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Surface tension investigation of ternary system: Copper surfactants - 2-amino-6-chloro benzothiazole complex, benzene and methanol at 311 K

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Abstract

Colloidal and micellar characterization of Cu (II) soap complex solutions in benzene + methanol mixture has been studied and analysed by measuring density and surface tension parameters. This study confirms that CMC values depend upon solvent mixture composition and it is observed that CMC decrease with increase in chain length of copper surfactant (caprylate, caprate and laurate). It has also been affected by the polarity of the solvents as non- polar benzene and polar methanol were taken to analyze this effect. Szyszkowski's empirical equation has been successfully applied to our referred system and it is found that the change in the behaviour of copper surfactant complex carried out at definite concentrations in different compositions of solvent mixture. It is also observed that the parachore of soaps solution increases with the mole fraction of the copper surfactant complex. The results show that there is justification in applying Hammic and Andrew's equation to these complex solutions in benzene methanol mixtures.

Keywords: Surfactants, Caprylate, Caprate, laurate, 2-amino, 6-chloro benzothiazole.

1. Introduction

Surfactants or surface-active agents are materials that tend not only to accumulate at surfaces, but also by their presence, change the properties of surfaces.[1] Benzothiazoles have been serving as the basis of a variety of drugs for over five decades. They constitute an important and interesting class of heterocyclic not only for synthetic investigations but also for their usefulness.[2-3] It is well known that benzothiazoles are derivative of anilines and play significant role in biological activities and having sufficient industrial and analytical applications.[4] Benzothiazole possesses nitrogen and sulfur atoms, which are responsible for their pharmacological activities.[5] They have been used as tranquilizers, anthelimintics, anti-inflammatory, neuroloptics, antihistamines, sedatives, antipsychotics, antiviral, diuretics, fungicides, anesthetics, bactericides, antimalarials etc. along with their activities.[6,7,8]

Number of solvents have been used to understand the micellar features of copper (II) soaps by viscosity, surface tension, parachor and electrical conductance, membrane incorporating heavy metal surfactants have been used to determine the surface activity by measuring membrane potential.[9-10]Viscometric studies at various temperatures, apparent molar volume, ultrasound, surface tension,

TGA, antifungal activities and photochemical degradation features of copper soap and their complexes derived from various edible and non -edible oils related with micellar features in various organic solvents have been earlier reported.[11,12,13,14,15] Several workers described the uses of copper soaps as stabilizers for nylon threads, synthetic polyamide and polyesters.[16,17] The protection of fabrics, nets, cordage etc. from fungi and decay by impregnating them in ammonical solution of copper soaps was described by several workers.[18-19] The effectiveness of copper soaps as fungicides, bacteriocides, insecticides and herbicides was also studied.[20] Present work has been initiated with a view to obtaining a profile as to micellar characterization and aggregation of Cu (II) soaps (caprylate, caprate and laurate) with 2-amino, 6-chloro benzothiazole in benzene + methanol mixtures of varying proportions in order to find out the critical micelle concentration CMC at constant temperature. Szyszkowski's empirical equation has been used to show that size and nature of micelles formed in two groups of solvent are different.

2. Experimental

The acids (n–caprylic acid, n–capric acid and n–lauric acid) have been taken for study and their purity was confirmed by the determination of melting points i.e. n - caprylic acid (16.3^0C) n - capric acid (31.2^0C), n - lauric acid (44.0^0C). Copper soaps were prepared by direct metathesis of the corresponding potassium soap by reported methods in literature.[21] Ligands were synthesized using thiocyanate on method.[22] The purity of the benzothiazoles has been checked by thin layer chromatography in various non-aqueous solvent systems. Separated solid complexes were filtered and washed successively with 5-ml portion of dry ethanol and dried. The dried sample was purified by repeated crystallization with dry ethanol. The metal was analysed by standard procedure. C, H, N, Cl and S analysis were performed at RSIC, CDRI Lucknow. In general, all the solid complexes (90% yield) with bluish green periphery were obtained (Table 1). These are soluble in ethanol, methanol, benzene and other organic solvents and insoluble in water. All the complexes are quite stable at room temperature up to 170^0C. On the basis of elemental analysis, the complexes have been assigned the composition $Cu_2(C_nH_{2n+1}COO^-)_4L_2$, n=7,9,11 and suggested 1:1 type stoichiometry (Fig. 1-3)

