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Physical Properties of Copper(II) Soap Complexes in Binary Solvent Mixture

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Copper(II) soap complexes were synthesized with the N-donar ligands *viz.*, benzothiazole and phenyl thiourea derived from *p*-methoxy aniline. These complexes were characterized by elemental analysis, molecular weight, melting point, IR, NMR and ESR spectral studies. In the present study, the solute-solvent interaction was investigated by density, molar volume and apparent molar volume measurements of different copper soap complexes in benzene-methanol mixtures. The critical micelle concentration were found to decrease with increase in average molecular weight of the soap complex. The apparent molar volume was examined in terms of masson equation. The limiting apparent molar volume (ϕ_v) was interpreted in terms of solute-solvent interaction while limiting slope (Sv) in terms of solute-solute interaction. The studies of various interactions suggest that solute-solvent interaction increases with the increase in carbon composition of fatty acid and lowering of molecular weight where as solute-solute interaction decreases.

Key Words: Copper(II) soap, Phenylthiourea, Benzothiazole, Density, Molar volume, Apparent molar volume.

INTRODUCTION

The copper(II) soaps in polar and non-polar solvents having remarkable interest and find their uses in various fields of applications like foaming, wetting emulsification and lubrication *etc.* due to the surface active properties of soaps[1,2]. Aniline and its derivatrives are used as intermediate for the manufacturing of various organic compound such as colarants, agrochemicals, pharmaceuticals, *etc*[3]. It has been found to be widely distributed in an aqueous environment and cause tetratosis in aquatic species[4].

Colloidal behaviour of copper(II) soap complexes play a significant role in their selection in various fields like preservatives, herbicidal, pesticidal activities, detergency, paints, lubrication *etc.*[5,6]. In biological systems, these agents are vital components and useful in many industrial process like stabilizers, printing, fabrics, photo sensitizers and indicator[7-9]. All these properties led us to study micellar features of various copper soap complexes for their possible uses and applications in agriculture and industries.

The density of soap solution has been investigated with a view to understand the nature, critical micelle concentration and micellar characteristics of the complexes.

EXPERIMENTAL

All chemicals used were of LR/AR grade.

Preparation of phenylthourea from 2-methoxy aniline[10-12]: 2-Methoxy aniline was firstly converted into phenyl thiourea by treating with NH_4SCN with mixture of HCl and water till the aniline hydrochloride is formed. This solution is now allowed to cool at room temperature and refluxed for 4 h on water bath. After cooling, solid is filtered, washed with cold water, dried and then recrystallized with ethanol.

Preparation of benzothiazole from 2-methoxy aniline[12,13]: It is synthesized by thiocynogenation of 2-methoxy aniline in the presence of thiocynogen gas, which is generated *in situ* by the reaction of cupric chloride and NH_4SCN. Mixture is refluxed for 1 h. After cooling Na_2CO_3 is mixed to neutralize the mixture.

Synthesis of soap and complexes[10,11,13]: Copper surfactants are prepared by direct metathesis of the corresponding potassium soap with slight excess of required amount of $CuSO_4$ at 65-70 ºC. After washing with hot water and alcohol the sample was dried and recrystallized with hot benzene.

The complexes are prepared by mixing the metal surfactants and ligands in the molar ratio 1:2, dissolving in ethanol and mixture is refluxed for *ca*. 1-2 h. The formation of complex was confirmed by using IR, NMR techniques and elemental analysis. The purity of the complex was confirmed by TLC[14]. The physical data of the synthesized complexes is given inTable-1.

TABLE-1
PHYSICAL DATA FOR COPPER(II)-SOAP COMPLEXES

Name of complex	Colour	m.p. (ºC)	Yield (%)	Average m.w.
$Cu[PTU]_A$	Grayish black	270	90	1624.92 (Dimer)
$Cu[BTA]_A$	Black	285	92	1622.92 (Dimer)

Purification of benzene-methanol was done by keeping over sodium wire for a couple of days and then distilled. The distillate was refluxed over sodium metal and again distilled. The fraction of 80 ºC was collected at 80 ºC. The calculated amount of the soap complex was weighted in a volumetric flask and solution made up to the mark by adding the required amount of benzene-methanol. Ostwald modification of the springel pyknometer with a volume of about 10 mL which allowed an accuracy of about one unit in the fourth place of decimal was used for measuring the density of the soap solution in a thermostated water bath at 301 K (± 0.1).

