Stability Constants of Ternary Complexes of Dioxouranium(VI) with Phthalic Acid & O-, O-, N & N, N Donor Ligands

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The ternary complexes of uranyl ion with phthalic acid (common ligand) and different ligands capable of complexing through O-, O- (oxalic, maleic, fumaric, succinic and salicylic acids and pyrocatechol), O-, N (8-hydroxyquinoline and o-aminophenol) or N, N (2,2'-bipyridyl and ethylenediamine) have been investigated pH-metrically at 25°C and \( \mu = 0.1 \text{M} (\text{KNO}_3) \) in aqueous medium. The stability constants of the ternary complexes have been evaluated by different methods depending on the nature of interaction between metal ion and the ligands. The results have been discussed in terms of donor atoms, sizes of the chelate rings, and electrostatic and metal-ligand interactions.

The formation of ternary complexes as important intermediates in many reactions in analytical chemistry and in biological processes has stimulated extensive investigations of these systems. Mixed-ligand complexes of transition metal ions of biological importance\(^1\) with some amines and amino acids, and ternary complexes of uranyl ion\(^5\) with simple and substituted carboxylic acids have been studied. In continuation of our earlier publications\(^3\),\(^4\), wherein we have reported the ternary complexes of Cu(II) with some biologically active ligands and also with the ligands under present investigation, we now report the stability constants of ternary complexes of dioxouranium(VI) employing phthalic acid (O-, O- donor ligand) as the common ligand and oxalic (OA), maleic (MA), fumaric (FA), succinic (SeA), salicylic (SA) acids, pyrocatechol (PC) (O-, O- donor ligands), 8-hydroxyquinoline (8-HQ), o-aminophenol (o-AP) (O-, N donor ligands) and 2,2'-bipyridyl (bipy) and ethylenediamine (en) (N, N donor ligands) in aqueous medium at 25°C and \( \mu = 0.1 \text{M} \text{KNO}_3 \).

Uranyl nitrate (AR) solution was standardised by oxinate method\(^8\). All other chemicals used were of AR grade. The ligands were recrystallised/distilled before use and their purity checked by TLC and m.p./b.p. All the solutions were prepared in doubly distilled water except the solution of 8-HQ which was prepared in 1% aq. ethanol. The experimental details and the method of measurement of pH have been given in our earlier papers\(^3\),\(^4\).

The formation of the mixed ligand complexes in solution was established by noting the pH of precipitation for MA, ML and MAL and by comparing the mixed ligand titration curve with the composite curve (Fig. 1) (Composite curve is drawn by the graphical addition of 1:1 MA/MAL curve to the titration curve of the free ligand A/L). The titration data reveal that the formation of ternary complexes takes place in the low pH region by the simultaneous interaction of PhA and OA, MA, FA, SeA, SA, en or 8-HQ with the metal ion, whereas PhA and PC, o-AP or bipy interact with the metal ion in a stepwise manner.

The ionization constants of ligands and stability constants of binary complexes of uranyl ion with the above ligands have been calculated by the method of Irving and Rossotti\(^9\),\(^10\) at 25°C and \( \mu = 0.1 \text{M} (\text{KNO}_3) \). Oxalic acid (OA), o-AP and bipy form 1:1 and 1:2 chelates while the remaining ligands form only 1:1 chelates. The absence or presence of a 1:2 chelate in solution has been confirmed by the procedure reported by Santappa and Rammoorthi\(^11\). The stability constants of ternary complexes are determined by suitable methods\(^9\),\(^12\) depending on the nature of interaction between the metal ion and the ligands. The accuracy in the ionization constants of ligands and stability constants of the binary and ternary chelates is
of the order of ± 0.05 log units. The data obtained are given in Table I.

There are two convenient ways to characterise the stabilities of mixed ligand complexes. One is by comparing the $\Delta \log K$ (Eq. 1)

$$\Delta \log K = (\log K_{MAL} - \log K_{MA}) = (\log K_{MAL} - \log K_{ML})$$

...(1)

(M = metal ion, A = primary ligand and L = secondary ligand; the selection of A and L as primary and secondary ligands respectively is purely arbitrary).