Table 1: Physical & analytical properties of Cu (II) surfactants complexes in benzene+ methanol at 311 K

Molecular Formula of Complex	Colour	% Yield	M.P. /^{o}C	%Cu	%C	%H	%O	%N	%S	%Cl
$Cu_2(C_7H_{15}COO^-)_4.(C_7H_5N_2SCl)_2$ $CC_{pl}ACB$	Dark Greenish Blue	90	175	11.67 [11.89]	51.07 [51.68]	6.23 [6.55]	11.72 [11.98]	5.02 [5.24]	5.89 [5.99]	6.56 [6.64]
$Cu_2(C_9H_{19}COO^-)_4.(C_7H_5N_2SCl)_2$ $CC_{pr}ACB$	Greenish Blue	92	190	10.54 [10.76]	54.85 [54.91]	7.03 [7.28]	10.78 [10.84]	4.59 [4.74]	5.22 [5.42]	5.98 [6.01]
$Cu_2(C_{11}H_{23}COO^-)_4.(C_7H_5N_2SCl)_2$ $CL_{rt}ACB$	Blue	94	205	9.80 [9.83]	48.06 [48.29]	7.77 [7.89]	9.81 [9.90]	4.25 [4.33]	4.86 [4.95]	5.38 [5.49]

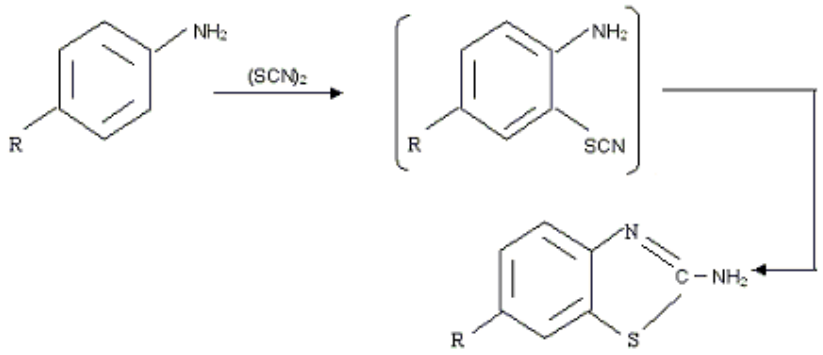

Figure 1: synthesis of ligand by thiocyanation method

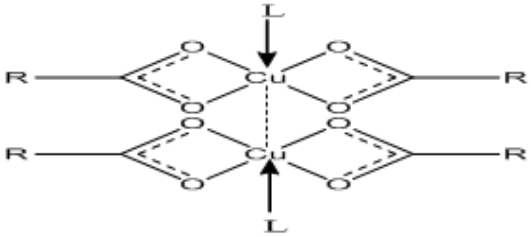

Figure 2: Proposed structure of copper soap

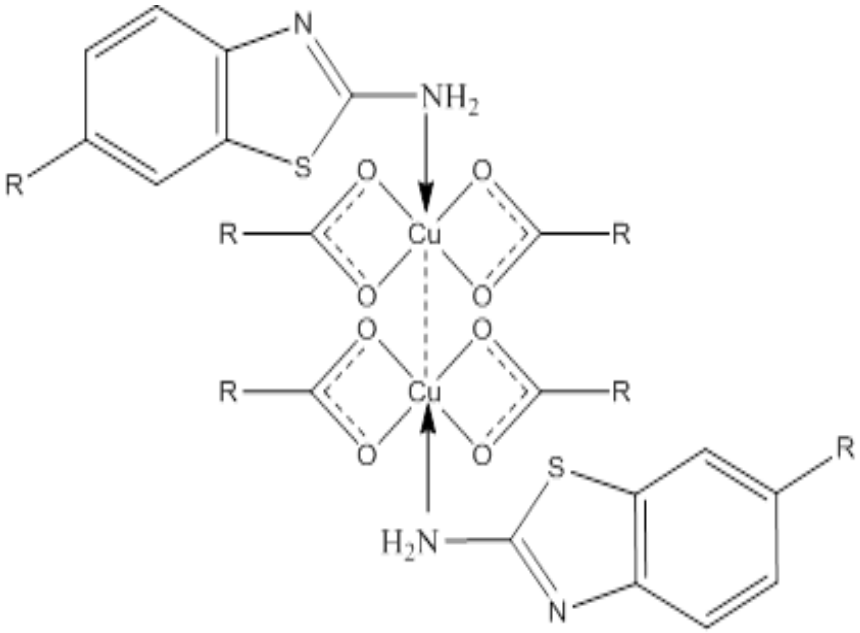

Figure 3: Proposed structure of copper soap complex

2.1 **Measurement of surface tension:**
Ostwald springel pyknometer was used for determination of the density of complex solutions. Traube's stalagmometer was used to measuring the surface tension of complex solutions by employing Harkins and Brown method of controlling the drops. The results were calculated by following formula.[23]

$$\frac{\gamma^0}{\gamma^1} = n^1 d^0 / n^0 d^1 \qquad (1)$$

Where γ_0 and γ_1 are surface tension of the known and unknown solution n_0, n_1 and d_0, d_1 are the corresponding number of drops and densities respectively. The reproducibility of the results was below 0.5%.

3. Results and Discussion:

