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NOTE

pH-metric and Thermodynamic Studies on Metal Chelates of Al(III), Cr(III) and Fe(III) Ions with Tridentate Biprotic Ligands

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The pH-metric studies on the metal chelates of trivalent Al(III), Cr(III) and Fe(III) ions with the tridentate biprotic ligands derived from dibenzoylmethane with *o*-aminobenzoic acid (H_2BB) and 2-aminopropanoic acid (H_2BP), respectively, have been carried out by employing Calvin-Bjerrum pH-titration technique at 25°, 35° and 45 ± 0.1°C ($\mu = 0.01, 0.05$ and 0.1 M $NaClO_4$) in aqueous media. The dissociation constants (pK_1 and pK_2), θ° and pk_m^H value of the ligands have been evaluated. The stability constants have been determined and these values follow the Irving-William order. The thermodynamic parameters (ΔG°, ΔH° and ΔS°) of the chelation have been evaluated and discussed.

A survey of literature[1–5] has revealed that no work has been done on trivalent Al(III), Cr(III) and Fe(III) metal chelates of tridentate ligands derived from dibenzoylmethane with *o*-aminobenzoic acid and 2-aminopropanoic acid, respectively. These two ligands are structurally similar and are expected to behave as a tridentate biprotic ligand.

All the reagents and chemicals used were of AnalaR grade and the solutions were made in double distilled carbonate-free water. A digital pH-meter (Century model CP901) equipped with a single electrode assembly were used for recording pH. The electrode system was calibrated before and after each titration.

Preparation of ligand: A mixture of equimolar alcoholic solutions of dibenzoylmethane and *o*-aminobenzoic acid (H_2BB) or 2-aminopropanoic acid (H_2BP) were refluxed in the presence of piperidine as a catalyst, on a water bath for 1 h. The resulting solutions were filtered while hot and dried at 35–37°C/0.01 mm/90 min. On cooling these give powdery pale yellow compound (H_2BB), m.p. 273 ± 1°C and dull yellow compound (H_2BP), m.p. 218.8 ± 1°C, respectively. These were recrystallized and preserved in a vacuum desiccator.

pH-metric technique: The Calvin-Bjerrum[6, 7] pH titration technique was used for the titration. The following three solutions: (i) 0.01 M ligand (ii) 0.05 M ligand and (iii) 0.1 M ligand and a metal ion (0.01 M) in 1 : 1 and 1 : 2 ratio, respectively, were prepared. The initial volume in each case was kept 40.0 cm^3 and ionic strengths were maintained at $\mu = 0.01, 0.05$ and 0.1 M by adding $NaClO_4$. These solutions were titrated against carbonate-free 0.01 M NaOH solution which was prepared by the Gran Method[8] at 25°, 35° and 45° ± 0.1°C, respectively, and the titration curves had usual shapes.

The values of dissociation constants of both the ligands suggest liberation of two protons, one from the carboxylic acid (—COOH) and the other from the enolic (—OH) group, *i.e.*, the ligands are biprotic.

Disssociation constants of ligands: The dissociation constants (pK_1 and pK_2) were determined by calculating $\bar{n}_A$ (average number of protons attached to free ligand) values at different pH, at 25°, 35° and 45°C. A graph is plotted between $\bar{n}_A$ and the corresponding pH values. The values of pK_1 and pK_2 increase with lowering in temperature.

θ and pK^H_m values: Harned et al.[9, 10] gave the relation $(pK^H - ct^2) = 2C\theta t + (pK^H_m - C\theta^2)$ where pK^H is pK at t°C, pK^H_m is minimum pK^H value at θ°C and 'C' is a constant having value $5.0 \times 10^{-3}\ deg^{-2}$. A plot of $(pK^H_m - C\theta^2)$ v/s t must be linear and this was found true in the present case. The values of θ° and pK^H_m for H_2BB are 3.78 and 10.53 and for H_2BP 4.12 and 10.81, respectively. The values of $\Delta H°$ obtained by Harned equation and Gibbs-Helmholtz equation were found in good agreement.

