STABILITIES OF MIXED LIGAND COMPLEXES OF MERCURY(II), UO_2^{2+}, BERYLLIUM(II) AND COPPER(II)

V.K. Mishra*, R.K.P. Singh and K.L. Yadava

Department of Chemistry, University of Allahabad, Allahabad-211002, India.

Electrophoretic mobility has been used to study mixed ligand complexes [1,2]. The present work is an extension of the method using Nitrilo triacetic acid (NTA) and 3-hydroxy benzoic acids as ligands.

EXPERIMENTAL

Electrophoretic equipment, method, pH measurement and temperature control are all as discribed earlier [2].

Solutions of perchlorates of mercury, uranyl ion, beryllium and copper and also glucose (5 mM in each case) are prepared as described earlier [2].

Stock solutions of 5.0 M perchloric acid (S.D.S. Analar), 2.0 M sodium hydroxide (A.R. grade), 10 mM 3-hydroxybenzoic acid (Aldrich, U.S.A.) and 1 mM nitrilotriacetic acid (NTA) (E Merck Darmstadt) were prepared by dissolving accurately weighed amount in water. Each solution was standardised using appropriate method.

The background electrolyte in the study of binary complexes consisted of 0.1 M perchloric acid and 10 mM 3-hydroxybenzoic acid/1 mM nitrilotriacetic acid(NTA). In the case of ternary complexes, the background electrolyte consisted of 0.1 M perchloric acid, 1 mM NTA and varying amounts (1 to 10 M Molar) of 3-hydroxy benzoic acid, and the pH adjusted to 10.

The paper strips were spotted with 1.0 µl of the sample solution and glucose (for making osmotic correction). Electrophoretogram was run as described earlier [2].

The spots were detected using the following solutions-H_2S solutions for detecting Hg(II), 0.5% solution of $K_4Fe(cW)_6$ for UO_2^{++}, 0.1% aluminon in ammonium acetate for detecting Be(II), 0.1% PAN in ethanol for Cu(II) and silver solution as discribed earlier to detect glucose.

RESULTS AND DISCUSSION

Metal-3-Hydroxybenzoic acid Binary System: As is evident from Figure 1, the plot of overall electrophoretic mobility of metal ion spot against pH gives a curve with two plateaus in each case. The first plateau corresponds to a region in which metal ions are uncomplexed. In this low pH region protnated species of 3-hydroxybenzoic acid is non-complexing. Beyond this region, metal ion spots have progressively decreasing velocity and hence complexation of metal ions should be taking place with some anionic species of the ligand whose concentration increases progressively with increase of pH. The figure shows the second plateau in each case with positive mobility indicating the formation of 1:1 complex of cationic nature. Further increase of pH has no effect on the mobility of metal ions. Hence it is inferred that the complexing species of 3-hydroxybenzoic acid is HL^- and not L^{2-}. This is in conformity with the findings of the other workers [3,4].

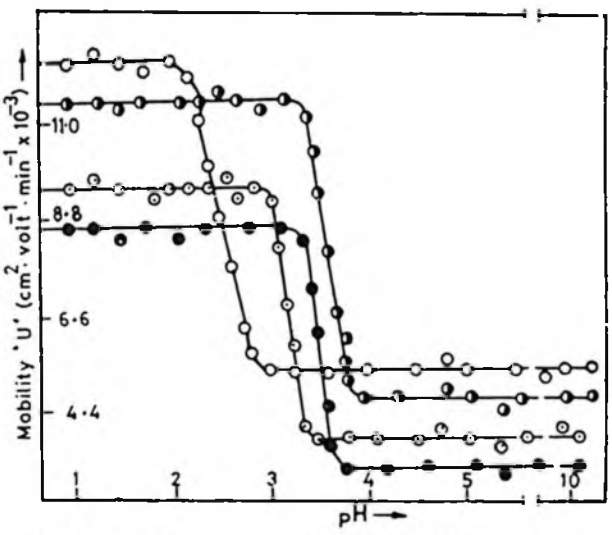


Fig.1 Mobility Curves [M(II)-3-Hydroxybenzoic Acid] System (Temperature = 35°C, Ionic Strength = 0.1)
○ Hg(II) ⊖ UO_2(II) ● Be(II) ⊖ Cu(II)

Stability constants (K_1 values) of the complexes of metal ions with 3-hydroxybenzoate ion is calculated by the fact that at the pH where K = 1/ [L], the overall mobility $u = \frac{1}{2}(u_0 + u_1)$. With the help of dissociation constants of 3-hydroxy-benzoic acid ($K_1 = 10^{-4.08}$, $K_2 = 10^{-9.96}$)[5], the concentration of 3-hydroxy-benzoate ion, [L], is determined at this pH and thus K can be calculated. The calculated values are given in Table 1.

