Studies of solute-solvent interactions and miceller behaviour of complexes of copper (II) palmitate with substituted phenylthiourea and 2-amino benzothiazole in methanol-benzene mixture

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Abstract

In this work, synthesis of copper (II) surfactants followed by the complexation of each other with the molar ratio of 1:2 dissolving in ethanol have been reported. The purity of the resulting complexes of the general formula- $CP(PTU)_T$, $CP(BTA)_T$ was checked by thin layer chromatography and characterized on the basis of elemental analysis. Their spectral studies are also included and data suggest that Cu (II) phenylthiourea mixed system binds through the donor ability of nitrogen to transition metal. The magnetic moment studies suggest the dimeric nature of the complexes. IR, NMR, ESR spectral details confirm that complexation has taken place successfully and dada suggest that the complexes possess elongated octahedral geometry. Density, Molar Volume, Apparent Molar Volume of these complexes was investigated in non-aqueous solvent at various concentrations by Springel Pyknometer to understand the nature, critical micelle concentration and micelle characteristics of the complexes. Overall, the CMC values were found to be decreased with increasing average molecular weight of soap complex. The solute - solute interactions were found to be greater before CMC whereas solute-solvent interactions were found greater after CMC.

Keywords: *Phenylthiourea ; Copper (II) Palmitate, Density ; Molar Volume ; Critical Micelle Concentration (CMC).*

1. Introduction

In the present research era, co-ordination chemistry is playing an important role. It has been the most active field of current scientific development and research. This definitely shows that due to its interrelated concern it has received considerable attention. Chemistry of transition metal complexes with nitrogen and sulphur donor ligands (special emphasis on copper complexes) is of much more importance largely due to their catalytic and bioorganic application. This combination of catalytic and bioorganic application is found to be highly eco-friendly and biodegradable in nature. Therefore, in order to examine briefly about the applicability of abovementioned complexes we can précis the following details. These complexes have been used extensively as preservatives, herbicides, insecticides, pesticides, detergents, paints, lubrication etc. They are of much importance due to their antimicrobial [1], antitumor [2-4], anticancer [5]**,** antibacterial [6,7], antifungal [8,9], antihelmintic, antiviral [10], anti-inflammatory, antihistamine, neuroleptic, sedative and biocidal properties [11-16]. As far as biological systems are concern, these are essential components and useful in many industrial processes like photosensitizers, fabrics, painting, stabilizers, indicators. These heterocyclic compounds have unique extraordinary performance in polar and non-polar solvents due to change in surface active properties [17,18], due to which they are used extensively in dispersing agents, foaming, wetting, emulsification and lubrications [19-22] .

Due to all above application we are able to synthesize complexes based upon their extensive applicable performance. All complexes were categorized by elemental analysis, melting points, IR, NMR, ESR spectral studies. In this study benzene-methanol has been selected as co-solvents because mixed solvents show affinity to interact with complex molecules and result in affecting the aggregation of complex molecule. Investigation of density of complexes has been done deeply in order to understand the nature of critical micelle concentration and micelle characterization. The accurate measurements of density are very important in estimation of apparent molar volume. Apparent molar volume of a solute reflects the cumulative effect of solute–solvent and solute–solute interactions and also provides important information for understanding the various interactions before and after CMC.

2. Materials and methods

All chemicals were used were LR/AR grade

*2.1. **Synthesis of substituted 2-amino benzothiazole***

Substituted 2-amino benzothiazoles were synthesized using thiocyanogenation method. In this method (0.1 mol) p-Methyl aniline was treated with a mixture of 7.6 gm ammonium thiocyanate and 80 ml glacial acetic acid in a 250 ml three necked round bottom flask, with stirrer, dropping funnel and reflux condenser at room temperature for one and half hour. The thiocyanogenation of aryl amine takes place in the presence of thiocynogen gas, which is generated insitu by the reaction of cupric chloride and ammonium thiocynate. After cooling the reaction mixture, add 100 ml concentrated HCl and heat again for half an hour, then cool it and then saturated solution of sodium carbonate (Na_2CO_3) is added to neutralize it, till the solid was formed. The solid separated out was filtered and washed with cold water, dried and recrystallised with ethanol [33].