The surface tension, γ of the solutions of copper surfactant complex solutions in mixture of varying composition of benzene and methanol shows an increasing trend up to CMC and after CMC it decreases in the complex concentration. This may be due to increasing tendency of complex molecules, to form aggregates in the form of micelles and decreasing effects in the surface energy of the solvent. Further, it is suggested that usually in adsorbed mono layer phase, the surface pressure develops on account of kinetic pressure, cohesive pressure and electrical pressure which favours the decrease in the surface tension of surfactant solution. The plots of surface tension γ, against the complex concentration c, (Fig 4) characterised by two straight lines corresponding to CMC of complex. At the CMC, hydrocarbon chain structure of complex molecules allows an extensive contact between adjacent chains, possibly accompanied by change in vibrational and rotational degree of freedom of methylene group. The plots of the surface tension γ, against the complex concentration c, have been extrapolated to zero complex concentration and values of the surface tension for zero complex concentration γ_0, are recorded in Table-2.

Table 2: Values of X, Y, XlnY for Cu (II) surfactants - 2-amino-6-chloro benzothiazole complex, benzene + methanol at 311 K

% volume of methanol	Soap Complex	X	Y	XlnY	A
		$X_1\times10^2$ $X_2\times10^2$	Y_1 Y_2	$(XlnY)_1$ $(XlnY)_2$	$A_1\times10^{-3}$ $A_2\times10^{-3}$
40%	$CC_{pl}ACB$	+2.2893 -3.3488	0.1103 0.1088	+0.2226 -0.2843	+6.1339 -2.8260
	$CC_{pr}ACB$	+1.7147 -2.9555	0.1108 0.1093	+0.1678 -0.2652	+6.5192 -2.2021
	$CL_{rt}ACB$	+1.8489 -2.8420	0.1110 0.1150	+0.1935 -0.2489	+7.1186 -2.3300
80%	$CC_{pl}ACB$	+2.1244 -4.0867	0.1069 0.1157	+0.1411 -0.2583	+5.4058 -3.3299
	$CC_{pr}ACB$	+3.0198 -3.7757	0.1039 0.1010	+0.1139 -0.0390	+4.5064 -3.6042
	$CL_{rt}ACB$	+1.8588 -4.8374	0.1033 0.1011	+0.0607 -0.0524	+6.3210 -3.8131

