

tion with TRIS seems to have reached to a maximum of 2 instead of four or six for both.

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Potentiometric Study of Be(II) Salicylates

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Formation constants of the complexes of Be(II) with salicylic acid and substituted salicylic acids have been determined by potentiometric titrations in aqueous solutions containing 0.10M NaClO₄. The results have been discussed with reference to the effects of substitutions in the ligand.

THE complex formation of Be(II) with salicylic acid or substituted salicylic acid has been studied by several workers¹⁻⁸. In the present work, formation constants of complexes of Be(II) with a series of substituted salicylic acids have been determined potentiometrically.

The preparation of sulphocresotic acids and their stock solutions were described earlier⁹. Potentiometric titrations were carried out under CO₂-free nitrogen atmosphere with carbonate-free 0.1000M KOH on well-stirred, thermostated (30° ± 1°) solutions containing 0.10M NaClO₄, 0.01M HClO₄ and ligand or metal and ligand in ratios of 1:10 and 1:20. Universal pH meter (model OP-204, Hungary, accuracy ± 0.02 pH unit) was used.

The formation constants (Table 1) of the 1:1 and 1:2 complexes were calculated by interpolation of \bar{n} values to 0.5 and 1.5. More precise values were obtained by linear plot¹⁰.

In all the titrations with Be(II) and salicylic acid, buffer regions were observed at 0 < a ≤ 2 (a = equivalent of base per mole of ligand) and 2 < a ≤ 4 with inflexions at a ≈ 2 and a ≈ 4 indicating the stepwise formation of 1:1 and 1:2 complexes. In non-sulphonated ligands, precipitations occurred at a ≈ 4. The \bar{n} value steadily increased with pH to ≈ 2 indicating the formation of 1:2 complex as the highest complex in Be(II)-salicylic acid system. Absence of disproportionation and constancy of \bar{n} in the pH range 7-10 in Be(II) complexes of sulpho-

TABLE 1 — FORMATION CONSTANTS (LOG K₁ AND LOG K₂) OF Be(II)-SALICYLATES AT 35° IN Aq. 0.1M NaClO₄

Ligand	pK [*] COOH	pK [*] OH	log K ₁	log K ₂
<i>o</i> -Cresotic acid (oCA)	2.84	14.14	13.05	8.78
<i>p</i> -Cresotic acid (pCA)	2.87	13.74	12.94	9.97
<i>m</i> -Cresotic acid (mCA)	2.94	13.54	12.87	9.89
Sulpho- <i>p</i> -cresotic acid (SpCA)	2.52	13.47	12.75	9.00
Salicylic acid (SA)	2.82	13.24	12.69	9.65
Sulpho- <i>o</i> -cresotic acid (SoCA)	2.54	12.58	12.04	8.99
5-Chlorosalicylic acid (ClSA)	2.43	12.50	11.97	9.30
5-Bromosalicylic acid (BrSA)	2.40	12.41	11.84	9.28
Sulpho- <i>m</i> -cresotic acid (SmCA)	2.68	12.33	12.72	9.25
5-Sulphosalicylic acid (SSA)	2.44	11.90	11.61	8.95
5-Nitrososalicylic acid (NO ₂ SA)	1.90	9.89	9.71	7.86

*Ref. 10.

salicylic acids point towards their resistance to hydrolysis.

Plot of log K₁ vs pK_{COOH} + pK_{OH} is linear with slope ≈ 1. Deviations from the linear plot are observed in case of *o*-cresotic (oCA) and sulpho-*m*-cresotic acids (SmCA). The unusually high stability of Be-SmCA complex could not be explained. The low stability of Be-oCA complex is probably due to the steric hindrance of -CH₃ group which is *ortho* to the -OH group. There should have been similar steric hindrance in Be-3-sulpho-*p*-cresotic acid (SpCA) and Be-sulpho-*o*-cresotic acid (SoCA) systems also but it appears that the coulombic attraction between dipositive Be(II) ion and trinegative ligand anion overcomes the hindrance due to *ortho* -CH₃ or -SO₃ groups during chelate formation. This assumption gains support from the plot of log K₂ vs pK_{COOH} + pK_{OH}. In the linear plot of slope ≈ 0.6, deviations towards low stability are observed in cases of oCA as well as SoCA and SpCA. Since formation of 1:2 complex involves a neutral or mononegative 1:1 complex and negatively charged ligand anion, there is no coulombic attraction between them and the steric factors become operative. The slope values of the curves indicate that in 1:1 complexes, substitution affects the stabilities of the metal-ligand complexes to the same extent as that of the corresponding proton-ligand complexes but in 1:2 complexes the effect of substitution on stabilities is 60% of the effect on basicities.