2.2. Synthesis of Substituted Phenylthiourea

0.1 mole of p-Methyl aniline was heated in 250 ml three necked flask with stirrer and reflux condenser with a mixture of 9ml HCl and 25 ml H_2O on water bath till aniline hydrochloride is formed. On cooling add NH_4SCN to it. Then the reaction mixture was refluxed for four hours, on water bath. After cooling the solid separate out was filtered, washed with cold water, dried and then recrystallised with ethanol [34].

3.3 Synthesis of copper surfactants

Copper palmitate was prepare by mixing one gm of palmitic acid into 25 ml ethyl alcohol, shake the mixture in hot water bath and then add one drop of phenolphthalein. A saturated solution of KOH in another beaker was prepared then it was added into palmitic acid solution drop by drop until the light pink color appears. Now again in another beaker prepare a saturated solution of $CuSO_4$ (about 2-3 g in 5 ml H_2O) and mix it into above solution with stirring till the blue colored soap is formed. Filtered and washed with warm water and 10% ethyl alcohol then dried and recrystallised with hot benzene [35].

3.4 Copper surfactants with substituted N-donor ligands

The purified copper stearate derived from stearic acid was refluxed with the ligands, substituted Benzothiazole and substituted phenylthiourea in 1:2 ratio using ethyl alcohol as a solvent for one and half hour, it was than filtered hot, dried, recrystallised and purified in hot benzene. In general all the complexes are solid, powdered in nature. They are insoluble in water but soluble in organic solvent. 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 calculated amount of the soap, ligands and complexes was weighted in a volumetric flask and solution made up to 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, ligands and complex solution in a thermostat water bath at 301 K (± 0.1) [36].

3. Results and Discussions

The density of benzothiazole and phenylthiourea of copper palmitate solutions initial stage was found to be increase slightly with the increase in complex concentration and then it starts decrease after a particular concentration corresponding to critical micellar concentration (CMC) [23] and after this concentration the density again increases with increase in concentration of complexes solution. The plot between density ‘d’ against complex concentration of ‘C’ (g.mol.l^{-1}) is showing an intersection of convex curve with respect to X-axis and straight line Fig. 1 and 2; at a definite complex concentration which corresponds to the CMC of the complex. It can be observed from the plot that after CMC the density values sharply increase with a definite straight line. It has been observed that CMC decreases by about one third per methyl group in aqueous solution because the energy required to transfer a methylene group form micelle to bulk is small as intermolecular forces are stronger in polar solvent (like methanol and water), whereas these intermolecular forces are weaker in nonpolar solvent(like benzene), the value of CMC order as follows.
CP(PTU)$_T$ > CP(BTA)$_C$

The above order shows that the CMC values are of CP(PTU)$_T$ higher as compared to CP(BTA)$_T$, because the average molecular weight of CP(PTU)$_T$ is lower as compared to CP(BTA)$_T$, so the interaction is lower and the formation of micelle is slower due to this the CMC obtain later. Larger molecule has the tendency to form micelle earlier and has lower value of CMC. Secondly the presence of methyl group at para position produces +I effect, hence the formation of micelle takes place slowly as compare to CP(BTA)$_T$ This difference clearly demonstrates that agglomeration of complex molecules initiates earlier in the predominance of non-polar solvent (benzene) as compared to polar solvent (methanol). According to the average molecular weight of the complex the CMC value follows the order.
CP (PTU)$_T$ > CP(BTA)$_T$

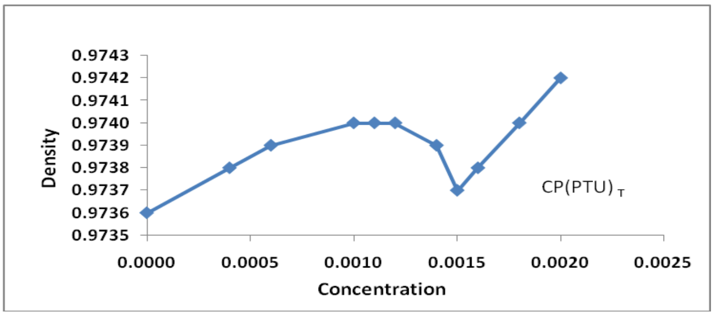

Figure 1: Density of complex of copper (II) palmitate with substituted phenylthiourea in 40% methanol-benzenne mixture.

