In the case of europium-crotonic acid system, a curvature obtained in the plot of $E_{1/2}$ versus $-\log C_2$ showed the formation of successive complexes. The Deford and Hume treatment as modified by Irving was applied and Eu(III) was found to form 1:1 and 1:2 complexes with crotonic acid with stability constant data, values of the degree of formation (Fig. 1) for each complex in a system have been calculated using Eq. 2 (ref. 10).

$$a_1 = \frac{-\beta_1[X]^1}{F_1[X]} \quad \ldots \quad (2)$$

Stability constant data show that the complexes of Eu(III) with crotonic acid are more stable than that with acrylic acid.

The reduction equilibrium for the formation of successive complexes reported above may be represented by Eqs 3 and 4:

$$\text{Eu}^{3+} + HX \leftrightarrow [\text{Eu}(X)]^{2+} + H^+ \quad \ldots \quad (3)$$

$$[\text{Eu}(X)]^{2+} + \text{HX} \leftrightarrow [\text{Eu}(X)]^{3+} + H^+ \quad \ldots \quad (4)$$

The percentage distribution of various complex species as a function of ligand concentration has been calculated in the case of Eu(III)-crotonic acid system. Based on this a polarographic method for the determination of microamounts of Eu(III) has been developed. Under optimum conditions Eu(III) in the range $4 \times 10^{-4} - 2 \times 10^{-2} M$ can be successfully determined in presence of different ions. The average percentage recovery of Eu(III) in the presence of various ions has been found to be 99.99% with a standard deviation of 0.192.

Metal ions like Ag(I), Au(III) and Te(IV) are precipitated. Metal ions like Se(VI), W(VI), Se(IV), Ti(IV) and Zn(IV) do not undergo reduction. Te(VI), Cr(VI), Sb(III) Cr(III), As(III), Pb(II), Ti(II), U(VI), Cu(II), Yb(III), Mn(II), Co(II), Ni(II) and Zn(II) undergo reduction at different potentials than that of Eu(III). Only Mo(VI), V(V), Cd(II) and In(III) interfere in the determination of Eu(III).

References


Formation Constants of Dioxouranium (VI), Cu (II), Ni(II), Zn (II), Co(II) & Mn(II) Complexes of Peonoloxime

V. Suresh Babu, D. UgaNdhar Raju & R. Raghava Naidu*
Department of Chemistry, Sri Venkateswara University, Tirupati 517502

Received 22 August 1978; accepted 27 January 1979

The metal-ligand stability constants $\log K_1$ and $\log K_2$ and the proton-ligand stability constant $\log K_1$ have been determined in 50% (v/v) dioxane-water, aceton-water, and 2-ethoxyethanol-water mixtures using the Bjerrum-Calvin pH titration technique as modified by Irving and Rosotti. The stability constants are in fair agreement with Irving-Williams rule. The results obtained are compared with the data available in the literature for structurally similar ligand complexes. Amongst the solvents used aceton-water shows abnormal behaviour.

In view of the analytical applications of peonoloxime (2-hydroxy-4-methoxyacetophenoneoxime), it is of interest to know the physico-chemical properties such as absorption spectral characteristics, thermal properties, magnetic susceptibility and stabilities of its metal complexes. Hence the authors have undertaken these studies and the present investigation deals with the determination of the stability constants of the complexes of UO$_2^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Co$^{2+}$ and Mn$^{2+}$ with peonoloxime by Calvin-Bjerrum titration technique as modified by Irving and Rosotti. Since the chelates were insoluble in water (except cobalt, zinc, and uranium) the study was carried out at 28°C in 50% (v/v) dioxane-water, aceton-water and 2-ethoxyethanol-water mixtures.

Peonoloxime was prepared according to literature method$^{6-7}$ and its solution (0.1 M) was prepared in the respective organic solvents. The metal nitrates solutions were prepared in doubly distilled water and standardised. Dioxane, aceton and 2-ethoxyethanol$^{8}$ were purified before use.

Elco (L1-10A) pH meter was used for pH measurements.

Procedure — The experimental procedure involved the titration of the following cart orthate-free solutions (total volume 50 ml) against standard sodium hydroxide (0.1025 M):

(a) 5 ml of (0.01 M) nitric acid + 25 ml of organic solvent + 20 ml of water.

(b) 1 ml of (0.1 M) ligand in pure organic solvent + 5 ml of (0.01 M) nitric acid + 24 ml of organic solvent + 20 ml of water.

(c) 0.5 ml of (0.01 M) metal solution + 1 ml of (0.1 M) ligand + 5 ml of (0.01 M) nitric acid + 24 ml of organic solvent + 19.5 ml of water.
The pH meter reading (B) was corrected for the nonaqueous medium following the procedure of Van Uitert and Hass25 (—log [H+] = B + log Uq) and others16,29.

