Magnetic Studies with Copper (II) Soaps in Non-aqueous Solutions

K. N. MEHROTRA, V. P. MEHTA and T. N. NAGAR

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The dispersion states of copper (II) soaps in non-aqueous solutions have been investigated by the determinations of the magnetic susceptibilities and magnetic moments of copper ions in copper soaps in non-aqueous solvents. The binuclear structure of copper soaps persists in hydrocarbons and in alcohols. The values of magnetic moments of copper ions in copper soaps are higher in hydrocarbons as compared with those in alcohols. The magnetic moments of copper ions in alcohols are independent of the chain length of the soap and of the soap concentration.

LIFSCHITZ and ROSENBOHM 1 pointed out that the molar susceptibility of cupric acetate monohydrate was anomalously low as compared to that for inorganic copper salts. The temperature variation of the susceptibility of hydrated copper acetate was studied by GUHA 2, FOEX and coworkers 3 and by FIGGIS and MARTIN 4. It was pointed out by HERRON and PINK 5 that the CURIE and WIESS law was not obeyed by copper soaps. An ionic pair hypothesis was proposed by BLEANEY and BOWERS 6 to account for these magnetic anomalies. A covalent chelate structure for copper laurate, based on magnetic measurements, was suggested by GILMOUR and PINK 7. SATAKE and MATUURA 8 examined the structures of copper stearate, oleate and their complexes by magnetic susceptibility measurements and observed that copper oleate takes a binuclear structure similar to that of copper stearate. MEHROTRA and RAI 9 confirmed the dimeric nature of copper soaps in chloroform and benzene and found that copper soaps have low values of magnetic susceptibility as compared to other copper salts. MARTIN and WHITLEY 10 and KONDO and KUBO 11 pointed out that the anomalously low magnetic moments of copper carboxylates corresponding to the binuclear structure persist in benzene and dioxane, whereas the moments in water and pyridine were slightly greater than the theoretical spin value, 1.73 B.M. SATAKE and MATUURA 12 investigated the dispersion states of copper stearate and oleate in non-aqueous solutions by the determinations of the magnetic susceptibilities of the solutions. The magnetic susceptibilities and the structure of urea complexes of copper alkonates were studied by KISHITA, INOUE and KUBO 13. The magnetic studies of amine substituted copper (II) alkonates were carried out by KOKOT and MARTIN 14.

The present paper deals with the magnetic studies of the solutions of copper (II) soaps (valerate, caproate, caprylate, caprate and laurate) in alcohols and hydrocarbons. The purpose of this paper is to investigate the dispersion states of copper soaps in non-aqueous solutions and to determine the values of the magnetic susceptibilities and magnetic moments of copper ion in solutions of copper soaps. The existence of micellar aggregates in soap solutions in hydrocarbons and alcohols were demonstrated from the studies of the heat of the solution and other physical properties in a previous communication 15.

8 I. SATAKE and R. MATUURA, Kolloid-Z. 176, 31 [1961].
15 K. N. MEHROTRA, V. P. MEHTA, and T. N. NAGAR, [Communicated].

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Experimental

Material

Merck or B.D.H. reagent grade organic solvents were used after purification. The acids were purified by distilling under reduced pressure. The purity of the reagents was confirmed by the determination of their melting or boiling points.

Copper soaps were prepared by the direct metathesis of the corresponding sodium soap with the slight excess of the required amount of copper sulphate solution at 50—55 °C. The dark green precipitated soaps were washed several times with hot distilled water and then with alcohol to remove the free precipitant and the acid, respectively. After initial drying in an air oven at 100—105 °C, the final drying was carried out under reduced pressure. The soaps were recrystallised in hot benzene, dried and ultimately analysed for the metal content.

Solutions were prepared by dissolving the respective soaps in organic solvents. Care was taken to avoid small traces of water which were found to hydrolyse the soap solutions.