Another method involves comparison of disproportionation constant given by Eq. (2)

$$K_{DAL} = K(MA + ML \leftrightarrow MAL + M)$$

...(2)

The $\Delta \log \beta_i$, [ $\Delta \log \beta = \log \beta_{MAL} - (4\log \beta_{AA} + \log \beta_{LL}) + 0.30$ (ref. 13)] is also useful to characterise the mixed ligand complexes in solution. Higher the $\Delta \log \beta_i$ value more is the stability of the complex.

The parameters $\Delta \log K$, $\log K_{DAL}$ and $\Delta \log \beta_i$ for all the systems have been calculated using the above equations and are included in Table I and discussed in terms of the donor atoms of the ligands.

$O^-$, $O^-$ donor ligands

The $\log K$ values for the systems containing uranyl ion-PhA and MA, ScA, OA and FA are negative (Table I). In all the systems the formation of the ternary complex takes place simultaneously in the lower pH region.

The order of stabilities of the ternary complexes in terms of $\Delta \log K$ is: MA > ScA > OA > FA. Though the complexes of maleic and succinic acids involve seven-membered rings, they are more stable than the oxalic acid complex which forms a five-membered ring chelate. This order is found to be unusual, but is observed in a good number of UO$_2$(V) complexes. This may be due to the fact that the repulsion between the electron pairs on oxygen atoms of dioxouranium ion and those of the oxygen atoms of the ligands decrease with the increase in the ring size.

The presence of $\pi$-electrons in maleic acid makes its ternary complex more stable than the succinic acid complex. The fumaric acid due to its trans-geometry may act as a monodentate ligand and thus forms less stable ternary complex. The $\log K_{DAL}$ values for these systems with reference to the secondary ligands, for the equilibrium MA + ML $\leftrightarrow$ MAL + M, and $\Delta \log \beta_i$ values confirm the conclusions drawn from $\Delta \log K$ values.

The $\Delta \log K$ value of the ternary complex with SA is positive while it is negative for the ternary complex containing PC, indicating that UO$_2$(V)-PhA-SA complex is more stable than the UO$_2$(V)-PhA-PC complex. This can be explained as follows: The carboxylate oxygen in SA is not directly bound to the benzene ring as the phenolate oxygen. It may therefore, adjust stereochemically more easily than the phenolate oxygen. In SA one donor atom is carboxylate oxygen and the other is a phenolate oxygen, while in the pyrocatechol both the donor atoms are phenolate oxygens, thus resulting in less stable ternary complex. The $\log K_{DAL}$ value for the UO$_2$(V)-PhA-SA is 0.62 while for UO$_2$(V)-PhA-PC it is -1.08, which are for the equilibria MA + ML $\leftrightarrow$ MAL + M, confirming the conclusions drawn from $\Delta \log K$ values. The $\Delta \log \beta_i$ values for these systems are in accord with $\log K_{DAL}$ values.

$O^-$, $N$ donor ligands

The $\Delta \log K$ value for 8-HQ complex is positive while that of 0-AP complex it is negative, indicating greater stability of 8-HQ complex, in accord with the observations recorded in literature$^{16,17}$. The $\pi$-interaction may be expected in both 8-HQ and 0-AP complexes. In order to see the possibility of inter-ligand $\pi$-interactions through metal ion $\pi$-orbitals the UV spectra of the ligands, binary complexes and the ternary complexes have been recorded. O-AP exhibits bands at 4329, 3521, 2296 cm$^{-1}$. The low energy band at 2296 cm$^{-1}$ corresponds to $\pi^*+\pi$ transition. The O-AP binary complex exhibits bands at 4347, 3546, 3067, and 2298 cm$^{-1}$ while the absorption