RESULTS AND DISCUSSION

The density of benzothiozole and phenylthiourea of copper stearate solution increases with increase in concentration then there is a decrease followed by linear increase. The plot of density *vs.* concentration assumes convex shape below CMC, thereafter remains linear (Fig. 1, Table-2). The plot of density *vs.* concentration is characterized by an intersection of a convex curve and a straight line at a definite soap complex concentration which corresponds to the CMC of the complex. This indicate that aggregation of molecules achieves critical array at this point. It is therefore concluded that the complex molecules do not aggregate adequately below CMC; whereas this definite soap concentration there is marked enhancement in the degree of aggregation of the soap molecules in benzene-methanol binary solvent. The density of soap complex follows the order $Cu[PTU]_A > Cu[BTA]_A$.

TABLE-2
PHYSICAL DATA OF $Cu(BTA)_A$ AND $Cu(PTU)_A$ COMPLEX IN METHANOL + BENZENE SOLUTION

Conc. (mol L^{-1})	Density		Molar volume		Apparent molar volume	
	$Cu(BTA)_A$	$Cu(PTU)_A$	$Cu(BTA)_A$	$Cu(PTU)_A$	$Cu(BTA)_A$	$Cu(PTU)_A$
0.0000	0.8506	0.8506	72.6747	72.6747	–	–
0.0002	0.8508	0.8510	72.6830	72.6656	-435	-1610
0.0004	0.8511	0.8516	72.6827	72.6393	-728	-2198
0.0006	0.8515	–	72.6739	–	-1022	–
0.0008	0.8516	0.8518	72.6911	72.6722	-728	-1022
0.0010	0.8512	–	72.7506	–	36	–
0.0012	0.8508	0.8519	72.8101	72.7136	545	-533
0.0014	0.8510	–	72.8184	–	405	–
0.0016	0.8512	0.8509	72.8266	72.8491	300	521
0.0017	–	0.8511	–	72.8445	–	395
0.0018	0.8516	0.8514	72.8177	72.8313	88	219
0.0019	–	0.8517	–	72.8181	–	60
0.0020	0.8518	0.8520	72.8260	72.8049	36	-82

The study of solute solvent interaction in binary solvent mixture is more complex than in pure solvents. In a pure solvent the composition of the microsphere of solvation of a solute, the so called cybolactic region is the same as the bulk solvent but in binary mixture (benzene + methanol) the composition in this microsphere can be different. The solute can interact to different degree with the components of the mixture. The effect of varying the composition of the mixture from the bulk solvent to the solvation sphere is called preferential solvation.

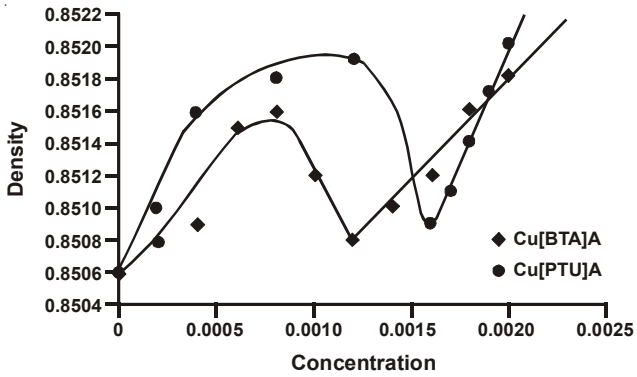

Fig. 1

The molar volume of the soap complex solution $\overline{V}$ has been calculated by the relationship

$$\overline{V} = \frac{x_1 m_1 + x_2 m_2 + x_3 m_3}{d}$$

where x_1 is the mole fraction of the complex of molecular weight m_1, where as x_2 and x_3 are the mole fraction of benzene and methanol of molecular weight m_2 and m_3 and 'd' stands for density of the solution.

The AMV has been calculated with the error limit of ± 0.02 % from the density using equation[15]

$$\phi_v = \frac{M}{d_o} + \frac{1000(d_o - d)}{Cd_o}$$

where d_o, d, M and C are density of solvent and solution, molecular weight of the complex and concentration of soution in g/mol, respectively.