Under our conditions, the following log \( U_{aq} \) values were obtained in different media under consideration: 0.10 (50% aq. acetone), 0.15 (50% aq. dioxa-ne) and 0.10 (50% aq. 2-ethoxyethanol).

The dissociation constant \((K_d)\) of the ligand is obtained from the formation curve of the proton-ligand system. The formation curve is constructed by plotting \( n_a \) (the number of protons attached to the ligand) against pH. From the titration curves using the solutions (a) and (b) \( n_a \) values were calculated at various pH values. For a ligand with a dissociation constant \( K_d \), the log \( K_d \) becomes equal to the pH corresponding to \( n_a = 0.5 \). Proton-ligand formation constants of the ligand in 50% aq. 2-ethoxyethanol, 50% aq. acetone and 50% aq. dioxan are 10.20, 11.00 and 11.20 respectively.

From the titration curves of solutions of (b) and (c), \( pL \) and \( pK_d \) values were calculated26-5. Metal-ligand formation constants of the complexes were calculated applying least square method2 to the \( n \) \( pL \) data (Table I).

The oxime behaves as a monobasic acid in the media studied. The acid dissociation constant of the ligand was found to increase in different media in the order acetone > 2-ethoxyethanol > dioxan. This order of stability follows the Irving-Williams rule16. This indicates that the nature of chelation and the type of bond in the chelate may be similar in all the metal ions studied. The order of stability of the complexes with respect to the solvent is dioxan > acetone > 2-ethoxyethanol. The dielectric constants for the pure as well as mixed solvents are in the order acetone > 2-ethoxyethanol > dioxan. This also shows the abnormal behaviour of acetone-water mixture. Similar abnormalities were reported in the literature18-19. This suggests that besides dielectric constant of the medium many other properties such as functional group present in the solvent may also play a significant role. The enhanced stability of the metal chelates in acetone-water may be due to the increased coordination of the chelate with acetone. A plot of log \( K_d \) versus ionisation potentials shows that the stabilities of the complexes can be better correlated with the second ionisation potential3 rather than the first.

A large difference between log \( K_1 \) and log \( K_2 \) values would be expected due to possible steric hindrance because of the linking of the second ligand molecule to the metal ion. The data presented in Table I show that the difference between log \( K_1 \) and log \( K_2 \) values is small and ratio of log \( K_1/K_2 \) is positive in all the cases. Separation factors between first and second formation constants are well within the expected range and the absence of high values indicates that there is little or no steric hindrance to the addition of second ligand molecule. It is also evident from the values of log \( K_1 \) and log \( K_2 \) that there is almost equal tendency for the formation of neutral complex species \( ML_2 \) as for species \( ML^+ \).

The values of overall stability constants (log \( \beta_n \)) of peonoxime complexes show that these chelates are more stable than the complexes of salicylaldehyde20, resacetopheononoxime18 and \( o \)-aminophenol21 but less stable than those of 8-hydroxyquinoline22 complexes. Calvin and Melchior16 suggested that the replacement of a chelated oxygen atom by a more basic nitrogen atom enhances the tendency of the coordination electron pairs to enter the d-orbital. Even though the structures of salicylaldehyde and peonoxime complexes are similar, the greater stability of the latter chelates can be attributed to a hardness-softness factor. Metal ions with greater number of d-electrons, preferably bind in the order \( N > O \). The higher stability of peonoxime chelates over \( o \)-aminophenol21 complexes may be ascribed to the presence of a conjugated six-membered ring in oxime complexes as compared to a five-membered chelate ring in \( o \)-aminophenol complexes. From the data presented in Table I in respect of complexes of peonoxime and that of resacetopheronoxime reported in the literature19 it appears that the introduction of \(-OCH_3\) group in place of \(-OH\) group tends to increase the stability of the chelates. This in turn suggests that the increase of electron density at the reactive centre increases the stability of the chelates. The greater stability of 8-hydroxyquinoline complexes22 can be accounted for by the presence of an additional aromatic ring and consequent higher electron density at the reactive centre.