As is evident from the table, the metal ions

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TABLE 1

STABILITY CONSTANTS OF SOME BINARY AND TERNARY COMPLEXES OF Hg(II), UO_2 (II), Be(II) AND Cu(II)

(Ionic strength = 0.1, Temperature = 35°C)

NTA anion = $:N(CH_2CO_2)^{3-}$
3-Hydroxybenzoic acid anion = $m\text{-}C_6^3H_5(OH)\ CO_2^-$

Literature Value of log K are given in brackets and their references in square brackets

Metal ion	$\log K^{M}_{M1}$	$\log K^{M}_{M\text{-}NTA}$	$\log K^{M\text{-}NTA}_{M\text{-}NTA\text{-}L}$
Hg(II)	3.55	13.54 (14.6)[9]	3.41
UO_2(II)	2.73	9.22 (9.56)[8]	2.52
Be(II)	2.42	6.91 (7.11)[8]	2.28
Cu(II)	2.36 (3.88)[3]	12.72 (13.05)[17]	2.17

$$K^{M}_{M\text{-}L} = \frac{[ML]}{[M].[L]} \quad ; \quad K^{M}_{M\text{-}NTA} = \frac{[M\text{-}NTA]}{[M]\ [NTA]}$$

$$K^{M\text{-}NTA}_{M\text{-}NTA\text{-}L} = \frac{[M\text{-}NTA\text{-}L]}{[M\text{-}NTA]\ [L]}$$

can be arranged in the following order in accordance with their decreasing complexation tendency with the liganding acid.

Mercury(II) > Dioxouranium(VI) > Beryllium(II) > Copper(II)

The mercury (II) has the strongest tendency to complex formation. This may be ascribed to the structural peculiarity of the ligand. The ligand has conjugated bonds in the benzene ring which may be coordinated to mercury (II) by extended conjugation of the ring as conjectured by Thomas [6]. The three metal ions, viz., dioxouranium(VI), beryllium(II) and copper (II) are in accordance with the Irving-Williams stability order as extended by Basolo and Pearson for all oxygen donor ligands [7]. The higher stability of the beryllium(II) complex compared to that of copper(II) may be ascribed to the smaller radius of the former and its greater affinity for the oxygen donor ligands.

Metal-Nitrilotriacetic acid (NTA) Binary Systems: The observations on overall mobility of metal ion spots in presence of nitrilotriacetic acid (NTA) at different pH of the background electrolyte are graphically represented in figure 2. As is evident from the figure, two plateaus are obtained with all the four metal ions. The mobility of the second plateau in each case lies in the negative region showing anionic nature of the complex species formed. Hence only one NTA anion is assumed to combine with one bivalent metal ion forming 1:1 M-NTA- complex. This is in conformity with the findings of the other workers [8-11]. The stability constants of the complexes of metal ions with NTA have been calculated in a manner analogous to that described earlier in the case of metal-3-hydroxybenzoic acid binary systems. The calculated values are given in Table 1.