The molar volume was calculated from density data and the comparison of results indicate that the value of $\overline{V}$ follows the order $Cu[PTU]_A < Cu[BTA]_A$. The plot of $\overline{V}$ *vs.* concentration show a change at CMC (Fig. 2). Below CMC the curve is concave, where as a linear trend is obtained after CMC. This suggests that the environment such as micellar clusterring, solvation of soap molecules, diminution mobility is entirely different below and above CMC.

The CMC of complex obtained from molar volume *vs.* concentraion plots follow again the same order which is found by density *vs.* concentration plot. This observation is in agreement with the fact that there is decrease in CMC value with the increase of the molecular weight of the soap[16-18].

The AMV of copper soap complex of stearic acid is calculated using eqn. 2. The plots of ϕ *vs.* $\sqrt{c}$ are characterized by an intersection of two straight lines corresponding the CMC of soap (Fig. 3). The value of ϕ_v show a sharp increase below CMC.

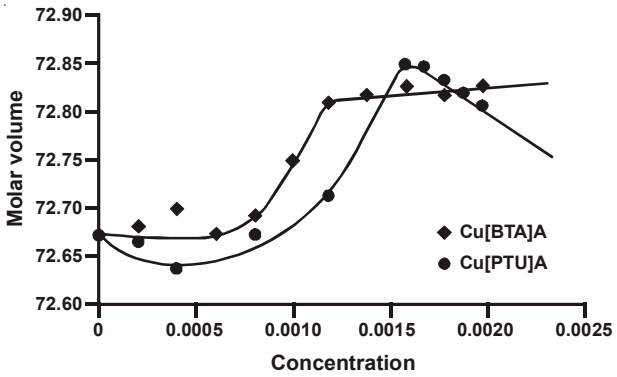

Fig. 2

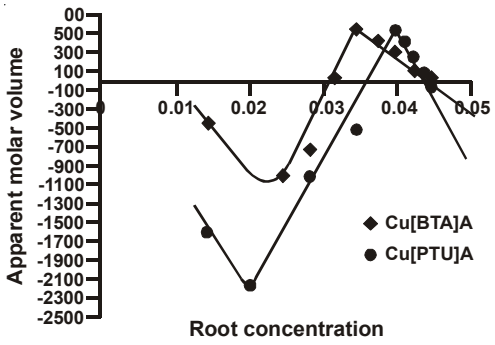

Fig. 3

The CMC obtained from plots of ϕ_v *vs.* $\sqrt{c}$ also follows the same order as for density and molar volume. CMCs obtained in this study is also confirmed by other physical properties studies like surface tension, parachor and viscosity[19,20]. The data has been analyzed in terms of masson equation[21]

$$\phi_v = \phi_v^o + S_v \sqrt{c}$$

This equation fits well both below and above CMC. The value of limiting apparent molar volume (ϕ_v^o) for these complex solution is obtained from extraplotation of ϕ_v *vs.* $\sqrt{c}$ plots to $c \rightarrow o$ and there are two values ϕ_v^o referred to as ϕ_{v1}^o (below CMC) and ϕ_{v2}^o (above CMC) as the masson equation is equally applicable to the two intersecting straight lines (Table-3).

TABLE-3
COMPUTED PARAMETERS OF MASON EQUATION FOR COPPER SOAP COMPLEXES DERIVED FROM STEARIC ACID AT 301 K

Complex	ϕ_{v1}^o	ϕ_{v2}^o	Sv_1	Sv_2
$Cu[PTU]_A$	–	2360	–	-2.9042
$Cu[BTA]_A$	–	5010	–	-1.0724

ϕ_v^o has been regarded as a measure of solute-solvent interaction[22]. Therefore, it is reasonable to assume that greater magnitude of ϕ_v^o may be regarded quantitatively as a measure of greater soap complex solvent interaction. It is thus obvious from ϕ_{v1}^o data that soap complex solvent interaction is more pronounced befor CMC.

In Fig. 3 both complexes formed one curved and one straight line, due to the formation of curved graph masson equation is not applicable. The parameter Sv in massons equation represents the limiting apparent slope and indicates the existence of solute solvent interaction.

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