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 ($\bar{V}_m$) was interpreted in terms of solute-solvent interaction while limiting slope ($S_v$) 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 whereas 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. Aniline and its derivatrives are used as intermediate for the manufacturing of various organic compound such as colorants, agrochemicals, pharmaceuticals, etc. It has been found to be widely distributed in an aqueous environment and cause tetratosis in aquatic species.

Colloidal behaviour of copper(II) soap complexes play a significant role in their selection in various fields like preservatives, herbicidal, pesticidal activities, detergent, paints, lubrication etc. In biological systems, these agents are vital components and useful in many industrial process like stabilizers, printing, fabrics, photo sensitizers and indicator. 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 phenylthiourea from 2-methoxy aniline**\(^{10-12}\): 2-Methoxy aniline was firstly converted into phenyl thiourea by treating with \(\text{NH}_4\text{SCN}\) with mixture of \(\text{HCl}\) 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 thio-cynogenation of 2-methoxy aniline in the presence of thiocynogen gas, which is generated \textit{in situ} by the reaction of cupric chloride and \(\text{NH}_4\text{SCN}\). Mixture is refluxed for 1 h. After cooling \(\text{Na}_2\text{CO}_3\) 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 \(\text{CuSO}_4\) at 65-70 °C. 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 in Table-1.

<table>
<thead>
<tr>
<th>Name of complex</th>
<th>Colour</th>
<th>m.p. (°C)</th>
<th>Yield (%)</th>
<th>Average m.w.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu[PTU](_A)</td>
<td>Grayish black</td>
<td>270</td>
<td>90</td>
<td>1624.92 (Dimer)</td>
</tr>
<tr>
<td>Cu[BTA](_A)</td>
<td>Black</td>
<td>285</td>
<td>92</td>
<td>1622.92 (Dimer)</td>
</tr>
</tbody>
</table>

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 °C was collected at 80 °C. 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>
<thead>
<tr>
<th>Conc. (mol L⁻¹)</th>
<th>Density</th>
<th>Molar volume</th>
<th>Apparent molar volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu(BTA)ₐ</td>
<td>Cu(PTU)ₐ</td>
<td>Cu(BTA)ₐ</td>
</tr>
<tr>
<td>0.0000</td>
<td>0.8506</td>
<td>0.8506</td>
<td>72.6747</td>
</tr>
<tr>
<td>0.0002</td>
<td>0.8508</td>
<td>0.8510</td>
<td>72.6830</td>
</tr>
<tr>
<td>0.0004</td>
<td>0.8511</td>
<td>0.8516</td>
<td>72.6827</td>
</tr>
<tr>
<td>0.0006</td>
<td>0.8515</td>
<td>–</td>
<td>72.6739</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.8516</td>
<td>0.8518</td>
<td>72.6911</td>
</tr>
<tr>
<td>0.0010</td>
<td>0.8512</td>
<td>–</td>
<td>72.7506</td>
</tr>
<tr>
<td>0.0012</td>
<td>0.8508</td>
<td>0.8519</td>
<td>72.8101</td>
</tr>
<tr>
<td>0.0014</td>
<td>0.8510</td>
<td>–</td>
<td>72.8184</td>
</tr>
<tr>
<td>0.0016</td>
<td>0.8512</td>
<td>0.8509</td>
<td>72.8266</td>
</tr>
<tr>
<td>0.0017</td>
<td>–</td>
<td>0.8511</td>
<td>–</td>
</tr>
<tr>
<td>0.0018</td>
<td>0.8516</td>
<td>0.8514</td>
<td>72.8177</td>
</tr>
<tr>
<td>0.0019</td>
<td>–</td>
<td>0.8517</td>
<td>–</td>
</tr>
<tr>
<td>0.0020</td>
<td>0.8518</td>
<td>0.8520</td>
<td>72.8260</td>
</tr>
</tbody>
</table>

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

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

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 $\pm$ 0.02 % from the density using equation

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

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

The molar volume was calculated from density data and the comparison of results indicate that the value of $V$ follows the order Cu[PTU]A < Cu[BTA]A.

The plot of $V$ 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 clustering, solvation of soap molecules, diminution mobility is entirely different below and above CMC.

The CMC of complex obtained from molar volume vs. concentration 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 soap15-18.

The AMV of copper soap complex of stearic acid is calculated using eqn. 2. The plots of $\phi$ vs. $\sqrt{c}$ are characterized by an intersection of two straight lines corresponding the CMC of soap (Fig. 3). The value of $\phi_v$ show a sharp increase below CMC.
The CMC obtained from plots of $\phi_v$ 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\textsuperscript{19,20}. The data has been analyzed in terms of masson equation\textsuperscript{21}

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

This equation fits well both below and above CMC. The value of limiting apparent molar volume ($\phi_v^o$) for these complex solution is obtained from extrapolation of $\phi_v$ vs. $\sqrt{c}$ plots to $c \rightarrow 0$ and there are two values $\phi_v^o$ referred to as $\phi_v^o$ (below CMC) and $\phi_v^o$ (above CMC) as the masson equation is equally applicable to the two intersecting straight lines (Table-3).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\phi_v^o$</th>
<th>$\phi_v^o$</th>
<th>$S\sqrt{c}$</th>
<th>$S\sqrt{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu[PTU]$_A$</td>
<td>–</td>
<td>2360</td>
<td>–</td>
<td>-2.9042</td>
</tr>
<tr>
<td>Cu[BTA]$_A$</td>
<td>–</td>
<td>5010</td>
<td>–</td>
<td>-1.0724</td>
</tr>
</tbody>
</table>

Table-3

COMPUTED PARAMETERS OF MASON EQUATION FOR COPPER SOAP COMPLEXES DERIVED FROM STEARIC ACID AT 301 K
φ_v has been regarded as a measure of solute-solvent interaction\textsuperscript{22}. Therefore, it is reasonable to assume that greater magnitude of φ_v may be regarded quantitatively as a measure of greater soap complex solvent interaction. It is thus obvious from φ_v data that soap complex solvent interaction is more pronounced before 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 masson’s equation represents the limiting apparent slope and indicates the existence of solute solvent interaction.

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