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Stability Constants & Thermodynamic Functions of Mg(II), Ca(II), Sr(II), Ba(II) & Pb(II) Complexes with Thiophene-2-carboxylic Acid

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The proton-ligand stability constant of thiophene-2-carboxylic acid and the stability constants of its 1 : 1 complexes with Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+} have been determined in aq. medium (μ=0·2*M*) using Calvin-Bjerrum *p*H titration techinique. The $\Delta G°$, $\Delta H°$ and $\Delta S°$ of the complexes have also been calculated using Gibbs-Helmholtz equation.

THE stability constants of the complexes of thiophene-2-carboxylic acid with Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+} have been evaluated using the Calvin-Bjerrum[1,2] titration technique as modified by Irving-Rossotti[3]. Thermodynamic parameters of the reactions have also been evaluated.

All the chemicals used were of BDH (AR grade). The standard solutions of the ligand and the metal salts were prepared in conductivity water. *p*H was measured on a Digicord *p*H-meter. The ionic strength was kept constant by $NaClO_4$ (1·0*M*) solution and the titrations were carried out at 30°, 40° and 50°C. For each set of experiments following three titrations were performed:

(a) Acid titration — $HClO_4$ (0·1*M*, 5 ml) + $NaClO_4$ (1·0*M*, 9·5 ml) + conductivity water (35·5 ml).

(b) Reagent titration — $HClO_4$ (0·1*M*, 5 ml) + $NaClO_4$ (1·0*M*, 9 ml) + Ligand (0·05*M*, 10 ml) + conductivity water (26 ml).

(c) Metal titration — $HClO_4$ (0·1*M*, 5 ml) + $NaClO_4$ (1·0*M*, 8·9 ml) + Ligand (0·05*M*, 10 ml) + metal solution (0·01*M*, 5 ml) + conductivity water (21 ml).

The initial volume of the solution was 50 ml in each case. The plots of *p*H of the solution against the volume of alkali added were of the usual shapes.

Proton-ligand and metal-ligand stability constants — The proton-ligand stability constant was obtained (Table 1) by Bjerrum half-integral method and also by point-wise calculation method at different points in the proton-ligand formation curve using Eq. (1)

$$\log K_1^H = pH + \log \bar{n}_H / 1 - \bar{n}_H \qquad ...(1)$$

The values of log K_1^H at 30, 40 and 50° are 2·95, 3·35 and 3·65 respectively.

The metal-ligand stability constants (Table 1) were determined by Bjerrum half-integral method[2] and also by point-wise calculation method from the corresponding formation curves using Eq. (2).

$$\log K_1 = pL - \log (1-\bar{n})/\bar{n} \qquad ...(2)$$

Thermodynamic parameters — The values of overall changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) have been determined using the Gibbs-Helmholtz equation[4] (Table 1).

In thiophene-2-carboxylic acid complexes $\bar{n}$-values remain less than one indicating the formation of 1:1 complexes. The data shows an increase in the value of long K_1^H with increase in temperature. The values of log K_1 are positive in all cases, and increase with increase of temperature. The values of $\Delta G°$ for the complexes become more negative indicating that the complex formation is a spontaneous process. The formation of all the complexes is an endothermic reaction and it explains the increase in the values of the formation constants with rise in temperature. The entropy change, $\Delta S°$, accompanying the formation of complexes, is positive in all the cases.

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Table 1 — Metal-Ligand Stability Constants and Thermodynamic Parameters of the Complexes at Different Temperatures

Metal ion	log K_1 at			$-\Delta G°$ (K joule/mole)			$\Delta H°$ (K joule/mole)	$\Delta S°$ (joule/mole/degree)
	30°	40°	50°	30°	40°	50°	40°	40°
Mg^{2+}	1·95	2·00	2·76	11·30	11·97	17·05	72·86	271·02
Ca^{2+}	2·01	2·09	2·21	11·65	12·51	13·65	18·22	98·18
Sr^{2+}	2·01	2·09	2·35	11·65	12·51	14·52	30·97	138·91
Ba^{2+}	2·06	2·09	2·51	11·94	12·51	15·51	40·99	170·93
Pb^{2+}	2·03	2·14	2·18	11·76	12·81	13·47	13·66	84·57