Influence of electrostatic effect on the stability of mixed-ligand complexes: Uranyl-complexone-phenol/phenolic acid ternary systems

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Abstract. The formation constants (log K_{MAL}^{MA}) of the complexes of the type $(UO_2.A.L]$ (where A = IMDA, NTA or EDTA; L = catechol, resorcinol, phloroglucinol, pyrogallol, β-resorcylic acid or protocatechuic acid) have been determined potentiometrically at 25°C and ionic strength, I = 0·2 (mol dm^{-3}, NaClO$_4$) using the Irving–Rossotti approach. The formation constants of the binary complexes (log K_{MA}^{M}) have been found to lie in the sequence IMDA < NTA < EDTA, whereas those for the mixed ligand complexes (log K_{MAL}^{MA}) follow the reverse sequence, IMDA > NTA > EDTA, due to the electrostatic effect.

Keywords. Ternary uranyl-complexone-phenol/phenolic acid complexes; electrostatic effect; formation constant; stability of mixed-ligand complexes.

1. Introduction

The statistical aspects of solution stabilities of mixed-ligand complexes have been discussed by some workers (Marcus and Eliezer 1961, 1962; Kida 1956, 1961; Dewitt and Watters 1954; Bhattacharya 1981). Bjerrum (1941) had proposed the so-called "total effect" in order to explain the gradual decrease in stability of the successive binary complexes of a given metal ion with a certain ligand. Astatisticality involved in the stability of some mixed-ligand complexes of the type [CuAL] (where A = 2,2'-dipyridyl, or o-phenanthroline, L = catechol or a similar secondary ligand) has been reported recently (Bhattacharya and Patel 1982). The effects of electrostatic and other astatistical factors on the stabilities of ternary lanthanide-EDTA complexes with alizarine-red sulphonic acid and some unsaturated aliphatic carboxylic acids have been reported by us (Limaye and Saxena 1984, 1985).

In the present work the formation constants of (1:1:1) mixed-ligand complexes of UO_2^{2+} have been determined using IMDA, NTA and EDTA as primary ligands and catechol (cat), resorcinol (res), phloroglucinol (phl), pyrogallol (pyr), protocatechuic acid (pca) and β-resorcylic acid (β-res) as secondary ligands. The role of electrostatic effect in the variation of stabilities of these ternary complexes has been discussed.

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2. Experimental

Uranyl nitrate of BDH analar grade and other chemicals of Merck GR or Fluka AR grade were used. The solutions were prepared in double distilled water. The metal-ligand formation constants were determined potentiometrically by using the Irving–Rossotti approach (Irving and Rossotti 1953, 1954; Chidambaram and Bhattacharya 1970) at 25°C and an ionic strength, $I = 0.2$ (mol dm^{-3}, NaClO$_4$). The usual titration sets (Limaye and Saxena 1982) were prepared and titrated after equilibration with a carbonate free 0.2 mol dm^{-3} NaOH solution using an Elico digital (model LI-120) pH-meter. Reproducible pH data were used for evaluating the formation constants. The proton-ligand formation constants of the secondary ligands were redetermined to obtain their values under experimental conditions. The experimental values of the formation functions were subjected to the Q-test (Pecsok *et al* 1976) so as to reject any suspect value. Only statistically valid values were used for calculating the formation constants. The formation constants, $\log K^{M}_{ML}$, $\log K^{MA}_{MA}$ and $\log K^{MA}_{MAL}$ (the terms have their usual meanings) are presented in table 1. The quantities in parentheses represent standard deviations.

3. Results and discussion

The formation of the mixed-ligand complexes in the present work (titration curves not shown) proceeds following the equilibria
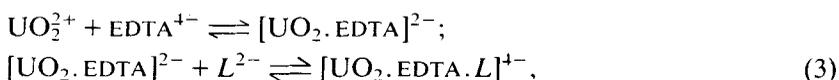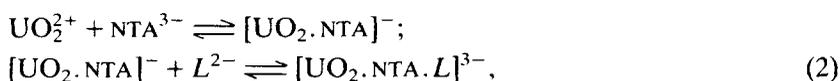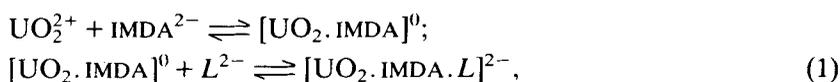
$$M + A \rightleftharpoons MA; \quad MA + L \rightleftharpoons MAL \quad \text{(charges omitted).}$$
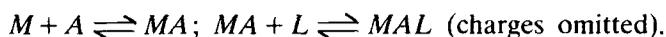
Chelation with the primary ligand takes place in a lower pH region (pH ≤ 3.0) and the primary complex MA remains stable up to a sufficiently high pH (~ 8.0). The secondary ligand L combines with MA in the pH range ~ 4.0–6.0. No hydrolysis of the complexes is indicated. Dilute solutions (1×10^{-3} mol dm^{-3}) were used to avoid any possibility of the formation of polynuclear species. Plots (not shown) of $\bar{n}/[L]$ vs $[L]$ ($\bar{n}$ = formation function of the complex, $[L]$ = free ligand concentration) were found to be smooth indicating the absence of any polynuclear species.

