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Studies on Mixed Micelles of Brij56 and CTAB

Paray Aijaz Ahmad

Department of Chemistry, University of Kashmir, Hazratbal, Srinagar J&K -190 0006
E-mail: parayaijazahmad@gmail.com

Abstract—*In this work we study Brij56 and CTAB surfactants and studied variation of CMC of one surfactant in presence of another. CMC of non ionic surfactants is much lower than cationic surfactants. We studied the interaction of Brij 56 and CTAB by using Rubing's model. Some surfactant mixture ratios show more strong interaction than others. This study will help us in making skin formulations with least skin irritations. Further micellar systems can solublize poorly soluble drugs which are otherwise insoluble hence can be used to make various drug formulations. The results of the present study may prove fruitful in optimizing the properties of surfactant mixtures relevant for many formulations.*

Keywords*: Brij56 and CTAB.*

1. INTRODUCTION

Surfactants are known to play an important role in many processes of interest in both fundamental and applied sciences. One important property of surfactants is the formation of colloid sized clusters in solutions, known as micelles, which have particular significance in pharmacy because of their ability to increase the solubility of springly soluble substances in water. Micellar systems can solublise poorly soluble drugs and thus increase their bioavailability, they can stay in blood long enough to provide gradual accumulation in the required area, and their size permit them to accumulate in areas with leaky vasculature. Now a day's mixed micelles are gaining more impotance than their individual components. Mixed micelles are being used in pharmaceutical and biological fields as they work better than their pure micelles [1-2].

2. EXPERIMENTAL DETAILS

2.1. Materials and Preparation

The cationic amphiphile cetyltrimethyl ammonium bromide CTAB used was a Sigma product and non ionic amphiphile polyoxyethylene (10) cetyl ether (Brij-56) was received from Fluka. The Stock solutions of Brij-56 and CTAB were prepared at concentrations of 15mM and 25mM respectively. The stock solutions were utilized to prepare the samples of desired concentration. All solutions were prepared in triple distilled water.

3. RESULTS AND DISCUSSIONS

3.1 CMC and surfactant-surfactant interactions

Surface tension of Brij56 and CTAB and their binary mixtures in aqueous solutions at 25 ^{o}C are present in Table 3.1 and 3.2. CMC's values of the surfactant solutions of Brij56 and CTAB as well as their mixtures were determined by plotting graphs between the surface tension (γ) and logarithm of the corresponding surfactant concentration. Figure 3.1 shows the experimental plots for Brij56 & CTAB respectively. As surfactant concentration is increased the surface tension decreases and then attains a constant value, joining the data points, point of intersection is obtained, which is used to determine critical micelle concentrations (CMC's) of individual surfactants and their mixtures. The CMC's of pure surfactants are given in Table 3.3 along with their CMC's reported in literature. The experimental values and literature values show good agreement. The low CMC value of the non-ionic surfactant are probably due to the fact that when they get into water, they distort the structure of water hence increasing the energy of the system and system responds by forcing the surfactant molecules to form micelles which leads to decreases the energy of the system.

Table 3.1: Surface tension data of CTAB and Brij56

Brij56		CTAB	
concentration (mM) × 103	**Surface tension (mN/m)**	**Concentration (mM) × 102**	**Surface tension (mN/m)**
2.78	69.4	4.99	72.8
3.57	65.5	9.96	70.3
5.54	63.9	14.91	65.6
7.87	60.0	19.84	63.7
11.72	56.7	29.64	58.4
15.50	52.4	39.37	55.3
19.23	50.2	49.02	51.9
22.90	49.4	58.59	49.3
26.52	47.9	68.09	47.2
30.08	47.1	77.52	44.9
33.58	48.4	86.87	43.0
37.04	48.0	96.15	41.4
43.80	48.5	105.36	41.1
47.10	47.7	114.50	41.0

		123.57	41.0
		132.58	41.2
		141.51	41.4
		150.38	41.3

Table 3.3 also lists the experimental CMC values of the mixtures, C_{12}^{Exp} , the values increase as the concentration of CTAB is increased, this is probably due to the reason as cationic component increases in the micelle its formation is less favoured due to electrostastic repulsions especially when CTAB mole fraction is more than half.