Apparatus

The magnetic susceptibilities of copper soaps were determined by a Gouy type magnetic balance at room temperature (30—40 °C). The field strength applied was about 9000 Gauss. Conductivity water and benzene (Analar) were used for calibration. The specific gram-susceptibility, \( \chi_{\text{soap}} \), of water was taken as \(-0.720 \times 10^{-6}\) and the value for benzene was found in complete agreement with the theoretical value. The specific gram-susceptibility of copper soap in solution was calculated from the following equation used by French and Trew \(^{16}\):

\[
\chi_{\text{soln.}} = \chi_{\text{solvent}} - \frac{k_{\text{air}}}{d_{\text{solvent}}} \left( \frac{d_{\text{solvent}} \times F_{\text{soln.}}}{d_{\text{soln.}} \times F_{\text{solvent}}} \right) + \frac{k_{\text{air}}}{d_{\text{soln.}}},
\]

where \( k_{\text{air}} \) was volume susceptibility of air \((=0.29 \times 10^{-6})\) and \( \chi_{\text{soln.}} \), \( \chi_{\text{solvent}} \), \( d_{\text{solvent}} \), \( d_{\text{soln.}} \), \( F_{\text{solvent}} \), \( F_{\text{soln.}} \) were respectively the magnetic susceptibilities, densities and resultant thrust of the solution and solvent.

The gram-susceptibility of the dissolved copper soap, \( \chi_{G}(\text{soap}) \), was then calculated from the following Weisemann’s equation:

\[
\chi_{G}(\text{soap}) = \chi_{\text{soln.}} - \left( 1 - \Theta \right) \chi_{\text{solvent}}
\]

where \( \Theta \) is the weight fraction of copper soap in the solution.

The molar susceptibility was calculated and Pascal’s diamagnetic correction factor was adopted for the diamagnetic contribution from the organic part of the soap. The magnetic moment, \( \mu \), was calculated from the expression:

\[
\mu = 2.84 \left[ (\chi_{y} - N_{a}) T \right]^{0.5}
\]

where \( N_{a} = 60 \times 10^{-6} \) was used to correct for the temperature independent paramagnetism of bivalent copper.

The specific gram-susceptibilities of the pure solvents were found as follows:

\[
\begin{array}{lll}
\text{Solvent} & \chi_{10^{-6}} & \text{Solvent} \\
\text{Benzene} & -0.716 & \text{Propanol-1} & -0.762 \\
\text{Chlorobenzene} & -0.587 & \text{Butanol-1} & -0.756 \\
\text{Xylene} & -0.746 & \text{Pentanol-1} & -0.752 \\
\end{array}
\]

Results and Discussion

The cupric ion has one unpaired electron and generally shows a magnetic moment of 1.73 B.M. or slightly more in magnetically dilute solutions. It has been shown by many workers that copper salts of both saturated and unsaturated fatty acids take binuclear structures in solid state, and hence the magnetic moments of copper soaps are anomalously low as compared to those of copper (II) salts. It is suggested that if the binuclear structures of copper soaps persist in solutions, the magnetic moments of copper soaps will retain their low values, but the moments will rise to the values usually observed for copper (II) salts provided that the binuclear structures are destroyed in solutions. The values of the magnetic susceptibilities of copper ions in copper soaps in various solvents at room temperature are shown in Table I and the values of magnetic moments calculated from the values of the susceptibilities are given in Table II.

It is evident from the anomalously low values of the magnetic moments of copper ions in copper