Table 1. Formation constants of the binary (MA and ML) and ternary (MAL) complexes of UO$_2^{2+}$. Temperature = 25°C; $I = 0.2$ (mol dm^{-3}, NaClO$_4$).

Formation constant	Primary ligand (A)	Secondary ligand (L)					
		cat	res	phl	pyr	pca	β-res
$\log K^{M}_{ML}$	–	14.90	9.66	8.34	13.81	15.47	8.10
		(± 0.002)	(± 0.01)	(± 0.0005)	(± 0.02)	(± 0.001)	(± 0.002)
$\log K^{MA}_{MAL}$	IMDA	13.80	8.96	7.46	13.55	15.04	7.41
		(± 0.002)	(± 0.00)	(± 0.02)	(± 0.02)	(± 0.003)	(± 0.002)
	NTA	13.40	8.64	7.08	12.85	14.50	6.97
		(± 0.004)	(± 0.002)	(± 0.05)	(± 0.002)	(± 0.008)	(± 0.003)
	EDTA	10.42	6.71	5.28	10.31	11.63	4.85
		(± 0.001)	(± 0.002)	(± 0.03)	(± 0.001)	(± 0.002)	(± 0.002)
$\log K^{M}_{MA}$	IMDA: 13.00 (± 0.02); NTA: 13.44 (± 0.04); EDTA: 15.37 (± 0.01)						

The log K_{MA}^M values are expectedly found to lie in the sequence IMDA < NTA < EDTA. The denticity of these ligands (three, four and six, respectively) causes gradually increasing chelate effect in this sequence. Further, the combination of the ligands A^{2-}, A^{3-} and A^{4-} (corresponding to IMDA, NTA and EDTA, respectively) with UO_2^{2+} should be associated with increasing entropy effect in this order. The metal chelates of these ligands with the 3*d*- and 4*f*- metal ions are actually reported (Ashcroft and Mortimer 1970) to be stabilised chiefly due to the entropy factor. The entropy effect should mainly originate from the rupture of the hydration sphere of the uranyl ion and the desolvation of the acetate groups of these ligands.

In contrast to the stability sequence of the binary *MA* complexes, a reverse order of stability has been observed (see table 1) for the ternary complexes, IMDA > NTA > EDTA. The complexation of the three chelons with the uranyl ion followed by a further chelation with the secondary ligand, L^{2-} may be represented as:

$$UO_2^{2+} + IMDA^{2-} \rightleftharpoons [UO_2. IMDA]^0;$$
$$[UO_2. IMDA]^0 + L^{2-} \rightleftharpoons [UO_2. IMDA. L]^{2-}, \tag{1}$$

$$UO_2^{2+} + NTA^{3-} \rightleftharpoons [UO_2. NTA]^-;$$
$$[UO_2. NTA]^- + L^{2-} \rightleftharpoons [UO_2. NTA. L]^{3-}, \tag{2}$$

$$UO_2^{2+} + EDTA^{4-} \rightleftharpoons [UO_2. EDTA]^{2-};$$
$$[UO_2. EDTA]^{2-} + L^{2-} \rightleftharpoons [UO_2. EDTA. L]^{4-}, \tag{3}$$

Equations (1), (2) and (3) clearly show that with IMDA the incoming secondary ligand (negatively charged) experiences no electrostatic repulsion during the formation of the mixed-ligand complex. With NTA and EDTA, however, gradually increasing electrostatic repulsion is involved. The $\Delta \log K$ (= log K_{MAL}^{MA} − log K_{ML}^M) values (table 1) are negative. Statistically also the combination of L^{2-} with *MA* in the three cases should be less favoured in the observed sequence. What is important here is not so much the negative value of $\Delta \log K$ but its magnitude which leads to a reverse order of stability of the ternary *MAL* complexes as compared to that of the binary *MA* complexes.

It is observed that in general the increase in charge (on *MA*) from − 1 to − 2 causes much greater increase in the numerical value of − $\Delta \log K$ as compared to the change from 0 to − 1. Statistically, therefore, the second step of complexation ($MA + L \rightleftharpoons MAL$) becomes much less favourable on going from NTA to EDTA than from IMDA to NTA which seems reasonable in view of their denticities.

The stability sequence (for binary, *ML* as well as ternary, *MAL* complexes) follows the order of ligand basicity pca > cat > pyr > res > phl > β-res. The effect of ring size of the chelate with the secondary ligand is also reflected in the stability. Both cat and pyr form similar five-membered rings; the presence of one additional −OH group in the latter causes a reduction in electron density over the two donor oxygens resulting in the sequence cat > pyr. Six-membered rings are formed by res and phl; the electron withdrawing property of the additional −OH in phl makes it less basic and hence the order res > phl. With pca chelation is expected to occur (Jejurkar *et al* 1972) through the two −OH groups (O^-–O^-); the presence of the −COOH group shows a positive inductive effect. Hence pca gives

higher values of log K_{ML}^M and log K_{MAL}^{MA} than those with cat, although both form otherwise similar five-membered rings. With β-res a six-membered ring involving the carboxylate and hydroxyl groups seems to be formed leaving behind one –OH group and hence the stability of β-res complexes is the least in the series.

Acknowledgements

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