic parameters (ΔG_m° , ΔH_m° , ΔS_m°) of the micelle formation were calculated from the temperature dependence on the CMC. The theories of Clint and Rubingh were applied to evaluate the expected CMC, the mole fraction of different components in the micelles, and the interaction parameter (β). The standard Gibbs free energies of adsorption ($\Delta G_{\text{ads}}^\circ$) and the excess free energies of micellization (ΔG_{ex}) of surfactant mixtures were also evaluated. Both $\Delta G_{\text{ads}}^\circ$ and ΔG_{ex} values are all negative and their magnitudes reveal that micelle formation is less spontaneous than adsorption while ΔG_{ex} values suggest that the mixed micelles are more stable than the micelles of individual components.

Keywords: critical micelle concentration, standard Gibbs free energy, surface tension, temperature dependence, tween 20, tween 80.

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INTRODUCTION

Nonionic surfactants made up of an aliphatic tail attached to a polar hydrophilic head chain are essential materials in many industrial applications such as; mineral flotation, corrosion inhibition, oil recovery, dispersion of solids, and detergency. The surface properties of surfactant mixtures were studied extensively because of their wide applications such as foaming, fabric softening, enhanced oil recovery, hydrate promoters etc.[1-2].

The aggregation behavior of binary mixtures of decylmethylsulfoxide, and decyldimethylphosphene oxide at 24°C was examined and the results show that the CMC of this mixed surfactant system could be calculated from the CMC values of the individual surfactants by assuming the phenomenological ideal mixed micelle model [3]. Direct microstructure imaging of aqueous mixtures of a nonionic surfactant C₁₂E₅ and two uncharged block copolymers — diblock copolymer poly(ethyleneoxide) – polybutadiene (EO₁₂₆-B₄₅) and triblock copolymer poly(ethyleneoxide)–poly(ethylene) – poly(ethyleneoxide) (EO₂₁-EE₃₅-EO₂₁) revealed that the shapes and sizes of mixed micelles change as functions of the surfactant-to-copolymer concentration ratio [4]. The CMC of pure surfactants polyoxyethylene (10) alkyl ether and N-decanoyl-N-methylglucamine and their mixtures were determined by surface tension measurements at different mixed ratios and temperatures. Interfacial parameters such as the maximum surface excess (Γ_{\max}) and the minimum area per molecule (A_{\min}) at the air/water interface and standard thermodynamic parameters of micellization and adsorption were also computed and discussed [5].

Mixed micellization of binary and ternary mixtures of anionic and nonionic surfactants, such as lithium dodecyl sulfate, Polyoxyethylene (23) lauryl ether, and polyoxyethylene-tert-octylphenylether, was studied in aqueous solution using tensiometric, conductometric, and spectrophotometric methods. Several parameters, cmc, free energies of micellization and interfacial adsorption, and the interaction parameter have been evaluated [6]. The aggregation behavior in mixed system of nonionic-nonionic surfactant solution was studied. The CMC from single and mixed nonionic surfactant system were compared and the effect of methanol to the CMC was also determined. They conclude that mixed surfactant solution system has lower CMC and addition of methanol lowered the CMC value for each single and thus decreased CMC of mixed nonionic surfactant solution system [7]. Non-ionic surfactants, polyoxyethylene sorbitan fatty acid esters (polysorbate) are chosen to examine the temperature effect on the CMC over a wide temperature range. The enthalpy and entropy of micelle formation are evaluated according to the phase separation model. It is found that ΔG_m° decreases monotonically as the temperature increases over the whole temperature range. Both ΔH_m° and ΔS_m° appear to be decrease monotonically with an increase in temperature [8].

