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Chemical Laboratories, B. NARAYANA, Autonomous Post-graduate S. BRAHMAJ V RAO.


MECHANISM OF THE SYNERGISTIC EFFECT IN THE ANION EXCHANGE UPTAKE OF Co(II) IN MIXED SOLVENT MEDIA

The anion exchange adsorption of cobalt(II) chloro-complex in mixed solvent media is compared with the solubility data and spectral data of quaternary ammonium chloro-complex of cobalt (II) and the similarity is pointed out.

The anion exchange adsorption of cobalt(II) at a lower hydrochloric acid concentration in mixed solvent media has been reported by the authors. The present studies have been carried out to understand the mechanism of the synergistic effect.

Ryan in his studies of the species involved in the anion exchange adsorption of quadrivalent nitrates \( \text{Pu(NO}_3\text{)}^4 \) and \( \text{U(NO}_3\text{)}^6 \) compared their anion exchange adsorption of these complexes with the solubility data. He found that a marked similarity exists between the anion exchange of these metal complexes and the solubility of the quaternary ammonium salts of these complexes.

Kraus and Michelson determined the solubility of tetramethylammonium and benzyl trimethylammonium chloroaurate in hydrochloric acid and lithium chloride and found that the solubilities of these are reminiscent of anion exchange behaviour of gold in these media.

In the light of above observations, it is considered worthwhile to examine the anion exchange uptake of cobalt from acetone-alcohol mixtures of different compositions in terms of solubility and spectral data.

**Experimental**

Preparation and Analysis of the complex:

Phenyl trimethyl ammonium chloride and anhydrous cobalt(II) chloride dissolved in alcohol are mixed in the ratio of 2:1 and HCl vapours are passed through this mixture while the solution is cooled. A blue crystalline precipitate separated on further cooling which is finally recrystallised from the ethanol, dried under vacuum and analysed (mp 208°C).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>CO₂O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>45-59</td>
<td>6-18</td>
<td>0-53</td>
</tr>
<tr>
<td>Required for ( (\text{C}_6\text{H}_5)\text{(CH}_3\text{)}_3\text{N})\text{CoCl}_4 )</td>
<td>45-68</td>
<td>5-90</td>
<td>0-55</td>
</tr>
</tbody>
</table>

The cobalt and the chloride ratios are determined by the volumetric method using EDTA and by Volhard’s method respectively. The Cl/Co ratio is found to be 4.

Solubility determination:

About 1 g of (phenyl trimethyl ammonium)₂ CoCl₄ complex is shaken with 10 ml portion of the 85% mixture of acetone and ethyl alcohol containing 1.5 M hydrochloric acid in a stoppered flask for one hour. After allowing the solid to settle down an aliquot of the clear supernatent liquid is taken out and the cobalt content is estimated colorimetrically with Nitroso-R-Salt on a Hilger Spekker Absorptometer using 520 nm colour filter. The solubility determinations in different acetone-ethanol mixtures are repeated until reproducible values are obtained.

Ion exchange distribution coefficients \( K_d \) were determined as already published.

Spectral data:

Spectra of the complex in mixed solvent media are taken on a Unicam SP 600 spectrophotometer.

**Results and Discussion**

The plot of the solubility of the cobalt complex in solvents of different compositions vs. mole fraction of acetone is given in Fig. 1. In the same figure the \( 1/K_d \) values of cobalt on the anion exchange resin as a function of solvent composition are also plotted. It can be seen that the curves show a trend similar to that observed by Ryan in the case of actinide nitratocomplexes in aqueous media.

The spectra of the complex in solvents of different compositions (Fig. 2) indicate that the \( e \) values are
greater in the mixed solvent media than in the individual solvents. The peak at 690 nm has been assigned to \( \text{CoCl}_2 \) species by Fine. A plot of \( \frac{1}{\varepsilon} \) value at this wave length as a function of solvent composition (Fig. 1) also shows a trend similar to the solubility plot. It is thus possible to conclude the synergistic effect is due to the enhanced formation of \( \text{CoCl}_2 \) in mixed solvent media as a result of structural changes of the medium arising from solvent-solvent interactions.

Department of Chemistry, Andhra University, Visakhapatnam-530003, December 26, 1977.

J. Subrahmanyan, M. N. Sastri.


A METHOD FOR FRACTIONATION OF BUFFALO SPERMATOZOA SUITABLE FOR THE STUDY OF FRUCTOSE METABOLISM

Two different methods for fractionation of buffalo spermatozoa into head, midpiece and tail have been described earlier which essentially require different molar concentrations of sucrose either separately or in the form of a gradient as the separation medium, and are satisfactory for the assay of various enzymes in the different fractions. However, both the techniques of fractionation were found to be unsuitable for the estimation of fructolysis in spermatozoal fractions and also such enzymes where the end product of the assay was fructose or glucose. Even repeated washings of the heads and midpiece fraction with distilled water or phosphate buffer did not eliminate the trace of sucrose present in the fraction.

Approximately 2 ml of freshly collected buffalo semen was centrifuged at 1400 \( \times \) g for 10 minutes. The seminal plasma was decanted. The sperm pack was resuspended in an equal volume of distilled water and centrifuged again for 10 minutes at 1400 \( \times \) g. This procedure was repeated twice. The washed sperm pack was diluted 3 fold with distilled water and disintegrated with the aid of vibriones ultrasonicator (model VPL P1) for 60 seconds at a frequency of 25 kilocycles per second. The ultrasonicated sample was centrifuged at 2000 \( \times \) g for 10 minutes in a refrigerated centrifuge. The supernatant was carefully drawn with the aid of a pasteur pipette. The supernatant comprised of tails which were fragmented almost to colloidal dimensions and its morphological entity was...