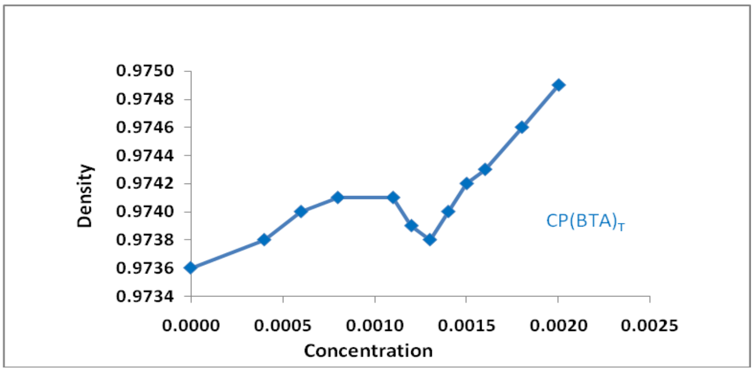

Figure 2: Density of complex of copper (II) palmitate with 2-amino benzothiazole in 40% methanol-benzene mixture.

The molar volume of the soap complex solution 'V' has been calculated by the relationship.

$$\overline{V} = \frac{X_1 M_1 + X_2 M_2 + X_3 M_3}{\rho}$$

Where X_1 is the mole fraction of the complex of molecular weight M_1, whereas X_2 and X_3 are the mole fraction of benzene and methanol of molecular weight M_2 and M_3 and 'ρ' stands for density of the solution.

The apparent molar volume has been calculated with the error limit of + 0.02% from the density using the following equation: [24]

$$\Phi = \frac{M + 1000(\rho_0 - \rho)}{\rho_0 \rho C}$$

Where ρ_0, ρ, M and C is density of solvent and solution, molecular weight of the complex and concentration of solution in (g.mol.l^{-1}) respectively. The apparent molar volume was calculated from density data and regarded quantitatively as a measure of soap complex solvent interaction or solute-solvent interactions.
CP $(PTU)_T$ > CP$(BTA)_T$

The plot of molar volume against concentration shows a change at CMC Fig. 3 and 4. It is clear from the graph, below CMC the curve is concave, whereas it is following a linear trend after CMC. Therefore, it suggests that the environment such as micellar clustering, mobility is entirely different below and above CMC. It has been observed that CMC of complex obtained from molar volume verses concentration plots follow again the same order which is found by density verses concentration plots.

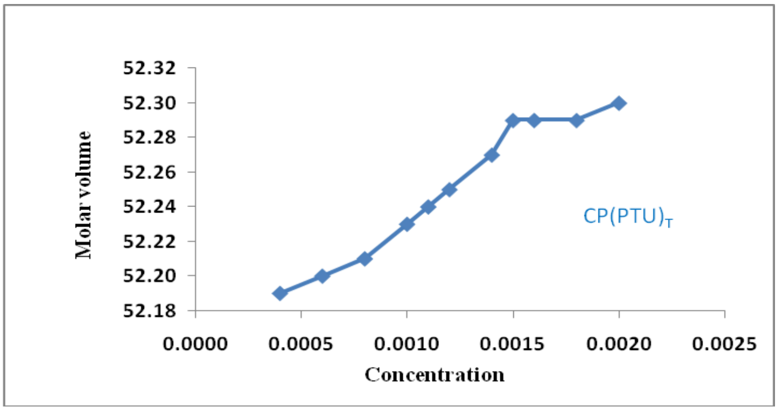

Figure 3: Molar volume of complex of copper (II) palmitate with substituted phenylthiourea in 40% methanol-benzene mixture.