The effect and interactions of polyethylene glycols of varying molecular mass (PEG 15000, PEG 6000, PEG 2000 and PEG 600) with the aqueous mixtures of Pluronic L64 and Igepal CO 720 was studied. The results indicate that Pluronic L64 and Igepal CO 720, belonging to two different categories of nonionic surfactants, behave differently in the presence of PEGs. The results analyzed in terms of CMC, Γ_{\max} , A_{\min} , and surface pressure (Π_{cmc}) [9]. The effect of the hydrophilic surfactant headgroup on the phase behavior of non-ionic surfactant mixtures was examined. They found that the hydrophilicity of the surfactant inhibits the tendency of the system to phase separate. Applying a classical phase separation thermodynamic model, the corresponding energy parameters were evaluated. In all cases, the parameters were found to depend on the type of nonionic surfactant, its concentration in the micellar solution and the presence of NaCl in the medium [10]. Surface and thermodynamic properties of tween 20 and tween 80 with diblock copolymer poly(oxyethylene/oxybutylene) (E39B19) at 298 K were studied. The results showed that the values of CMC of tween 20 and tween 80 were 0.05 mM and 0.019 mM respectively, which were observed to decrease to 0.012 mM and 0.016 mM respectively with the addition of diblock copolymer indicating that micellization is more favorable [11].

In this study, the adsorption studies of non-ionic surfactants (tween 20, and tween 80) and their mixture were conducted at water-air interface by ring detachment method with a du Nouy Tensiometer. Γ_{\max} was calculated from Gibb's equation while A_{\min} was computed from surface excess. Thermodynamic parameters (ΔG_m° , ΔH_m° , ΔS_m°) of the micelle formation were calculated from the temperature dependence on the CMC. The mixed cmc and interaction parameters (β) of surfactant system are determined experimentally and on the basis of the regular solution model.

EXPERIMENTAL

Tween surfactants are polyoxyethylene-sorbitan alkylates, which have a sorbitan ring bound to hydrophilic chains of 20 oxyethylene groups and a hydrocarbon tail. The surfactants in this group differ in the length of the alkyl chain only. The surfactants studied includes: Tween 20 (polyoxyethylene-20 sorbitan-monododecanoate with 12 C-atoms in the alkyl chain), and Tween 80 (polyoxyethylene-20 sorbitan-monooleate with 18 C-atoms and one double bond in the alkyl chain). They were obtained from Sigma Aldrich. Deionized water was employed in the preparation of solutions.

The surface tension of solutions was determined by means of DuNouys ring platinum on S.E.O. Co. Ltd, tension meter (Korea). Platinum ring was thoroughly cleaned before each measurement and the results were the average of three measurements.

RESULTS AND DISCUSSION

Individual surfactants

The surfactants surface tension(γ) was measured as a function of their concentration at 293, 303, 313, and 323 K, and the CMC for the two surfactants was then considered as the point of intersection between two continuous lines obtained by tensiometry (γ vs. $\log [\text{surf}]$). The results obtained are listed in Table (1) and shown in Figure (1).

Table 1: Interfacial and thermodynamic parameters for the individual surfactants

	T(K)	CMC (mM)	Π_{CMC} (mN/m)	$\Gamma_{\text{max}} 10^{-3}$ mmol/m ²	A_{min} Å ² /mole cule	$-\Delta G^{\circ}_{\text{ads}}$ kJ/mol	$-\Delta G^{\circ}_{\text{m}}$ kJ/mol	$\Delta H^{\circ}_{\text{m}}$ kJ/mol	$\Delta S^{\circ}_{\text{m}}$ J/mol.K
Tween20	293	0.0499	28.802	6.341	26.2	38.455	33.913	13.632	162
	303	0.0356	28.284	5.760	28.8	40.831	35.921	14.579	167
	313	0.0300	27.342	5.464	30.3	42.556	37.552	15.557	170
	323	0.0280	28.842	5.076	32.7	44.619	38.937	16.567	172
Tween80	293	0.0125	24,040	3.469	47.8	44.214	37.285	5.5670	146
	303	0.0110	26.119	1.823	91.0	53.207	38.880	5.953	148
	313	0.0107	26.798	3.104	53.4	48.868	40.235	6.220	148.5
	323	0.0160	21.086	2.016	82.3	50.899	40.440	6.765	146

