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Electrochemical Studies on the Composition, Stabilities and Thermodynamics of Zn^{+2}, Cd^{+2} and Pb^{+2} Complexes with Methylene bis Thio Acetic Acid

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Potentiometric and conductometric studies on the zinc, cadmium, lead—methylene bis thio acetic acid system in aqueous media reveal the formation of 1 : 1 and 1 : 2 (M : L) complexes in the pH range 3.4–5.1. Their stability constants have been determined at 20°, 30° and 40 °C by applying *Calvin* and *Melchior*'s extension of *Bjerrum*'s method. The overall changes in thermodynamic function ΔH, ΔG and ΔS accompanying complexation have been evaluated at 30 °C.

(Keywords: Conductometric; Potentiometric; Thermodynamics)

Elektrochemische Untersuchungen über Zusammensetzung, Stabilität und Thermodynamik von Zn*(II)-,* Cd*(II)- und* Pb*(II)-Komplexen mit Methylen-bis-thioessigsäure*

Potentiometrische und konduktometrische Untersuchungen an Zink-, Cadmium- und Blei-Methylen-bis-thioessigsäure-Systemen in wäßrigem Medium zeigten die Bildung von 1 : 1 und 1 : 2 (M : L)-Komplexen im pH-Bereich 3,4—5,1. Die Stabilitätskonstanten wurden bei 20°, 30° und 40 °C mittels der *Calvin-Melchior*-Methode (erweiterte *Bjerrum*-Methode) bestimmt. Die thermodynamischen Parameter ΔH, ΔG und ΔS der Komplexierung wurden für 30 °C ermittelt.

Introduction

Mercapto-acids and other sulphydryl compounds are strong complexing agents and hence *Saxena* and co-workers[1–4] have focussed their interest on the complexation of these compounds with various metals.

This communication reports the formation, composition and stability constants of Zn^{+2}, Cd^{+2} and Pb^{+2} complexes with methylene bis thio acetic acid, employing potentiometric and conductometric techniques. The $\log K_{stab}$ values determined at 20°, 30° and 40 °C by *Calvin* and *Melchior*'s extension of *Bjerrum*'s method have been further refined by least square method, correction term, and *Schrodinger*'s convergence formula. The thermodynamic parameters accompanying complexation have also been evaluated at 30 °C.

Experimental

Methylene bis thio acetic acid (referred herein as *MBTAA*) was obtained from Evan's Chemetics Inc. New York and other chemicals used were of AnalaR grade. The contents of zinc, cadmium and lead from their respective solutions were estimated by standard methods. The solutions were prepared in doubly distilled air-free conductivity water.

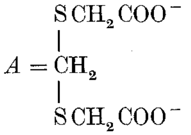
A Toshniwal digital *pH* meter (accuracy ± 0.01 *pH*) and the electronic eye type conductometer were used for *pH* and conductance measurements respectively. The experimental procedure described earlier[3, 4] consists of a series of *pH* and conductometric titrations of *MBTAA* with standard 0.1 *M* NaOH in the absence and presence of metal ion at various ligand to metal ratios.

Results and Discussions

Stoichiometry

The stoichiometry of the reaction between M^{+2} (Zn^{+2}, Cd^{+2} and Pb^{+2}) and methylene bis thio acetic acid was determined by *pH* and conductometric titrations of mixtures of reactants in various ratios against standard alkali (Fig. 1).

The appearance of only one inflection (Fig. 1, curve 1) after two mole of base per mole of ligand [*MBTAA*] has been added, corresponds to the neutralisation of two carboxyl hydrogen in a single step. Hence if free methylene bis thio acetic acid, having two replaceable hydrogen ions is denoted as H_2A where



$$A = \begin{array}{l} SCH_2COO^- \\ | \\ CH_2 \\ | \\ SCH_2COO^- \end{array}$$

the reaction between "*m*" interval of O-2 may be represented in a single step by the equation

$$H_2A + 2\,OH^- \rightarrow A^{-2} + 2\,H_2O \qquad (1)$$

The absence of an inflection at 1 mol of NaOH indicates that the acidities of both the hydrogens are fairly comparable in magnitude and that the two ligand species H_2A and HA^- exist in equilibrium in the *pH* ranges corresponding to the values of O-2 moles of NaOH.

Addition of an equimolar concentration of Zn^{+2}, Pb^{+2} or Cd^{+2} ions (Fig. 1, curve 4) alters the shape of the free ligand titration curves as a result of chelate formation. It is seen that the reaction of the ligand and metal ion results in the lowering of buffer region and the displacement of hydrogen (at different *pH* values for different metal ions) to form 1 : 1 chelate which may be given by the equation

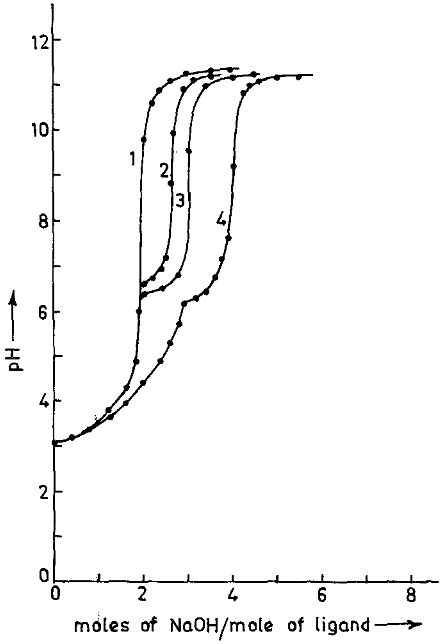


Fig. 1. *pH* meteric titration of the solution; curve (1) $4\cdot10^{-3}M$ *MBTAA*; (2) $4\cdot10^{-3}M$ *MBTAA* $+ 1\cdot33\,M\,Zn^{+2}$; (3) $4\cdot10^{-3}M$ *MBTAA* $+ 2\cdot10^{-3}M\,Zn^{+2}$; (4) $4\cdot10^{-3}M$ *MBTAA* $+ 4\cdot10^{-3}M\,Zn^{+2}$