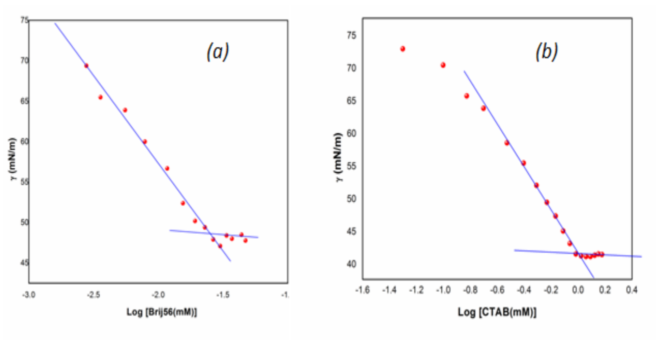

Figure 3.1: Plot of Surface tension versus logarithm of: (a) Brij56, (b) CTAB concentration.

The Clint equation [3]

$$\frac{1}{C_{12}^{Ideal}} = \frac{x_1}{C_1} + \frac{1-x_1}{C_2} \qquad (3.1)$$

gives the CMC of ideal binary surfactant mixtures formed from components 1 & 2 with C_1 & C_2 as their respective CMC's. The ideal CMC values,C_{12}^{Ideal}, for Brij56 and CTAB so obtained are incorporated in Table 3.3. The experimental values and ideal value when compared indicate synergism between the surfactants forming mixed micelles. Similar nonideal and synergistic behavior has been reported for other cationic-nonionic mixed micelles previously [4-5]. The ideal CMC's of Brij56 and CTAB mixtures must lie in-between that of CMC of Brij56 and CMC of CTAB because incorporating non ionic surfactants in the ionic surfactant decreases electrostatic repulsions and favour their formation. The experimental mixed CMC of binary mixture with Brij56 mole fraction 0.5 or more is even lesser than that of pure Brij56, suggesting that these mixtures have much enhanced tendency of micelle formation possibly due to decrees in the strong steric hindrances if only Brij56 molecules would have been present.

Table 3.2: Surface tension data for Brij56+CTAB mixture.

Brij56 & CTAB [1:1 ratio]		Brij56 & CTAB [3:7 ratio]		Brij56 & CTAB [7:3 ratio]	
Concentration (Mm) × 103	Surface stension (Mn/m)	Concentration (Mm) × 102	Surface tension (Mn/m)	Concentration (Mm) × 102	Surface tension(Mn/m)
0.64	72.8	0.64	59.2	0.32	56.4
1.28	64.7	1.28	51.2	0.64	49.1
1.92	61.4	1.92	47.8	0.96	48.8
2.55	58.9	2.55	46.9	1.28	46.6
3.19	56.0	3.19	45.0	1.59	44.1
3.82	55.4	4.77	44.6	1.91	43.4
4.46	55.3	6.35	43.9	2.23	43.3
5.09	52.3	7.92	43.2	2.54	42.9
5.72	54.0	9.49	43.5	2.86	42.8
6.35	52.6	11.05	43.2	3.17	43.3
6.98	53.9	12.60	43.3	3.49	43.0
7.82	51.4	14.15	43.0	3.80	42.3
10.11	51.5	15.69	43.0	4.12	42.3
11.67	47.8	17.22	42.6	4.43	42.1
13.22	46.8	18.75	42.8	4.74	42.3
14.76	46.6	20.27	43.1	5.06	41.6
16.30	45.8	21.79	43.2	5.37	41.9
19.36	45.0	23.30	42.8	5.68	41.8
22.40	44.7	24.81	42.7	5.99	41.6
25.41	44.2	26.31	43.0	6.30	41.6
28.40	44.6	27.80	42.8	6.92	41.3
31.36	44.6	30.77	42.6	7.23	41.2
34.30	44.0	33.72	42.6	7.54	41.6
40.12	44.1	36.64	42.7	7.84	41.6
45.85	44.0	39.54	42.6		

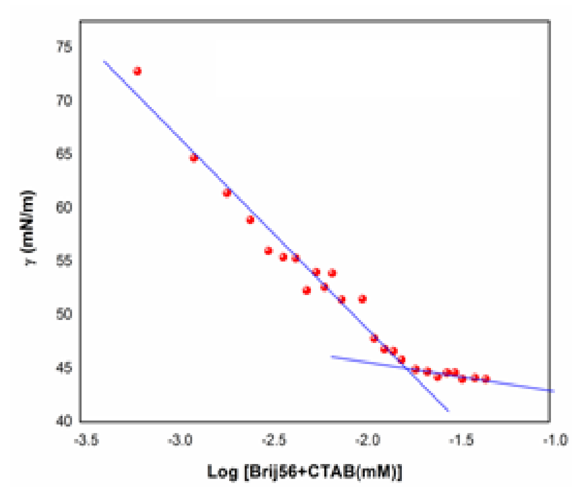

Figure 3.2: Plots of surface tension versus surfactant concentration for binary Brij56 and CTAB system.