One of the possible reasons for this, besides statistical and coulombic factors, is that 1:2 complexes form at relatively higher pH values than 1:1 complexes and there is a pronounced effect of the competition of hydroxyl ions with ligand anions for 1:1 complexes.

The higher stability of complexes of sulphocresotic acids give the corresponding ligands an edge over sulphosalicylic acid (SSA) as complexing agents for Be(II). It has been shown¹⁰ that if salicylic acid (SA) is regarded as reference substance, then in the case of metal complexes of substituted sali-

cyclic acids, the wavelength of maximum absorption and molar extinction coefficient increase in presence of $-\text{SO}_3\text{H}$ and $-\text{CH}_3$ groups. This possibility together with lower water solubility and stronger beryllium affinity for oCA, pCA and mCA in comparison to SA makes the cresotic acids as potentially better extracting agents for Be(II) than SA.

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Some Mixed Ligand Complexes of Th(IV)*

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The stability constants of mixed ligand chelates of Th(IV) with EDTA and DTPA as primary ligands and kojic acid, Tiron, oxine and N-phenyl-N-benzoylhydroxylamine as secondary have ligands been determined. The study has revealed a coordination number of ten for Th^{4+} ion.

THOUGH the existence of mixed ligand complexes has been known for a long time, the detailed investigation of their equilibria has received attention only recently^{1,2}. In our previous communications^{3,4}

we have reported stability constant data on some mixed ligand complexes of thorium and lanthanide ions. Some further work on some more mixed ligand chelates of Th(IV) is described in this note. The primary ligands chosen were EDTA (hexadentate), diethylenetriaminepentaacetic acid (DTPA, octadentate) and triethylenetetraaminehexaacetic acid (TTHA, decadentate). The secondary ligands used were kojic acid, Tiron, oxine and N-phenyl-N-benzoylhydroxylamine (BPHA).

Thorium nitrate (Indian Rare Earths Ltd. purity >99.9%) was dissolved in 0.1M nitric acid and standardized by titration with EDTA using xylenol orange as indicator. BPHA (Koch-Light) was recrystallized from hot ethanol-water and vacuum-dried. Kojic acid (BDH, biochemical grade) was recrystallized from ethanol using animal charcoal to give buff-coloured needles. Tiron (Fluka), oxine (E. Merck GR), EDTA disodium salt (E. Merck GR), DTPA free acid (K & K Laboratories) and TTHA (Sigma Chemical Co., USA) were used as such. The primary ligands were standardized against zinc solution prepared from zinc granules (analar grade).

The experimental set-up and the method of calculation of the constants has been described previously³. Titrations for kojic acid and Tiron were carried out in an aqueous medium while those for oxine and BPHA in 20% ethanol-water medium to ensure solubility of these ligands.

Titrations were performed at 28°C and the ionic strength maintained at 0.10M by addition of KNO_3 . pH measurements were made with a Beckman model G pH meter using Beckman 40495 (0-14 pH) or a Toshniwal GA 110 (0-14 pH) glass electrode.

Titration curves for ThY-kojic acid system (where Y is the anion of the primary ligand) are depicted in Fig. 1 while the formation constants for the addition reactions of the secondary ligands are summarized in Table 1.

It is now generally recognized that elements in the fifth and subsequent periods can extend their coordination to accommodate more than six ligand atoms. Thorium ion after combination with a hexadentate ligand like EDTA is still coordinately unsaturated and can further combine with suitable secondary ligands. The present study reveals that the primary Th-EDTA complex is capable of adding on two molecules of bidentate ligands. The primary complex with the octadentate ligand (DTPA) could, however, combine only with one molecule of the

TABLE 1 — STABILITY CONSTANTS

Reagent	EDTA						DTPA log K	
	log K_1^H	log K_2^H	log K_1	log K_2	log β_2	2 log α^* (pH=5.5)		log β_2 (cond.)
Oxine	10.16	4.98	8.12	5.56	13.68	9.50	4.18	5.76
BPHA	8.88	—	7.04	4.80	11.84	6.76	5.08	5.10
Tiron	12.60†	7.60(3)	13.20(3)	7.70(3)	20.90	18.40	2.50	10.76
Kojic acid	7.81	—	6.95	5.04	11.99	4.62	7.37	4.73

$$*\alpha = 1 + K_1^H [H^+] + K_1^H K_2^H [H^+]^2$$

†Literature value.

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