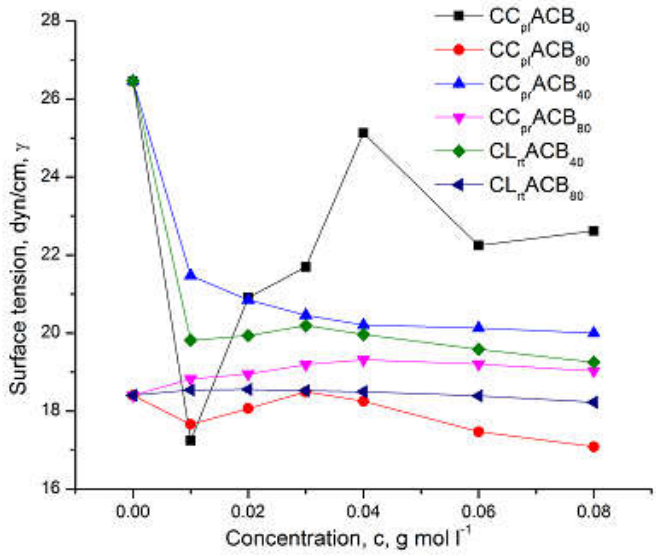

Figure 4: Plots of surface tension v/s concentration of Cu (II) surfactants complex in benzene + methanol at 311 K

It is observed that the extrapolated value of surface tension for zero complex concentration is in close agreement with actual surface tension of the solvent mixtures. It is significant to mention about the typical behaviour of the surface tension, which decreases with the increase in volume percent of methanol in the solvent mixture. The observed change in 40% methanol and in 80% methanol may be due to change in the nature of the solvent as the compositions of the mixed solvent vary.[24]

The plots of γ v/s log c, (Fig-5) are characterised by an intersection of two straight lines for all the compositions of the solvent mixtures. The linear variation, of γ against log c is in agreement with Szyszkowskis empirical equation for solution of fatty acids.[25]

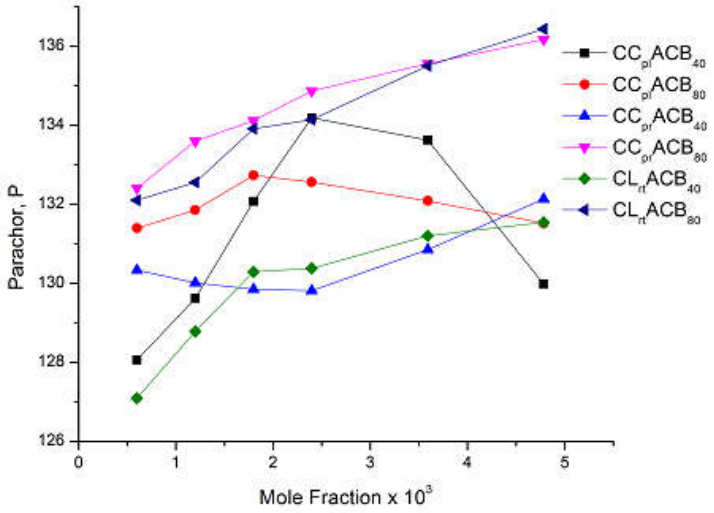

Figure 5: Plots of Parachor v/s mole fraction Cu (II) surfactants complex in benzene + methanol at 311 K

$$\frac{\gamma}{\gamma^0} = 1 - X ln \frac{c}{Y} \qquad (2)$$

Where γ and γ_0 are surface tension of the solution of concentration c (g mole l^{-1}) and of the pure solvent respectively and X and Y are constants.