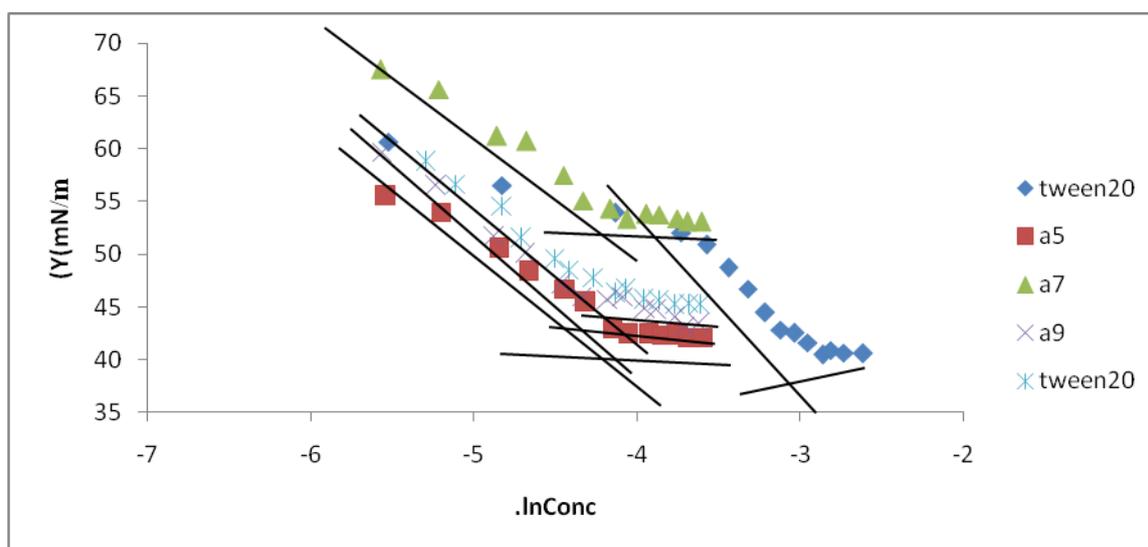


Fig 1: Surface tensions (γ) versus ($\ln[C]$) for individual and typical mixed surfactant systems

The data in Table (1) indicate that in the temperature range studied the CMC of tween 20 surfactant decreases as the temperature increased. This may be due to decrease in hydration of hydrophilic group which favors micellization. The same behavior was observed for tween 80 in the temperature range 293-313 K, but when the temperature increased to 323K the CMC increases with temperature which indicate that the increase in temperature also causes the increase in breakdown of the structured water surrounding the hydrophobic group which disfavors micellization[12-13]. This behavior agrees well with the reported in the references[11], [14] and [15].

The temperature dependence of the CMC of the surfactant has been used to obtain the thermodynamic parameters of micellization [8, 10-11]. The standard free energy of micelle formation ΔG_m° was calculated by the equation:

$$\Delta G_m^\circ = RT \ln X_{CMC} \text{--- (1)}$$

Where X_{CMC} is the mole fraction of surfactant at the CMC, R is the gas constant, and T is the temperature. The enthalpy of micellization ΔH_m° was obtained by applying the Gibbs-Helmholtz equation to the equation above:

$$\Delta H_m^\circ = - RT^2 (\partial \ln X_{CMC} / \partial T) \text{---(2)}$$

ΔH_m° was evaluated from the slope of the plot of $\ln X_{CMC}$ versus temperature. The entropy of micellization process ΔS_m° was estimated from the equation:-

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ \text{---(3)}$$

ΔG_m° , ΔH_m° and ΔS_m° that have been obtained by applying the above equations for tween 20 and tween 80 surfactants are reported in Table (1).

From the results presented in Table (1), it can be generalized that ΔG_m° is negative in the whole temperature range studied which indicates that the micellization process is spontaneous. ΔH_m° is negative and increased as temperature increased which indicates the micellization is exothermic. The entropy of micellization, ΔS_m° , is positive in all temperature range and decreases with increase in temperature. This is due to the fact that the head group is more hydrated than the hydrophobic tail with increasing temperature which leads to an overall ordering of the system hence, the lowering of the entropy with increase in temperature [16].