Table 3.3: Experimental CMC (CMC^{Exp}) and ideal CMC (CMC^{Ideal}) of the binary mixtures of CTAB with Brij56.

S. No.	Mole fraction of Brij56 in the mixture	CMCExp (Mm)	CMCIdeal (Mm)
1	0.0	1.03 (0.815) [6]	-
2	0.1	0.095	0.212
3	0.3	0.038	0.082
4	0.5	0.017	0.051
5	0.7	0.018	0.037
6	0.9	0.020	0.029
7	1.0	0.026 (0.036) [7]	-

3.2 Mixed Micellization and Interaction Parameter

To take into account the non-ideal mixing of Brij56 and CTAB, Rubing's model [8] of mixed micelle formation, which is based on the Regular Solution Theory, was applied. According to this model the equation applicable for mixed micelle formation is:

$$\frac{X_1^2 ln(C_{12}\alpha_1/C_1X_1)}{(1-X_1)^2 ln\{C_{12}(1-\alpha_1)/C_2(1-X_1)\}} = 1 \quad (3.2)$$

where α_1 represent the overall mole fraction of the component 1 in the binary surfactant system, C_1, C_2 and C_{12} are the CMC's of components 1, 2 and that of the mixture respectively. X_1 and $X_2 = (1-X_1)$ are the mole fractions of the components 1 and 2 in mixed micelles. The interaction parameter, β, of mixed micelle formation is given by the equation:

$$\beta = \frac{ln(C_{12}\alpha_1/C_1X_1)}{(1-X_1)^2} \quad (3.3)$$

and is related to activity coefficients of surfactants within the micelle by the equation:

$$f_1 = \exp\{\beta(1 - X1)^2\} \quad (3.4)$$

$$f_2 = \exp\{\beta X_1^2\} \quad (3.5)$$

Table 3.4 presents the different parameters calculated for binary mixtures at different stoichiometric compositions, obtained from Rubing's model. Negative value of interaction parameter β, indicte that there are strong attractive intractions between the components in the mixed micelle. The sign of β values has commonly been attributed to the nature of interaction between the head groups on the one hand and that between the hydrophobic tails on the other. It is evident that generally the β values become more and more negative as mole fraction of CTAB in mixed micelle decreases probably due to decrease in electrostatic repulsions in the micelle. Similar results have been previously reported for other cationic-nonionic mixed amphiphiles [8-9]. However much lower concentration of CTAB in the micelle leades the β value to become less negative possibly due to increase in the steric hindrance among Brij56 surfactant molecules. The highest interaction occurs when CTAB and Brij56 are in equimolar proportions. This highest interaction at 1:1 ratio might be due to the fact that such a micelle would have minimum steric hindrance among Brij56 molecules, minimum electrostatic repulsions among CTAB molecules and maximum attractions between the molecules of two components.

Table 3.4: Micellar composition, X_1, interaction parameter, β, activity coefficients, f_1 and f_2, at 25 °C of binary mixture of Brij56 and CTAB at different stoichiometric compositions, α_1, obtained by Rubing's model are as

α_1 (Brij56)	CMC_{12}^{Exp} (Mm)	CMC_{12}^{Ideal} (Mm)	B	X_1	f_1	f_2
0.0	1.03	1.03	-	-	-	-
0.1	0.095	0.212	- 3.83	0.63	0.59	0.22
0.3	0.038	0.082	-5.06	0.70	0.63	0.09
0.5	0.017	0.051	-7.69	0.69	0.47	0.03
0.7	0.018	0.037	-7.02	0.75	0.64	0.02
0.9	0.020	0.029	-6.63	0.83	0.82	0.01
1.0	0.026	0.026	-	-	-	-

4. CONCLUSIONS

- The cationic surfactants were found to have higher CMCS then non ionic surfactants of comparable chain length.
- In Brij56 and CTAB mixture CMC's first increases with increase in mole fraction of Brij56 reaching at its highest value and then decreases. Lowest CMC was found when mole fraction of Brij56 in the binary mixture was 0.5 in the solution.
- Rubing's model also showed highest interaction of components in the binary mixed micelle when mole fraction of Brij56 in the solution is 0.5.

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