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Potentiometric Study on the Ternary Complexes of Chromium(III) Metal Ion at Different Ionic Strengths

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The stepwise equilibria of 1 : 1 : 1 Cr(III)-A-L mixed ligands systems where A = salicylic acid (SA)/monosodium salt of 5-sulfosalicylic acid (SSA) and 3,5-dinitrosalicylic acid (DNSA) and L = 2-hydroxyacetophenone (HAP), 2,5-dihydroxy acetophenone (DHAP) and 5-chloro-2-hydroxyacetophenone (CHAP) have been investigated potentiometrically at 0.05 M, 0.10 M and 0.15 M ($NaNO_3$) ionic strengths in ethanolic-aqueous (20% v/v) medium at 25°C.

INTRODUCTION

The stability constants of ternary complexes are of interest for understanding the role of metal ion and the nature of two ligands in determining the stability of the ternary complexes[1]. The biological significance and function of the Cr(III) ion as an essential micro element have been described by Mertz[2–4] and other authors[5]. Recent observations led to the conclusion that the biological activity of Cr(III) largely depends on the chemical nature of chromium(III) complexes.

Salicylic acid and substituted salicylic acids have been established as potential antimicrobial agents and drugs[6–10] and form binary and ternary complexes with transition elements[11–15]. Binary and ternary complexes of transition elements with 2-hydroxyacetophenones and related compounds have been studied but the information is scanty[16–17]; therefore, it is worth while to study the binary and ternary complexes using above biologically active chelating ligands with Cr(III) metal ion.

EXPERIMENTAL

All the reagents employed were of analytical grade. The solutions of salicylic acid (SA), sulfosalicylic acid (SSA) and 3,5-dinitrosalicylic acid (DNSA) were prepared in aqueous solution while solutions of 2-hydroxyacetophenone (HAP), 2,5-dihydroxyacetophenone (DHAP) and 5-chloro-2-hydroxyacetophenone (CHAP) were prepared in absolute alcohol by direct weighing. Chromium(III) metal ion solution was prepared and standardised by usual method.

The experimental procedure consists in titration of the following thermostated

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mixtures of solutions with a 0.10 M sodium hydroxide solution and recording the pH after each addition of standard sodium hydroxide solution.

1. Mixture (A): 10mL of 0.01 M HNO_3 solution.
2. Mixture (B): Mixture (A) + 5 mL of 0.01 M ligand.
3. Mixture (C): Mixture (B) + 5 mL of 0.01 M metal solution.
4. Mixture (D): Mixture (A) + 5 mL of 0.01 M ligand L solution.
5. Mixture (E): Mixture (D) + 5 mL of 0.01 M metal solution.
6. Mixture (F): Mixture (E) + 5 mL of 0.01 M ligand A solution.

The ionic strengths of the above titration mixtures were maintained to 0.15 M, 0.10 M and 0.05 M ($NaNO_3$) by adding the required volume of 1.0 M sodium nitrate solution, keeping the total volume of 50 mL with 20% (v/v) ethanolic-aqueous medium and appropriate corrections in pH meter reading were made[12, 20] to get true pH values.

RESULTS AND DISCUSSION

Proton dissociation constants and 1:1 metal-ligand stability constants have been obtained by modified algebraic method[22].

In the ternary complex Cr(III)-A-L system it is examined that the 1:1:1 mixed ligand titration curve runs superimposed on the 1:1 binary Cr(III)-A titration curve upto a = 1.9 and pH ≈ 4.5 indicating that the L (CHAP/DHAP/HAP) does not participate in complex formation up to this stage. The formation of ternary complexes is evidenced by the diversion of mixed ligand titration curve from the binary system in the regions $2 \le a \le 3$ and pH ≈ 5.0 reveals the formation of ternary complexes of the type Cr(III)-A-L through stepwise equilibria:

$$\mathrm{Cr(III)} + \mathrm{H_2A} \xrightarrow{0 \le a \le 2} [\mathrm{Cr\text{-}SA}]^+ + 2\mathrm{H}^+$$

$$[\mathrm{Cr\text{-}SA}]^+ + \mathrm{HL} \xrightarrow{2 \le a \le 3} [\mathrm{Cr\text{-}A\text{-}L}]^0 + \mathrm{H}^+$$

In case of SSA which is taken as H_2A-the charges on the binary and ternary complexes would be 0 and −1 respectively.

The formation of ternary complexes is further supported by apperance of yellowish-green colour at pH ≈ 4.5 during the titration of mixed ligand system indicating the interaction of Cr(III)-A complex with ligand L and formation of Cr(III)-A-L complex species.

The total concentrations of ligand H_2A, HL and metal M at any pH on the mixed ligand titration curve from a = 0 to 3 are given by the following expressions:

$$C_A = [H_2A] + [HA] + [A] + [MA] + [MAL]$$

$$C_L = [HL] + [L] + [ML] + [MAL]$$

$$C_M = [M] + [MA] + [ML] + [MAL]$$

$$aC_M = [HA] + 2[A] + 2[MA] + [L] + [ML] + 3[MAL]$$

a = moles of alkali per mole of metal in the ternary system.
(Charges are omitted for simplicity)

Substituting the proton-dissociation constants of the ligands and the equilibrium constants of their binary complexes, the free ligand concentrations [A] and [L] were calculated by Newton-Raphson method[22, 23]; thereby the concentrations of other species were obtained. These values were used for the calculation of equilibrium constants of the ternary complexes and representative species distribution curves for the Cr(III)-SA-HAP system.