Interfacial properties

The values of different surface properties, Γ_{max} , A_{min} , Π_{CMC} and thermodynamic parameter, ΔG_{ads}° (the standard Gibbs energy of adsorption) were obtained for the surfactants and are listed in Table 1. These parameters were calculated using the following equations [17-20].

$$\Gamma_{max} = - \frac{1}{nRT} \left[\frac{d\gamma}{d \ln C} \right] \text{--- (4)}$$

Where C is the concentration of the surfactant in solution and n is the number of species constituting surfactant. The $d\gamma/d \ln C$ factor was obtained from the slopes of the linear plots of γ vs. $\ln C$ (Fig. 1). Γ_{max} values follow regular trend with temperature. The temperature effect is due to an increase in molecular motion; resulting in poor packing at the liquid–air interface¹⁵. Γ_{max} values were used to calculate A_{min} at the air/solvent interface using the relationship:

$$A_{min} = 1/ N\Gamma_{max} \text{--- (5)}$$

Where N is Avogadro’s number. The trend in A_{min} values is the reverse to that of Γ_{max} as expected from the reciprocal interdependence. The values of Π_{CMC} were obtained from Eq. (6)

$$\Pi_{CMC} = \gamma_o - \gamma_{CMC} \text{--- (6)}$$

Where γ_0 is the surface tension of pure solvent and γ_{CMC} being the surface tension at the CMC. Π_{CMC} values are not following any regular trend with temperature. ΔG_{ad}° at the air/water interface is calculated from the relation:

$$\Delta G_{ad}^\circ = \Delta G_{m-}^\circ (\Pi_{CMC} / \Gamma_{max}) \quad \text{--- (7)}$$

Both ΔG_{m-}° and ΔG_{ads}° are negative at all temperature studied and their magnitudes reveal that the ΔG_{ads}° to be more spontaneous which leads them toward air/water interface. From this, it is concluded that micelle formation is less spontaneous compared to adsorption [21].

Mixed surfactants

The ideal mixed micelles CMC for a binary surfactant system, as proposed by Clint [22], is given by the following equation:

$$\frac{1}{C_{mix}} = \frac{\alpha_1}{C_1} + \frac{\alpha_2}{C_2} \quad \text{--- (8)}$$

where α_1 and α_2 are the mole fraction of surfactant 1 and surfactant 2 in the total mixed solute respectively, and C_1 , C_2 and C_{mix} are critical micelle concentrations for components 1, 2, and mixture respectively. The CMC obtained experimentally at 293 K and their calculated from equation (8) are listed in Table (2). The experimentally mixed CMC values decreased as α_1 increased and at $\alpha_1 = 0.9$ a synergistic effect was observed which give CMC value of 0.0115 mM. For comparison between ideal and non ideal mixtures, the mixed CMC values of the system studied as a function of mole fraction of surfactant 1 are given in Fig. 2 which shows the experimental CMC values deviate from the ideal CMC values in the whole mixing range, indicating that an attractive interaction exists in the mixed micelle formation process [23].

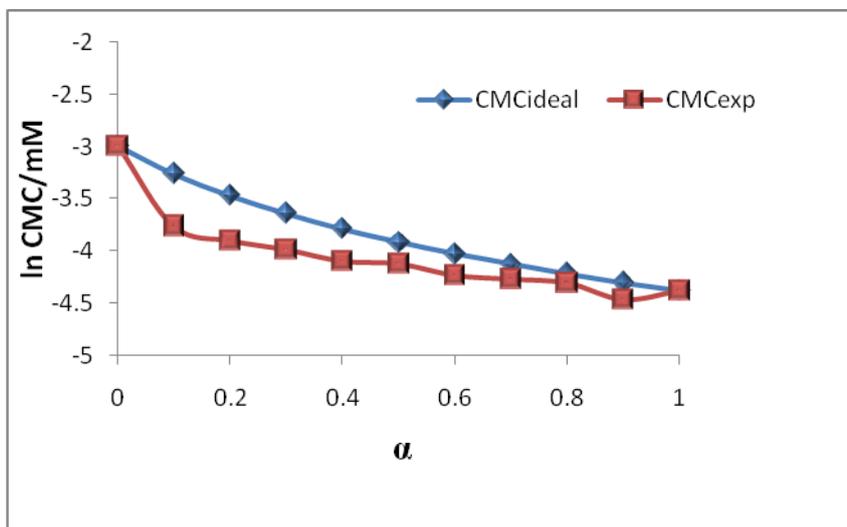


Fig 2: variation of mixed CMC values with alpha

Table 2: The interaction parameters values for Tween 20 / Tween 80 mixed surfactant systems at 20C°.

