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Studies on metal-diethylenetriamine pentaacetic acid complexes as ligands

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Abstract : Potentiometric studies have been carried out on H_3ML complexes where M represents divalent metal ions Cd, Hg, Co, Ni, Cu, Ca and Ba and L represents Diethylenetriamine pentaacetic acid (DTPA) using pH-titration technique. The protonation constants of H_3ML complexes in solution have been determined at an ionic strength μ= 0.1 M KNO_3 at 20^0C and 40^0C.The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complex formation have also been evaluated.These values are found quite favourable for the systems under study.

(**Key words:** Potentiometry/protonation constant/ thermodynamic parameters/DTPA/H_3ML type ligand).

Introduction

H_3ML type complexes with multidentate ligands can themselves act as ligands to form their bimetallic complexes of the type M_2L or MM'L. There is considerable literature in the equilibrium studies of the former whereas very little information is available regardingthe equilibria involved in the formation of MM'L complex. Only recently some studies have been reported on such systems[1,2]. Such H_3ML complexes still retain dissociable protons and donor sites. Thus they themsleves can act as ligands in forming bimetallic complexes.Practically no effort has been made to study the behaviour of protonation equilibria of theH_3ML type complexes with multidentate ligands and therefore in the present paper we are reporting our work on determination of proton-ligand equilibria of H_3M(II)DTPAcomplexes. The "practical" proton- ligand stability constants of the ML^{3-} complexes have been obtained by Bjerrum-Calvin[3] titration technique as modified by Irving and Rossotti[4].

Experimental

Materials and Method

Solutions of Cd (II), Hg (II), CO (II), Ni (II), Cu (II), Ca (II) and Ba (II) metal ions were prepared and standardized by EDTA titrations[5]. A 0.1 M solution of diethylenetriamine pentaacetic acid (DTPA) was prepared by dissolving it into two equivalent of alkali (NaOH)which was parepared in double distilled water and had earlier been standardised against a standard oxalic acid solution Solutions of carbonate free sodium hydroxide (E. Merck)and perchloric acid (A.R.) were standardised potentiometrically.A digital pH-meter (Century-model CP 901-S) with a glass electrode was used to determine the changes in hydrogen ion concentration. The pH-meter has a reproducibilityof $\pm$ 0.01 pH. The three reaction mixtures :

(A) 10.0 ml KNO_3 (0.5 M) + 10.0 ml $HClO_4$ (0.1 M) + water.
(B) 10.0 ml KNO_3 (0.5 M) + 10.0 ml $HClO_4$ (0.1 M) + 5.0 ml DTPA (0.1 M) +water.
(C) 10.0 ml KNO_3 (0.5 M) + 10.0 ml $HClO_4$ (0.1 M) + 5.0 ml DTPA (0.1 M) +5.0 ml M (II) ion soln. (0.2 M) + water.

containing acid, acid + ligand and acid + ligand + metal ion were prepared such that the concentration of the common ingredients were identical in all the cases. The total volume in each case was kept 50.0 ml. The ionic strength (0.1M KNO_3) and free acid concentration(0.02M $HClO_4$) were also kept the same in each case. The ratio between the metal and ligand was kept 2 : 1. The values of ΔG, ΔH and ΔS have been calculated by using the method[6] described elsewhere.

Results and Discussion

The proton-ligand equilibria for the H_3ML complexes can be expressed as:

$ML^{3-} + H^+ \leftrightarrow HML^{2-} K_1^H$

$HML^{2-} + H^+ \leftrightarrow H_2ML^- K_2^H$

$H_2ML^{-1} + H^+ \leftrightarrow H_3ML K_3^H$

The above equilibria have been investigated for the bivalent metal ions Cd (II), Hg (II),Co (II), Ni (II), Cu (II), Ca (II) and Ba (II). The logarithmic values of $ß_1$, $ß_2$ and $ß_3$ withrespect to H_3Cd(II)DTPA, H_3Hg(II) DTPA, H_3Co(II)DTPA, H_3Ni(II)DTPA, H_3Cu(II)DTPA, H_3Ca(II)DTPA, and H_3Ba(II)DTPA have been determined by using graphical method[7] described elsewhere and are given in Table 1.

Table - 1

Table 1- Proton-ligand stability constants of H_3M (II) DTPA complexes ($\mu = 0.1$ M)

System	Temp (°C)	log $ß_1$ (log K_1^H)	log $ß_2$ (log K_1^H + log K_2^H)	log $ß_3$ (log K_1^H + log K_2^H + log K_3^H)
H_3Cd(II) DTPA	20	4.79	8.01	10.31
	40	4.72	8.06	10.37
H_3Hg(II) DTPA	20	5.12	8.69	11.32
	40	5.01	8.61	11.02
H_3Co(II) DTPA	20	5.74	10.00	12.02
	40	5.7	19.48	11.50
H_3Ni(II) DTPA	20	6.30	10.63	12.52
	40	6.16	10.23	12.22
H_3Cu(II) DTPA	20	5.73	9.50	11.87
	40	5.54	9.24	11.62
H_3Ca(II) DTPA	20	7.11	14.06	16.77
	40	7.01	12.47	16.47
H_3Ba(II) DTPA	20	7.61	14.83	19.32
	40	7.33	13.33	18.46

Relative error $\pm$0.1

The K_1^H, $K_2^H$and K_3^Hvalues for DTPA (L^{5-}) and ML^{3-} (1: 1 M(II) -DTPA complex)represent the successive protonation equilibria of same carboxylic groups. It can be safely assumed that the two highly ionizable protons of DTPA (i.e. K_4^H and K_5^H) are completely replaced in M(II) DTPA complex. A comparison of the K_n^H values of DTPA as reported inliterature[8]. (K_1^H= 10.57, K_2^H = 8.61, K_3^H= 4.31) at 20 ° C and ionic strength 0.1M with thatof M(II) DTPA complex shows that the protons are less strongly bound in the M(II) - DTPAcomplex as compared to the DTPA. The extent of destabilization is more for $K_1^H$and least for K_3^H. So far as the effect of metal ions are concerned K_1^H decreases for the M(II) DTPAcomplexes in the order: Ca> Ba> Co> Ni> Cu> Hg> Cd. These results also lead tothe conclusion that formation of metal complex causes the multidentate ligand to becomeinflexible and thus makes intra-hydrogen bonding difficult and dissociation of protons easier.The values of ΔG, and ΔH are most favourable (i.e. negative) for Ca and Ba systems whereas the ΔS value is most favourable (i.e, positive) for Ni (II) system (Table 2).

Table -2
The values of ΔG, ΔH and ΔS for H_3M(II) DTPA complexes *

System	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS($JK^{-1}mol^{-1}$)
H_3DTPA	-62.53 (-65.91)	-13.16	+168.54 (+168.52)
H_3Cd(II) DTPA	-30.84 (-29.35)	-52.69	-74.47 (-74.46)
H_3Hg(II) DTPA	-31.98 (-31.74)	-35.11	-10.73 (-10.72)
H_3CO(II) DTPA	-40.66 (-38.97)	-65.41	-84.40 (-84.48)
H_3Ni(II) DTPA	-36.73 (-37.77)	-21.93	+50.53 (+50.54)
H_3Cu(II) DTPA	-34.53 (-33.53)	-48.28	-47.06 (-47.08)
H_3Ca(II) DTPA	-47.67 (-44.03)	-100.95	-181.83 (-181.84)
H_3Ba(II) DTPA	-47.64 (-44.96)	-87.82	-136.91 (-136.92)

* Values given in the bracket are at 40 ° C, Relative error $\pm$0.2.

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