<table>
<thead>
<tr>
<th>Metal</th>
<th>50% (v/v) aq. 2-ethoxyethanol</th>
<th>50% (v/v) aq. acetone</th>
<th>50% (v/v) aq. dioxan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \log K_1 )</td>
<td>( \log \beta_2 )</td>
<td>( \log K_2 )</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>9.29±0.05</td>
<td>18.06±0.06</td>
<td>8.77±0.08</td>
</tr>
<tr>
<td>UO( ^{2+} )</td>
<td>9.02±0.04</td>
<td>16.19±0.07</td>
<td>7.18±0.08</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>6.18±0.03</td>
<td>11.74±0.03</td>
<td>5.36±0.04</td>
</tr>
<tr>
<td>Zinc</td>
<td>5.83±0.03</td>
<td>10.95±0.04</td>
<td>5.12±0.03</td>
</tr>
<tr>
<td>Co(II)</td>
<td>5.63±0.03</td>
<td>10.64±0.03</td>
<td>5.01±0.04</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>4.42±0.04</td>
<td>8.47±0.05</td>
<td>4.05±0.06</td>
</tr>
</tbody>
</table>
The authors are thankful to the CSIR, New Delhi, for the award of junior research fellowships to two of them (V.S.B. & D.U.R.).

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Dibromamine-T as an Analytical Reagent : Estimation of Thiourea Alone or in Its Metal Complexes

M. S. AHMED & D. S. MAHADEVAPPA*

Department of Post-graduate Studies and Research in Chemistry, University of Mysore, Manasa Gangotri, Mysore 570 006

Received 22 November 1978; accepted 22 December 1978

A simple and rapid method for the estimation of thiourea (tu) alone or in its metal complexes, [M tu]X, where M = Zn, Cd or Hg with dibromamine-T has been developed. Both visual and potentiometric methods of detecting the end point, with an Andrews type of titration in the former, are proposed. Oxidation involves an eight-electron change per thiourea molecule. The products of oxidation have been identified. The proposed method is useful for computing the number of ligand molecules in a metal-thiourea complex.

The number of suitable oxidants available in non-aqueous and partially aqueous redox titrimetry is limited. Jacob and Nair introduced the organic halooamines, dichloramine-T (DCT) and dibromamine-T (DBT) as redox titrants in non-aqueous media. Dibromamine-T (N,N'-dibromo-p-toluene-sulphonamide) has been employed in our laboratories for the estimation of thiocyanate, cyanide, thiosemicarbazide alone or in their metal complexes, in the presence of KBr and sodium acetate. The present paper reports the extension of these studies to the estimation of thiourea (tu) alone or in its metal complexes. An eight-electron change per ligand molecule was noticed in a direct titration of the latter with DBT, when visual and potentiometric methods of detecting the end point were employed. Addition of a little KBr was found essential for smooth oxidation of the reductant, while it served as an indicator to detect the end point in an Andrews type of titration using an organic liquid such as CCl4 or CHCl3. The method is rapid and is helpful for computing the number of ligand molecules in a thiourea complex.

Thiourea is a well-known metal complexing agent and is used as a stabiliser and anti-oxidant for a number of compounds such as vitamins, alkaloids, fats and polymers. Several reagents such as hypophosphate, bromine in acid medium, N-bromosuccinimide, lead tetracetate and iodine trichloride have been employed for determining thiourea and substituted thioureas in solution. A direct titration between thiourea and chloramine-T has been reported by Singh et al. while a rapid back titration procedure has been developed by Aravamudan and Rao. The latter method is useful for estimating thiourea in metal thiourea complexes in solution by chloramine-T.

Thiourea (AR, E. Merck) was recrystallized from aqueous solution and its purity checked. Metal complexes, Zn tu2C12, Zn tu2(CH3COO)2, Zn tu2SO4, Zn tu2Cl2, Cd tu2Cl2, Cd tu2(C2O4)2, Cd tu2(HCO3)2, Cd tu3(SO4)2, Pb tu2(ClO4)2 and Hg tu2Cl4 were prepared by methods reported in literature. The purity of complexes was checked by elemental analyses. All other reagents were of accepted grades of purity.

Aqueous solutions (~5 mg/ml) of thiourea and of its metal complexes were prepared (~1 mg/ml in the case of Cd tu2 (NCS)2 and the mercury complex). Preparation of DBT and standardization of its solution in glacial acetic acid were carried out by the method of Nair and Indrasenan.

Recommended procedure : (a) Visual end point — To an aliquot of thiourea or its complex solution were added 1 M KBr solution (0.5 ml), CCl4 (1 ml) and enough water to retain the organic layer. The solution was titrated against DBT to the appearance of a faint yellow colour in the organic layer. Blank correction was 0.05 ml of 0.1N DBT.

(b) Potentiometric end point — A potentiometric titration, using a potentiometer with Pt-SCE electrode assembly of thiourea and its metal complexes was practicable in the presence of KBr (~0.5 ml of 1M solution). A large potential jump of ~200–400 mV was noticed for the addition of 0.1 ml of 0.1N DBT at the equivalence point. The reaction mixture was generally stirred for 5 sec and the readings were recorded after about 2 min.

Some typical results of analyses, presented in Table I, show that every g-atom of sulphur present