alpha	CMCideal (mM)	CMCexp (mM)	X1	theta	f1	f2	Delta Gex J/mol
0.1	0.0384	0.0233	-	-	-	-	-
0.2	0.0312	0.0202	-	-	-	-	-
0.3	0.0263	0.0185	0.047	0.948	0.423	0.997	-105

0.4	0.0227	0.0166	0.245	1.071	0.543	0.937	-484
0.5	0.0199	0.0162	0.352	-1.911	0.454	0.784	-1061
0.6	0.0178	0.0145	0.413	-2.508	0.421	0.652	-1482
0.7	0.0161	0.0140	0.456	-2.853	0.430	0.553	-1723
0.8	0.0147	0.0135	0.5	-3.357	0.432	0.432	-2045
0.9	0.0135	0.0115	0.547	-4.735	0.378	0.243	-2857
1	-	0.0125	-	-	-	-	-

Surfactant interactions was analyzed by using regular solution theory (RST), which is allowed to calculate the micelle mole fraction (X_1) and interaction parameter (β) by using the following equations (Rubingh model) [24]:

$$\frac{(X_1) 2 \ln \left(\frac{\alpha_1 C_{mix}}{X_1 C_1} \right)}{(1 - X_1) 2 \ln \left[\frac{(1 - \alpha_1) C_{mix}}{(1 - X_1) C_2} \right]} = 1 \quad \text{--- (9)}$$

$$\beta = \frac{\ln \left(\frac{\alpha_1 C_{mix}}{X_1 C_1} \right)}{(1 - X_1) 2} \quad \text{--- (10)}$$

Where X_1 is the micelle mole fraction of surfactant 1 in the mixed micelles and β is the interaction parameter which indicates the magnitude of interaction between the two components in the mixed micelle. Eq. (9) was solved iteratively for X_1 values and β values are obtained by substituting X_1 in Eq. (10). The values of X_1 and β are given in Table 2.

The results showing that X_1 values of $\alpha = 0.3$ is very small and increases with increasing α of surfactant 1. The values of β indicate the extent of interactions between two surfactants which leads to deviation from ideal behavior. The β values of systems $\alpha = 0.3$ to $\alpha = 0.9$ are all negative which can be ascribed to the interaction between the head groups leading to electrostatic stabilization [24].

Maeda [25] proposed that in addition to electrostatic interactions, the chain/chain interaction play a major role in the formation of mixed micelles, especially for the dissimilar chain lengths. In the present study, chain/chain interactions contribute to the attractive interaction, whereas, these are also head group contributions to attractive interaction.

The activity coefficients (f_1 and f_2) of the two surfactants within the mixed micelle are related to the interaction parameter (β) through equations:

$$f_1 = \exp[\beta (1 - X_1)^2] \quad \text{--- (11)}$$

$$f_2 = \exp(\beta X_1^2) \quad \text{--- (12)}$$

The values of activity coefficients, f_1 and f_2 calculated from Eqs. (11) and (12), are found to be less than unity showing non-ideal behavior of the mixed systems. The activity coefficients can be used to calculate excess free energy of mixing (ΔG_{ex}) by the relation [26]:

$$\Delta G_{ex} = RT[X_1 \ln f_1 + (1 - X_1) \ln f_2] \quad \text{--- (13)}$$

Table 2 show that all the calculated ΔG_{ex} values are negative which suggests that the mixed micelles are more stable than the micelles of individual components and the maximum value are observed in case of $\alpha = 0.9$ system.

CONCLUSIONS

- 1-From the study of the temperature dependence of the CMC of tween 20 and 80 in aqueous solution, we have observed that the micellization process is favorable when the temperature increased.
- 2-Thermodynamic adsorption data showed that the adsorption of the surfactant and micelle formation occur spontaneously and becomes more spontaneous at higher temperatures.
- 3- The variation of CMC of mixtures of surfactant show nonideal behavior in micelle formation and the β values can be ascribed to the interaction between both the head groups and chains.
- 4- ΔG_m° and ΔG_{ads}° magnitudes reveal that micelle formation is less spontaneous than adsorption. Also ΔG_{ex} values suggest that the mixed micelles are more stable than the micelles of individual components.

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