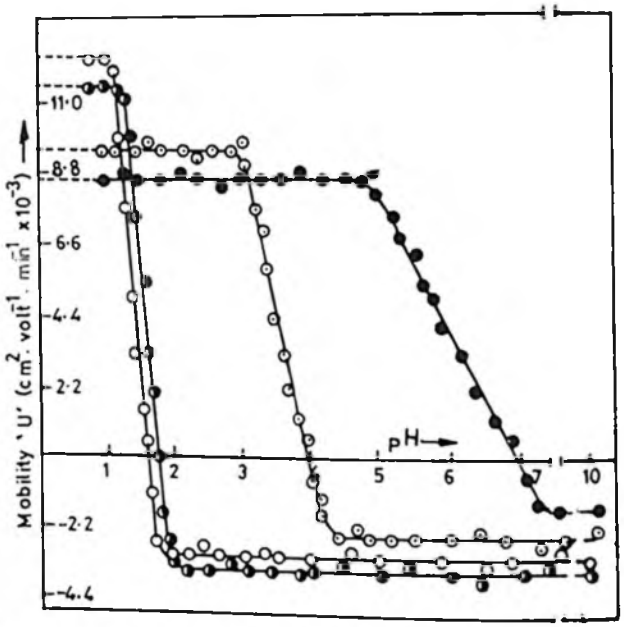


Fig.2 Mobility Curves [M(II)-NTA] Systems 35°C, Ionic Strength = 0.1
○ Hg(II) ⊙ UO_2(II) ● Be(II) ◑ Cu(II)

The specificity of a ligand as elucidated by Sidgwick in his exhaustive work on different ligands is also shown here. As is evident from Table 1, the coordination powers of metal ions with 3-hydroxybenzoic acid and nitrilotriacetic acid are different. In the latter case mercury (II) is superior followed by copper(II), dioxouranium(VI) and beryllium (II). It appears that for polydentate NTA mercury(VI) and then copper(II) fit in the spatial configuration of orbitals of the ligand more easily than dioxouranium(VI) and beryllium(II)

Metal-NTA-3-Hydroxybenzoic acid Ternary Systems: The plot of overall mobility against logarithm of the concentration of 3-hydroxybenzoic acid for all the four bipositive metal ions is shown in Figure 3. As is evident from the figure, two plateaus are obtained in each case. The mobility in the range of first plateau corresponds to the mobility of 1:1 M-NTA complex as can also be seen by comparing these mobilities with the mobilities of 1:1 M-NTA complexes shown in Figure 2. The mobilities of the second plateau in each case are seen to be more negative than that of the first plateau and this shows the formation of more negatively charged complex species. It is inferred, therefore, that 3-hydroxybenzoate ion has coordinated with the 1:1 M-NTA complex resulting in the formation of 1:1:1 metal-nitrilotriacetate-3-hydroxybenzoate mixed ligand complex.

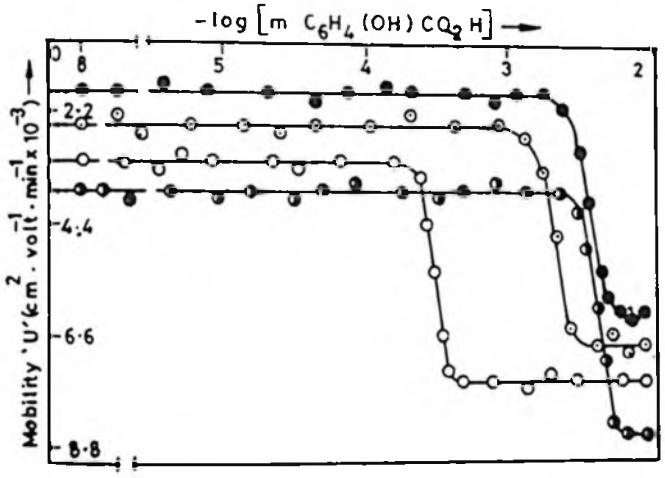


Fig. 3 Mobility Curves [M-NTA-3-Hydroxybenzoic Acid] System (Temperature = 35°C Ionic Strength = 0.1)
○ Hg(II) ⊙ UO_2(II) ● Be(II) ◐ Cu(II)

From Figure 3, the concentration of 3-hydroxybenzoic acid at which the overall mobility is mean of the two plateaus is determined. The concentration of 3-hydroxybenzoate ion at pH 10.0 for this total 3-hydroxybenzoic acid concentration is calculated K' is, obviously, equal to 1/[L], where [L] is the concentration of 3-hydroxybenzoate ion. The value of K' for all the four metal ions are given in Table 1.

The stability of the mixed ligand complexes, as is evident from their overall stability constants, follows the order :

$$[Hg(NTA)HL]^{2-} > [UO_2(NTA)HL]^{2-} > [Be(NTA)(HL)]^{2-} > [Cu(NTA)(HL)]^{2-}$$

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