| Table I—Formation Constants of Ternary Complexes, Phthalic Acid (A)-UO$_2$(VI)-Ligand(L) | \( (\mu = 0.1 \text{ M} \text{KNO}_3; \log K_{MAL} = 5.13; \text{temp.} = 25^\circ\text{C}) \) |
|---|---|---|---|---|---|---|---|---|
| Ligand(L)| $K_{MAL}$| $K_{MLA}$| $\log K_{MAL}$| $\log K_{MLA}$| $\log K_{MAL}$| $\log K_{MLA}$| $\Delta \log K$| $\log K_{DAL}$| $\Delta \log \beta_i$ |
| Oxalic acid| 4.48| 3.95| 7.24| 2.11| 2.76| -2.37| -2.37| -2.44 |
| Maleic acid| 4.80| 9.05| 3.92| 4.25| -0.88| -0.88| -1.18 |
| Fumaric acid| 3.47| 6.15| 1.02| 2.68| -2.45| -2.45| -2.75 |
| Succinic acid| 4.38| 8.51| 3.18| 4.13| -1.00| -1.00| -1.30 |
| Salicylic acid| 11.30| 17.05| 11.92| 5.75| 0.62| 0.62| 0.32 |
| Pyrocatechol| 13.23| 17.28| 12.15| 4.05| -1.08| -1.08| -1.38 |
| 8-Hydroxyquinolione| 9.66| 17.33| 12.20| 7.67| 2.54| 2.54| 2.24 |
| 2,2'-Bipyridyl| 3.77| 3.15| 10.44| 5.31| 6.67| 1.54| 1.54| 1.55 |
| Ethylenediamine| 9.02| 12.97| 7.84| 3.95| -1.18| -1.18| -1.48 |
The spectrum of its ternary complex exhibits bands at 43478, 35461, 30488 and 22989 cm\(^{-1}\). These data show that there is no shift in band position in the lower energy region indicating no \(\pi\)-interaction. The absorption bands of 8-HQ and its binary and ternary complexes appear at 41494, 39370, 31847 (8-HQ); 40816, 38760 and 31847 cm\(^{-1}\) [UO\(_2\)(VI)-8-HQ] and 41667, 38760 and 28169 cm\(^{-1}\) [UO\(_2\)(VI)-8-HQ-PhA]. The shift of 40816 cm\(^{-1}\) band of the binary complex to 41667 cm\(^{-1}\) in the ternary complex and appearance of a new band at 28169 cm\(^{-1}\) in the ternary complex indicate \(\pi\)-interaction between the ligand and metalion orbitals. From this it can be deduced that the 8-HQ complexes are more stable than the \(\sigma\)-AP complexes. The \(\log K\) values confirm the above stability order.

**N, N donor ligands**

The \(\Delta \log K\) value of UO\(_2\)(VI)-bipy-PhA complex is positive while that of UO\(_2\)(VI)-en-PhA complex it is negative, indicating greater stability of the former complex. In the formation of MA\(_2\) type complexes, where A is a bidentate oxygen donor ligand, the electrostatic repulsion between the metal ion electrons and the lone pair of electrons (which are not involved in coordination) makes the approach of the second ligand molecule more difficult, thus resulting in negative \(\Delta \log K\) \((\log K_2 - \log K_1)\). In the ternary complex UO\(_2\)(VI)-bipy-PhA the metal ion initially forms a bipy complex and then coordinates with the O\(^-\), O\(^-\) donor phthalate ion and in this the repulsion is reduced to a minimum by the back donation of charge from metal ion to the vacant orbitals of the bipy. No such \(\pi\)-interaction can be expected in the case of ethylenediamine (en) as it is an open chain, saturated neutral molecule. Thus the ternary complex of bipy is more stable than that of en. The positive value of \(\log K\) and \(\Delta \log K\) for bipy confirm greater stability of its ternary complex than that of en. The higher \(\log K\) and \(\Delta \log K\) values for UO\(_2\)(VI)-PhA-8-HQ (2.54 and 2.24) and UO\(_2\)(VI)-bipy-PhA (2.15 and 1.54) indicate that these complexes are the most stable complexes among all the complexes studied in the present investigation.

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**References**