The equation can be written as:

$$\gamma = \gamma^0 (1 + X \ln Y) - \gamma^0 X \ln c \qquad (3)$$

On differentiating equation (2) we get:

$$\frac{d\gamma}{d} lnc = -X\gamma_0 \qquad (4)$$

by substitution in Gibb's adsorption equation, the adsorption excess, Γ, (i.e. the excess concentration of the solute per unit area of surface)[26] is found to be

$$\tau = -1 /RT \frac{d\gamma}{d} lnc = -X\gamma_0 /\text{RT} \qquad (5)$$

Hence, the surface area, A, covered by the complex micelles formed by 1 g. mole of the complex

$$A = RT/ X\gamma_0 \qquad (6)$$

The values of X evaluated from the slops (-2.303γ_0X) and values of Y and (-XlnY) calculated from the intercept {γ_0 (1+XlnY)} of the plots of γ v/s log c are summarised in Table-3.A perusal of results shows that the parameter X, Y and XlnY are not independent of the composition of the solvent mixtures.[27]

Table 3: Extra plotted values of surface tension of Cu (II) surfactants- 2-amino-6-chloro benzothiazole complex, benzene + methanol at 311 K

% Volume of methanol	Solvent mixture	Name of Complex		
		$CC_{pl}ACB$	$CC_{pr}ACB$	$CL_{rt}ACB$
40%	26.4638	34.0146	28.3242	21.0422
80%	18.4039	21.0123	20.5421	19.5244

It is interesting to note that:

1. A perusal of the results reveals that the numerical value of X for all the complexes in 40% and 80% methanol-benzene mixture below CMC are higher than above CMC.
2. Two values of Y have been enumerated below and above CMC.
3. X ln Y, too have been stipulated from the referred equation and two such values corresponding to below and above CMC.

From the data it is concluded that micellar features of soap complex in 40% methanol is quite different than 80% methanol mixture. Furthermore, it is argued that the ordering of micelles structure is more pronounced at 80% methanol because methanol being polar solvent having resultant dipole moment, exhibit a less perturbing effect on the micelles due to its electric fields. A theoretical subscription to higher CMC value and delay in orderly orientation of the micelles at 40% methanol may be ascribed to the fact that in the predominance of non-polar solvent, complex-solvent interaction increases.[28]

The approximate values of the surface area occupied by the micelle formed by 1 g. mole of the complex in the mixed solvents. It is noteworthy to point out that the area covered by 1 g. mole of the $CC_{pl}ACB$ decreases gradually from 40% methanol to 80% methanol. Here it is pertinent to suggest that at 40% methanol, the disarray in the clustering of benzene molecules in the peripheral region of the micelles and their incorporation in the micelles lead to scattering of agglomerates. However, from this consideration it may be concluded that the nature and size of the micelles at 40% methanol and

80% methanol are quite different, the values of X, Y, (X ln Y) and A for $CC_{pl}ACB$ show a marked change in 40% methanol to 80% methanol concentration. Hence there is a justification in applying Szskowskis's equation to find out the nature of the micelles formed in such system.[29]

The value of CMC in the solution containing 80% methanol is lower as compared with the CMC values in solution containing higher volume percent of benzene. It is suggested that methanol and benzene takes place quite different position in the palisade layers and complex exhibits different degree of aggregation in the mixed solvent of varying composition.

3.1 Parachor

The parachor P, of solution is written as[30]

$P = M\gamma^{1/4}/D = V\gamma^{1/4}$ (7)

Where M, D, V and γ are the molecular weight, density, molar volume and surface tension of the solution respectively.

According to Hammic and Andrew's mixture law equation, the parachor of the solution may be written as[31]

$P = XPcomplex + (1 - X)Psolvent$ (8)

Where, P, $P_{complex}$ and $P_{solvent}$ refer to the parachor of the complex solution, complex and solvent respectively and X is the mole fraction of the complex in the solution.

Since $P_{complex}$ and $P_{solvent}$ are constants, as such the equation (8) can be written as:

$P = XPcomplex + (1 - X)Psolvent = XK_1 + K_2$ (9)

Where K_1 is equal to ($P_{complex}$ - $P_{solvent}$) and K_2 is equal to $P_{solvent}$ .Hence, from equation (8) and (9) we have:

$P = XK_1 + K_2 = V\gamma^{1/4}$ (10)

The equation shows that the plots of $V_0\gamma^{1/4}$ against X should be linear.