$$M^{+2} + H_2A + 2\,OH^- \rightleftharpoons MA + 2\,H_2O \qquad (2)$$

On further addition of NaOH, an inflection at $\simeq$ 3 mol of NaOH per 1 mol of ligand is observed, which may be attributed to the disproportionation of the 1 : 1 chelate into the more stable 1 : 2 chelate and corresponding hydroxide in accordance with the equation

$$MA + OH^- \rightleftharpoons 1/2\,[M(A)_2]^{-2} + 1/2\,[M(OH)_2] \qquad (3)$$

Addition of NaOH beyond 3 mol of NaOH per 1 mol of ligand causes another inflection at $\simeq$ 4 mol of NaOH per mol of ligand due to the decomposition of 1 : 2 chelate into disodium salt of acid and metal hydroxides in accordance with the equation

$$1/2\,[M\,(A)_2]^{-2} + 2\,\mathrm{OH}^- \rightleftharpoons A^{-2} + 1/2\,M\,(\mathrm{OH})_2 \qquad (4)$$

When 2 mol of ligand are added to M^{+2} (Fig. 1, curve 3) the curve shows two inflections at 2 and 3 mol of NaOH per mol of ligand which corresponds to the formation of 1 : 2 chelate and its decomposition into disodium salt of acid and hydroxide in accordance with the equation:

$$1/2\,M^{+2} + \mathrm{H}_2A + 2\,\mathrm{OH}^- \rightleftharpoons 1/2\,[M\,(A)_2]^{-2} + 2\,\mathrm{H_2O} \qquad (5)$$

$$1/2\,[M\,(A)_2]^{-2} + \mathrm{OH}^- \rightleftharpoons A^{-2} + 1/2\,M\,(\mathrm{OH})_2 \qquad (6)$$

which have been further confirmed by the inflection at $\simeq$ 2 and 2.66 mol of NaOH per mol of ligand (Fig. 1, curve 2) when the ratio of metal to ligand has decreased to 1 : 3.

Conductometric Studies

Conductometric titrations of the solutions containing metal ions and the ligand mixed in different ratios were also performed against standard 0.1 *M* NaOH and the titration curves revealed the formation of 1 : 1 and 1 : 2 complexes in all cases as obtained from *pH* titration curves.

Computation of Stability Constants

Calvin and *Melchior*'s[5] extension of *Bjerrum*'s[6] method was used for determining the stability constants of the complexes from potentiometric titration data and their values were further refined by least square treatment[7], convergence formula[7] and the correction term[8] method.

The results (Table 1) reveal that Pb^{+2}, Zn^{+2} and Cd^{+2} form 1 : 1 and 1 : 2 complexes and the sequence of stability has the order

$$\mathrm{Pb}^{+2} > \mathrm{Zn}^{+2} > \mathrm{Cd}^{+2}$$

which is in accordance with the *Irving-Williams* series. The values of overall stability constants increase with temperature which shows that higher temperature is favourable for the formation of complexes and for their stabilities.

Table 1. *Values of the stability constant for* Pb^{+2}, Zn^{+2} *and* Cd^{+2} *complexes with MBTAA at 20°, 30° and 40 °C*

Methods[a]	Constants[b]	20 °C			30 °C			40 °C		
		Pb^{+2}	Zn^{+2}	Cd^{+2}	Pb^{+2}	Zn^{+2}	Cd^{+2}	Pb^{+2}	Zn^{+2}	Cd^{+2}
[A]	$\log K_1$	3.00	2.92	2.84	3.38	3.27	3.16	3.83	3.57	3.45
	$\log K_2$	2.65	2.74	2.65	2.74	2.88	2.74	2.94	3.08	2.94
	$\log \beta$	5.65	5.66	5.49	6.12	6.15	5.90	6.77	6.65	6.39
[B]	$\log K_1$	3.02	2.88	2.82	3.35	3.28	3.10	3.85	3.52	3.48
	$\log K_2$	2.60	2.72	2.63	2.75	2.77	2.80	2.85	3.10	2.92
	$\log \beta$	5.62	5.60	5.45	6.10	6.05	5.90	6.70	6.62	6.40

[a] [A] and [B] represent *Bjerrum*'s and the least square methods, respectively.

[b] The log K_{stab} values obtained by correction term and *Schrodinger*'s convergence formula are in close proximity with those obtained from [A] and [B] but they are not recorded for the sake of brevity.

Thermodynamic Functions

From the variation of stability constants of the complexes with temperature, the values of change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying the complexation reactions have been determined at 30 °C by applying the standard equations[9] (Table 2).

Table 2. *Thermodynamic parameters*

Metal complex	$(-)\ \Delta G$ (K cal/mol)	$(-)\ \Delta H$ (K cal/mol)	$(-)\ \Delta S$ (cal/deg/mol)
Pb^{+2}	8.46	22.60	42.40
Zn^{+2}	8.44	20.70	40.44
Cd^{+2}	8.17	18.28	33.34

The negative values of ΔG show that the driving tendency of the complexation reaction is from left to right and the reaction tends to proceed spontaneously. The values of enthalpy changes are negative indicating the exothermic nature of the reaction and the changes in entropy (negative) is related to the decrease in the number of particles on complex formation.

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