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Name of the soap</th>
<th>Valerate</th>
<th>Caproate</th>
<th>Caprylate</th>
<th>Caprate</th>
<th>Laurate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>754</td>
<td>843</td>
<td>704</td>
<td>871</td>
<td>1001</td>
<td></td>
</tr>
<tr>
<td>(36)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>961</td>
<td>931</td>
<td>687</td>
<td>993</td>
<td>956</td>
<td></td>
</tr>
<tr>
<td>(36)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>808</td>
<td>755</td>
<td>884</td>
<td>871</td>
<td>863</td>
<td></td>
</tr>
<tr>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td>(40)</td>
<td>(40)</td>
<td>(40)</td>
<td></td>
</tr>
<tr>
<td>Propanol-1</td>
<td>547</td>
<td>544</td>
<td>585</td>
<td>542</td>
<td>522</td>
<td></td>
</tr>
<tr>
<td>(37)</td>
<td>(36)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td></td>
</tr>
<tr>
<td>Butanol-1</td>
<td>462</td>
<td>490</td>
<td>511</td>
<td>545</td>
<td>508</td>
<td></td>
</tr>
<tr>
<td>(40)</td>
<td>(39)</td>
<td>(39)</td>
<td>(39)</td>
<td>(39)</td>
<td>(39)</td>
<td></td>
</tr>
<tr>
<td>Pentanol-1</td>
<td>638</td>
<td>620</td>
<td>579</td>
<td>627</td>
<td>762</td>
<td></td>
</tr>
<tr>
<td>(36)</td>
<td>(36)</td>
<td>(38)</td>
<td>(38)</td>
<td>(38)</td>
<td>(36)</td>
<td></td>
</tr>
</tbody>
</table>

Table I. Values of \( \chi_{\text{copper}} \times 10^{6} \) in C.G.S. The temperatures at which measurements were made are given within brackets below the magnetic susceptibility values.

MAGNETIC STUDIES WITH COPPER (II) SOAPS

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Name of the soap</th>
<th>Valerate</th>
<th>Caproate</th>
<th>Caprylate</th>
<th>Caprate</th>
<th>Laurate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.32</td>
<td>1.40</td>
<td>1.25</td>
<td>1.45</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.55</td>
<td>1.46</td>
<td>1.25</td>
<td>1.53</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>1.37</td>
<td>1.32</td>
<td>1.42</td>
<td>1.43</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>Propanol-1</td>
<td>1.10</td>
<td>1.10</td>
<td>1.15</td>
<td>1.09</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>Butanol-1</td>
<td>1.01</td>
<td>1.04</td>
<td>1.07</td>
<td>1.11</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>Pentanol-1</td>
<td>1.20</td>
<td>1.18</td>
<td>1.14</td>
<td>1.19</td>
<td>1.32</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Magnetic moments in B.M. of copper ions in copper soaps in various solvents.

soaps in non-aqueous solutions that the binuclear configuration exists in these soap solutions and the dispersion unit is the binuclear molecule having the structure represented as:

\[
\text{structure image}
\]

where L represents solvent.

It is suggested that the sub-dispersion units are bound together by weak polar forces which arises due to the interaction between 3 \(d_x\) and 3 \(d_y\) orbitals of the two copper atoms in conjunction with the hydrocarbon chain attached to the carbon atoms involved in the dimeric unit. The intramolecular exchange interaction reduces the effective moment in the soap solutions whereas the subnormal magnetic moments of solid copper soaps are due to the intermolecular exchange demagnetization through lateral overlapping of 3 \(d_{x'}\) and \(3 d_{y'}\) orbitals on each copper ion which has been identified as \(\delta\) bond by Figgis and Martin. The subnormal magnetic moments may be accounted for by the contribution of lower diamagnetic state.

It has been observed that the magnetic moments of copper ions in copper soaps in hydrocarbons are higher as compared to those in alcohols. The lower values of magnetic moments in alcohols may be due to the fact that the solvent molecules, present at the two terminal positions indicated by L, enhance the overlapping of 3 \(d_x\) and 3 \(d_y\) orbitals. It may be pointed out that the values of magnetic moments in alcohols are independent of the chain length of the soap and of the soap concentration.

It is also observed that the magnetic moments of copper ions in laurate and caprate in hydrocarbons are slightly higher than the magnetic moments of solid copper soaps. This may be due to the fact that the residual exchange intermolecular forces existing in the solid state are eliminated in the solution and this results in the increase in the magnetic moment of copper ion in the soap in these solutions.

The values of the magnetic moments of copper ions in copper soaps in non-aqueous solutions confirm that the binuclear structures exist in these solutions and the dispersion unit is the binuclear molecule.

The green color of the soap solutions in these organic solvents also corresponds to the fact that the dispersion unit is the binuclear molecule.

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