On differentiating equation (10) we get:

$dV_0\gamma^{1/4}/dx = K_1$ (11)

This shows that quantity $d(V_0\gamma^{1/4})/dx$ should be equals to i.e.($P_{complex}$- $P_{solvent}$).The values of K_1 have been calculated by using equation (11) for the solution of $CC_{pl}ACB$ complex in mixture of benzene and methanol and have been compared with the values obtained graphically be plotting $V_0\gamma^{1/4}$ against X. The results are summarised in Table-4-9.

Table 4: Parachor of $CC_{pl}ACB_{40}$ in benzene + methanol at 311 K

Concentration of soap complex (g. mole l^{-1})	X (10^3)	$P=(V\gamma^{1/4})$	$d(V\gamma^{1/4})$	dx ×10^3	K_1 Calculated	K_1 Graphical	K_2 Graphical
0.01	0.6003	128.0571	----	----	----		
0.02	1.2000	129.6243	+1.5672	0.5997	+2613.31		
0.03	1.7989	132.0726	+2.4483	0.5989	+4087.99	(+1150.4)	(129.57)
0.04	2.3971	134.1879	+2.1153	0.5982	+3536.11	(-0624.9)	(133.14)
0.06	3.5914	133.6236	-0.5643	1.1943	-0472.25		
0.08	4.7829	129.9851	-3.6385	1.1915	-3053.71		

Table 5: Parachor of $CC_{pl}ACB_{80}$ in benzene +methanol at 311 K

Concentration of soap complex (g mole l^{-1})	X (10^3)	P=($V\gamma^{1/4}$)	d($V\gamma^{1/4}$)	dx ×10^3	K_1 Calculated	K_1 Graphical	K_2 Graphical
0.01	0.6003	131.3960	----	----	----		
0.02	1.2000	131.8571	+0.4611	0.5997	+0768.88		
0.03	1.7989	132.7327	+0.8756	0.5989	+1462.01	(+1279.9)	(130.67)
0.04	2.3971	132.5609	-0.1718	0.5982	-0287.20	(-0600.9)	(133.89)
0.06	3.5914	132.0884	-0.4725	1.1943	-0395.60		
0.08	4.7829	131.5183	-0.5701	1.1915	-0478.47		

Table 6: Parachor of $CC_{pr}ACB_{40}$ in benzene +methanol at 311 K

Concentration of soap complex (g mole l^{-1})	X (10^3)	P=($V\gamma^{1/4}$)	d($V\gamma^{1/4}$)	dx ×10^3	K_1 Calculated	K_1 Graphical	K_2 Graphical
0.01	0.6003	130.3379	----	----	----		
0.02	1.2000	130.0129	-0.0325	0.5997	-0541.94		
0.03	1.7989	129.8483	-0.1646	0.5989	-0274.84	(-404.0)	(128.0)
0.04	2.3971	129.8122	-0.0361	0.5982	-0060.35	(+965.7)	(130.5)
0.06	3.5914	130.8514	+1.0392	1.1943	+0870.13		
0.08	4.7829	132.1363	+1.2849	1.1915	+1078.39		

Table 7: Parachor of $CC_{pr}ACB_{80}$ in benzene +methanol at 311 K

Concentration of soap complex (g mole l^{-1})	X (10^3)	P=($V\gamma^{1/4}$)	d($V\gamma^{1/4}$)	dx ×10^3	K_1 Calculated	K_1 Graphical	K_2 Graphical
0.01	0.6003	132.4070	----	----	----		
0.02	1.2000	133.5987	+1.1917	0.5997	+1987.16		
0.03	1.7989	134.1187	+0.0520	0.5989	+0868.26	(+965.7)	(131.6)
0.04	2.3971	134.8660	+0.7473	0.5982	+1249.25	(+383.9)	(134.4)
0.06	3.5914	135.5590	+0.0693	1.1943	+0580.26		
0.08	4.7829	136.1724	+0.6134	1.1915	+0514.81		