TABLE-1

EQUILIBRIUM CONSTANTS OF THE LIGANDS AND Cr(III) COMPLEXES

	$\mu = 0.15$ M		$\mu = 0.10$ M		$\mu = 0.05$ M		$\mu \to 0$	
Proton dissociation constant	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
SA	2.97	12.37	3.11	12.61	3.17	12.83	3.43	
SSA	2.92	10.68	3.03	10.78	3.10	10.91	3.33	
DNSA	1.51	7.37	1.66	7.52	1.88	7.75	2.12	
HAP	10.62		10.78		10.92		11.23	
DHAP*	10.08		10.21		10.35		10.65	
CHAP	9.79		9.95		10.15		10.42	
Binary complexes	$\log K^{Cr}_{Cr\text{-}A}$		$\log K^{Cr}_{Cr\text{-}A}$		$\log K^{Cr}_{Cr\text{-}A}$		$\log K^{Cr}_{Cr\text{-}A}$	
Cr(III)-SA	12.39		12.50		12.59		12.78	
Cr(III)-SSA	10.49		10.57		10.65		10.85	
Cr(III)-DNSA	7.60		7.69		7.78		7.96	
	$\log K^{Cr}_{Cr\text{-}L}$		$\log K^{Cr}_{Cr\text{-}L}$		$\log K^{Cr}_{Cr\text{-}L}$		$\log K^{Cr}_{Cr\text{-}L}$	
Cr(III)-HAP	9.82		9.90		9.99		10.17	
Cr(III)-DHAP*	9.38		9.45		9.53		9.71	
Cr(III)-LHAP	9.71		9.80		9.89		10.09	

*In DHAP the second proton does not undergo dissociation up to pH 11.5.

Formation constants of mixed ligand complexes along with Δ log K and per cent of relative stabilization [(%) R.S.] values for ternary complexes are given in Table-2. Δ log K and (%) R.S. may be given by the following expressions:

$$\Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$$

$$(\%)\ \text{R.S.} = \frac{\Delta \log K}{\log K^{M}_{ML}} \times 100$$

TABLE-2
FORMATION CONSTANTS OF MIXED LIGAND COMPLEXES

Complexes	$\mu = 0.15$ M $\log K^{Cr}_{Cr\text{-}A\text{-}L}$	$\mu = 0.10$ M $\log K^{Cr}_{Cr\text{-}A\text{-}L}$	$\mu = 0.05$ M $\log K^{Cr}_{Cr\text{-}A\text{-}L}$	$\mu \to 0$ $\log K^{Cr}_{Cr\text{-}A\text{-}L}$	log K	(%) R.S.
Cr(III)-SA-HAP	7.24	7.31	7.39	7.47	–2.70	–26.55
Cr(III)-SSA-HAP	7.30	7.37	7.45	7.59	–2.58	–25.37
Cr(III)DNSA-HAP	7.72	7.79	7.85	7.99	–2.18	–21.44
Cr(III)-SA-DHAP	6.76	6.84	6.91	7.09	–2.62	–26.98
Cr(III)-SSA-DHAP*	6.93	7.01	7.10	7.29	–2.42	–24.92
Cr(III)-DNSA-DHAP*	7.27	7.35	7.42	7.61	–2.10	–21.63
Cr(III)-SA-CHAP	7.16	7.23	7.30	7.45	–2.64	–26.16
Cr(III)-SSA-CHAP	7.22	7.30	7.36	7.58	–2.51	–24.88
Cr(III)-DNSA-CHAP	7.61	7.69	7.76	7.92	–2.17	–21.51

* In DHAP the second proton does not undergo dissociation up to pH 11.5.

The numerical values of (%) R.S. are uses for a quantitative estimation of the relative stabilizations of those ternary systems at a given temperature and ionic strength. (%) R.S. values for all the ternary systems are found to be negative indicating that the secondary ligand L binds better to metal-aquo ion than to the binary [(CrIII)-A] complex. Such a higher stability of binary complexes compares to that of ternary complexes due to greater attraction forces between the Be^{2+} and L- than the [Cr-A] complexes, coupled with the availability of lesser number of coordination sites for the second ligand on the Cr-A complexes of free Cr(III)-aquo ion.

In general, for a series of similiar ligands the ligands the higher the basicity of the ligands, greater is the stability of the metal complexes as found true in the Cr-(III)-A and Cr(III)-L binary complexes and ternary complexes with respect to secondary ligand (L). While reverse investigated for the ternary systems, the order of stability of ternary complexes with respect to primary ligand (A), is in the order, DNSA > SSA > SA which can be explained on the basis of the fact that the electron withdrawing nature of nitro and sulfo groups/group present in DNSA and SSA are/is making effectively a more electropositive Cr(III) metal ion in Cr(III)-SSA/DNSA complex, than Cr(III)-SA, enabling the secondary ligand to coordinate more effectively and form more stable complexes with respect to SA.

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