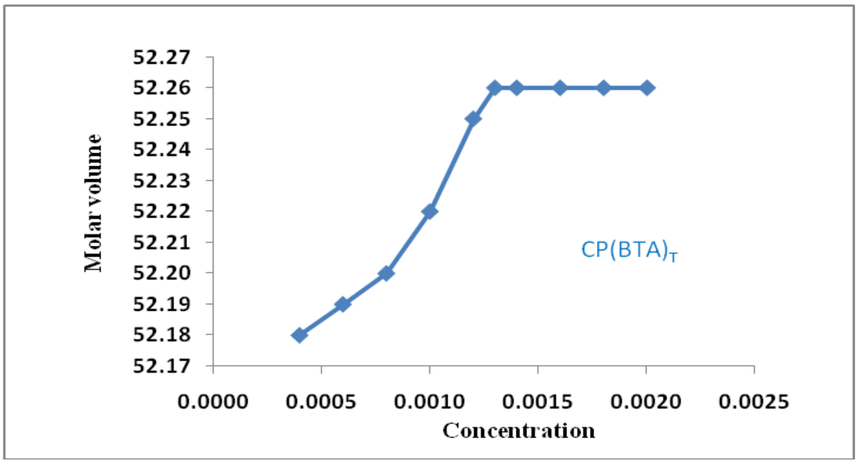

Figure 4: Molar volume of complex of copper (II) palmitate with 2-amino benzothiazole in 40% methanol-benzene mixture.

This observation is in concurrence with the statement that there is decrease in CMC value with the increase of the molecular weight of the soap [25-38].

Equation (3) has been used for the calculation of apparent molar volume of copper soap complex of palmitic acid. CMC of the complex is characterized by an intersection of two straight lines at a point in the plots of Φ_v verses $\sqrt{C}$, Fig. 5 and 6. As shown in the plots the value of Φ_v shows a sharp increase below CMC. The CMC obtained from plots of Φv verses √C also follows the same order as for density and molar volume. In this study, CMC so obtained, is also confirmed by other physical properties studies like surface tension, parachore and viscosity [29-30]. The data has been analyzed in terms of Masson equation. [31]

$$\Phi_V = \Phi^0_V + \delta_V \sqrt{C}$$

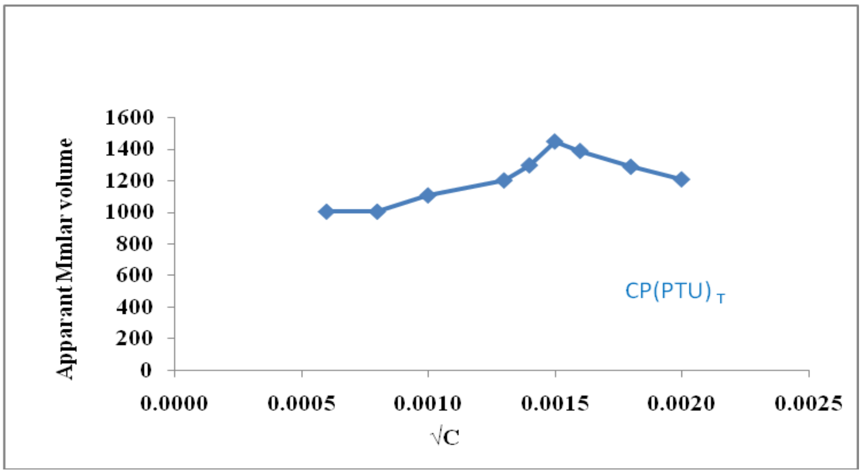

Figure 5: Apparent molar volume of complex of copper (II) palmitate with substituted phenylthiourea in 40% methanol-benzene mixture