Table 8: Parachor of $CL_{rt}ACB_{40}$ in benzene +methanol at 311 K

Concentration of soap complex in (gmole l^{-1})	X (10^3)	P=($V\gamma^{1/4}$)	d($V\gamma^{1/4}$)	dx ×10^3	K_1 Calculated	K_1 Graphical	K_2 Graphical
0.01	0.6003	127.0910	----	----	----		
0.02	1.2000	128.7845	+1.0133	0.5997	+1689.72		
0.03	1.7989	130.2942	+1.5097	0.5989	+2520.79	(+1327.0)	(128.43)
0.04	2.3971	130.3811	+0.0869	0.5982	+0145.27	(+0240.5)	(129.86)
0.06	3.5914	131.2007	+0.8196	1.1943	+0686.26		
0.08	4.7829	131.5422	+0.3415	1.1915	+0286.61		

Table 9: Parachor of $CL_{rt}ACB_{80}$ in benzene +methanol at 311 K

Concentration of soap complex in (g mole l^{-1})	X (10^3)	$P=(V\gamma^{1/4})$	$d(V\gamma^{1/4})$	dx $\times10^3$	K_1 Calculated	K_1 Graphical	K_2 Graphical
0.01	0.6003	132.1023	----	----	----		
0.02	1.2000	132.5535	+0.4512	0.5997	+0752.38		
0.03	1.7989	133.9131	+1.3596	0.5989	+2270.16	(+781.3)	(131.0)
0.04	2.3971	134.1439	+0.2308	0.5982	+0385.82	(+404.0)	(134.29)
0.06	3.5914	135.5055	+1.3616	1.1943	+1140.08		
0.08	4.7829	136.4380	+0.9325	1.1915	+0782.63		

It is observed that the values of parachor of the complex solution of $CC_{pl}ACB$ increase with increase in the mole fraction and volume percent of methanol below CMC and decrease above CMC.[32]The parachor P, have been plotted against the mole fraction, X, of the complex to test the validity of the equation (10).It is observed that the plots of parachor against the mole fraction of the $CC_{pl}ACB$ complex are characterised by an intersection of two straight lines at a point that corresponds to the CMC of the complex. The values of CMC are in good agreement with those obtained from γ v/s c plots. A perusal of results shows that, there is a concordance in the extrapolated values of parachor to zero complex concentration (blow CMC) and the corresponding values for the specific solvent mixture (Fig-6). This however shows that there is not sufficient aggregation below CMC.[33,34,35,36,37,38] The plots of the parachor against the mole fraction of the complex show a change at a point corresponding to the CMC of the complex, which may be attributed to the fact that the complex exists in different forms below and above CMC (Table 10).

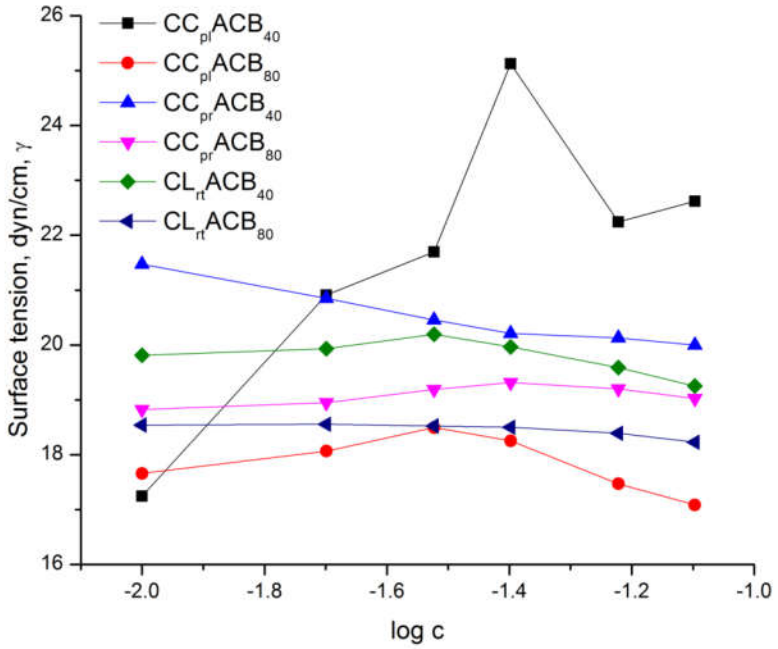

Figure 6: Plots of surface tension v/s log c of Cu (II) surfactants complex in benzene + methanol at 311 K