Stability constants: The values of '$\bar{n}$' (formation function) for all the metal chelates of both ligands do not go beyond 1.13 which suggest formation of the one complex species having 1 : 1 (metal : ligand) ratio in the solution. The formation curves for metal chelate were drawn by plotting a graph between various values of $\bar{n}$ and corresponding $-\log [A^-]$. The values of stability constants ($\log \beta_1$) read directly from the curves at $\bar{n} = 0.5$. The values were further refined by computational methods[11], namely, interpolation at half $\bar{n}$ values, successive approximation and correction term and average values are summarized in Table-1.

TABLE-1

THE VALUE OF DISSOCIATION CONSTANTS OF H_2BB AND H_2BP, STABILITY CONSTANT AND THERMODYNAMIC PARAMETERS OF THEIR METAL COMPLEXES.

Ligand/ metal-chelate		Average value of pK/log β_1			$\Delta G°$ (kJ/mole)			$\Delta H°$ (kJ/mole)	$\Delta S°$ (kJ/deg/mole)
		25°C	35°C	45°C	25°C	35°C	45°C	35°C	35°C
H_2BB	pK_1	3.29	3.03	2.82	76.46	75.43	74.10	111.59	607.20
	pK_2	10.01	9.88	9.66					
H_2BP	pK_1	2.70	2.36	2.19	74.63	72.42	71.11	127.02	647.53
	pK_2	10.47	9.99	9.54					
Al(III)		6.79	6.44	6.19	47.36	44.94	42.92	109.78	502.00
		(6.56)	(6.13)	(5.74)	(54.94)	(53.09)	(52.12)	(68.95)	(396)
Cr(III)		9.20	8.84	8.60	61.11	58.56	55.65	142.44	652.60
		(8.62)	(8.23)	(7.76)	(67.33)	(66.41)	(65.61)	(78.02)	(468)
Fe(III)		10.50	10.14	9.84	67.50	65.34	62.96	135.18	651.04
		(10.20)	(9.69)	(9.19)	(75.66)	(75.08)	(74.59)	(86.18)	(523)

* Values in parentheses are for H_2BP.

Al(III) acts as a Lewis acid and has tightly held outer electrons and also an empty orbital. The basic atoms as oxygen, sulphur and nitrogen could coordinate by donating electrons to empty orbitals of Al(III), forming a complex with different stabilities in acidic media[12]; hence it may be expected that the ligands under investigation would form a stable complex with Al(III). The results show that Al(III) form chelate only in 1 : 1 (M : L) ratio in solutions. Though Al(III) forms stable complexes but since the ions of transition metals have vacant d-orbital, which can readily accommodate the electron pairs donated by the ligands, their exponential tendency for complex formation can be readily understood. In the present investigation the Fe(III) and Cr(III) metal chelates with both the ligands were found more stable than Al(III) complexes. The greater stability of Fe(III) chelates may be attributed to d^5 configuration conforming to the Irving-William order[13] of stability.

The sequence of stability constants of trivalent metal-ion chelates of both the ligands is Fe(III) > Cr(III) > Al(III) which is in agreement with natural order. The values of stability constants are summarised in Table-1.

Thermodynamic study: The thermodynamic stability constants were obtained by extrapolation of the measured stability constants at different ionic strengths to zero ionic strength from the graph plotted between stability constants and $\sqrt{\mu}$, where 'μ' is the ionic strength. The thermodynamic functions such as change in the free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) accompanying complexation were determined with the standard relations[10] (Table-1).

$$\Delta G° = 2.303RT \log K;$$

$$\Delta H° = 2.303RT_1T_2/(T_2 - T_1) \log K$$

$$\Delta S° = (\Delta G° - \Delta H°)/T$$

The negative value of $\Delta G°$ shows that chelation reactions tend to proceed spontaneously and the values are more negative at lower temperature suggesting that low temperature favours chelation. The very large entropy change is also justified by considering the greater availablity of coordination sites to these ions. All the chelation reactions are associated with negative $\Delta H°$ values indicating exothermic nature of the reactions. The values of $\Delta H°$ for Cr(III) and Fe(III) are higher than Al(III) chelates. Since $\Delta H°$ is a measurement of the strength of covalent bonding[5], it may be concluded that Fe(III) complexes are more strongly bonded than Cr(III) and Al(III).

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