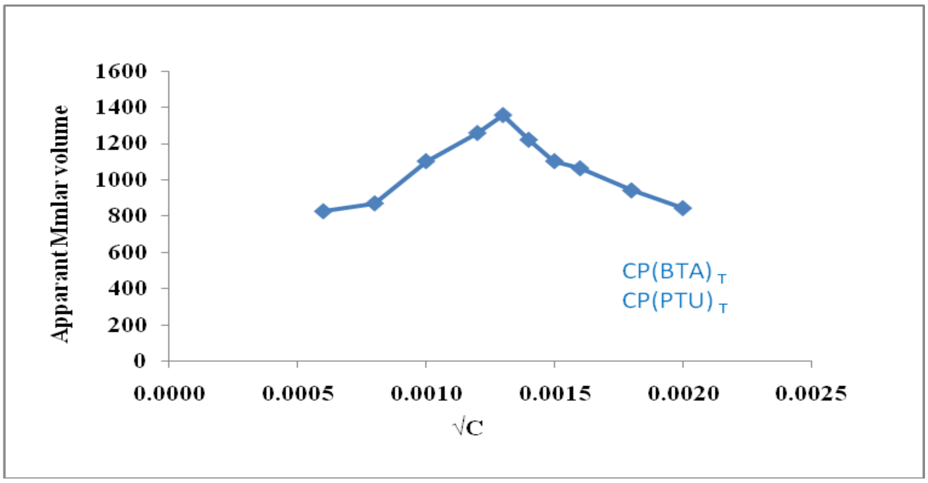

Figure 6: Apparent molar volume of complex of copper (II) palmitate with 2-amino benzothiazole in 40% methanol-benzene.

It has been observed that the above equation fits well both below and above CMC. The value of limiting apparent molar volume (Φ_V) for these complexes is obtained by the extrapolation of Φ_V verses √C plots to C→0. The two value of Φ_V have been obtained, first as a Φ_{V1} (below CMC) and second as a Φ_{V2} (above CMC). It has been shown by several researchers that Φ_V is a measure of solute solvent interaction [32], therefore, it is logical to assume that greater magnitude of Φ_V shall quantitatively be referred to as greater solute-solvent interaction are more pronounced after CMC as compared to before CMC. In table shown the computed parameters of Masson's equation for complexes of Copper (II) palmitate with substituted phenylthiourea in methanol-benzene mixture.

Name of Complex	**Volume of Methanol (20 %)**			
	$\Phi^0 v_1$	**$\Phi^0 v_2$**	**δv_1**	**δv_2**
CP(PTU)$_T$	-500	1860	58333	30000
CP(BTA)$_T$	-220	3300	65000	64000

The solute-solvent interaction follows the order for both of the complexes.

$\Phi v_2 > \Phi_{V1}$

From the above discussion it has been observed that the solvent-solute interactions are higher in the dominance of polar solvent than in the solvent mixture. The parameter δv in Masson's equation represents the limiting apparent slope and is indicative of existence of solute-solute interaction. It is again reasonable to determine two value of parameter δv one below CMC and another above CMC designated as δv_1 and δv_2 respectively. The data reveal that $\delta v_1 > \delta v_2$ for both CP(PTU)$_T$ and CP(BTA)$_T$ complexes. Thus, it is obvious that solute-solute interactions are more pronounced below CMC in both of the complexes.

In this study, it has been observed that the density parameters are important to understand the colloidal behaviour, CMC characteristics and nature of the complexes. These studies are indirectly helpful in identifying the structural insight, physical and biochemical properties of above class heterocyclic complexes. The above studies will definitely help future researchers to apply these novel binuclear complexes in multiple interlinked fields based on their widest applicability. Overall, the present course of study helps us to understand the characteristic nature and application of biological active metal complexes of nitrogen and sulphur donor ligands with copper soap. Above study definitely generates a new hope in biological, pharmacological and therapeutic testing.

4. Conclusion

In this study, it has been observed that the density parameters are important to understand the colloidal behaviour, CMC characteristics and nature of the complexes. These studies are indirectly helpful in identifying the structural insight, physical and biochemical properties of above class heterocyclic complexes. The above studies will definitely help future researchers to apply these novel binuclear complexes in multiple interlinked fields based on their widest applicability. Overall, the present course of study helps us to understand the characteristic nature and application of biological active metal complexes of nitrogen and sulphur donor ligands with copper soap. Above study definitely generates a new hope in biological, pharmacological and therapeutic testing.

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