Table 10: Values of CMC for Cu (II) surfactants - 2-amino-6-chloro benzothiazole complex, benzene and methanol at 311 K

Parameter	CC_{pl}ACB		CC_{pr}ACB		CL_{rt}ACB	
	Volume % of methanol in the solvent mixture					
	40%	80%	40%	80%	40%	80%
Surface tension(dyne/cm)	0.0360	0.0344	0.0350	0.0322	0.0340	0.0311
Parachor	0.0378	0.0353	0.0344	0.0320	0.0311	0.0302

The parachor behaviour may be represented by two linear equations having different values of the constant, K_1 and K_2 below and above CMC respectively.[39,40,41,42]The suggested structure of micelle at CMC shown in Fig. 7

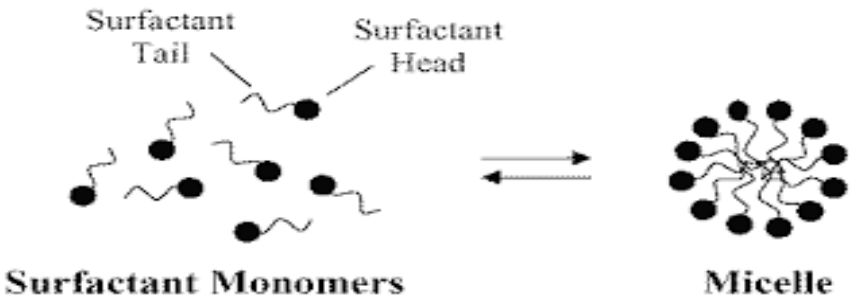

Figure 7: Formation of micelle from surfactants monomers at CMC (Structure of micelle)

It is observed that the calculated values of K_1 using equation (10) are in complete agreement with the values obtained graphically.[43]The values of K_2i.e.the parachor of the solvent obtained graphically are in close agreement with the corresponding experimental values of the parachor of the solvent mixtures of benzene and methanol. Hence there is a justification in applying Hammic and Andrews's equation to the solution of CC_{pl}ACB complex in mixtures of benzene and methanol. The values of CMC are higher for the predominance of non-polar solvent (benzene) as compared to the predominance ofpolar solvent (methanol).[44,45] With regard to chain length of the soap segment of the complex molecule, CMC follow the order: $C_6>C_8>C_{10}$.

4. Conclusion

The present study also gives an account of our understanding of several aspects of micelle formation of copper soap-complexes in the mixed non-aqueous solvents. Attempts have also been made to study the physico-chemical properties of Cu (II) soap-complexes in methanol + benzene solvent mixtures. Surface tension studies of copper (II) soap complex solutions confirm that cmc values depend upon the composition of the solvent mixture and are found to decrease with increase of chain length of the soap segment of the complex. From Szyschkowski's empirical equation it is observed that the values X, Y and (-X ln Y) lead to the conformation of the fact that the change in the behaviour of the complex in 40% methanol is quite different than 80% methanol concentration. It is apparent from the studies that the process of agglomeration of the complex molecules into micelles in 40% methanol is quite different than 80% methanol. The results show that there is justification in applying Hammic and Andrew's equation to this complex solution.

The copper soap complexes referred in this study form micellar aggregates and the CMC determined is found dependent of the nature and composition of solvent but as well as chain length of anion. The longer hydrophobic group of soap ion is geometrically favorable for the micelle formation. Szyszkowski's empirical equation is able to explain the behavior of copper soap complexes in

benzene-methanol solvent mixtures. All data are showing that these surfactants definitely play the role of surface activity and are useful colloids which will be importance in industry private sectors and research laboratories.

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