Stability constants and Related Thermodynamic Functions of Cu^{+2}, Ni^{+2}, Co^{+2} and Mn^{+2} complexes of Methylenebis (thioacetic acid)

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Summary: The stability constants of Cu^{+2}, Ni^{+2}, Co^{+2} and Mn^{+2} complexes of methylenebis(thioacetic acid) have been determined in aqueous media at μ=0.1M ($NaClO_4$) and 20°, 30° and 40°C employing Bjerrum-Calvin pH titration technique and refined by alternative methods. The stability of complexes follows the order:-

$$Cu^{+2} > Ni^{+2} > Co^{+2} > Mn^{+2}$$

The free energy, enthalpy and entropy changes involved in the complexation have also been evaluated at 30°C.

Introduction

Mercapto compounds have several applications in biological, pharmaceutical and other chemical fields and are well known to form complexes with various metals. Saxena and coworkers [1-3] have carried out significant investigations on the electrochemical behaviour of several biologically active organo-sulphur compounds and their complexation behaviour with metals. This communication reports the formation and composition of Methylenebis (thioacetic acid) complexes with Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2} and determination of their stability constants at 20°, 30° and 40°C emplying Bjerrum-Calvin pH titration technique and evaluation of changes in free energy, enthalpy and entropy accompanying the complexation.

Experimental

Methylenebis (thioacetic acid) (referred herein as MBTAA) was obtained from Evan's Chemetics Inc. New York and all other chemicals used were of Analar grade. Metal salts viz. copper sulphate, nickel sulphate, cobalt chloride and manganese chloride were used and the metal contents were estimated by standard methods from their respective solutions. Fresh solutions of MBTAA were prepared to avoid any effects of ageing and oxidation.

pH measurements were made on a Toshniwal digital pH meter (accuracy $\pm$ 0.01 pH) with glass calomel electrode assembly. Conductance was measured on an electronic eye type conductometer. The temperature of the cell was maintained by thermostat having an accuracy of $\pm$ 0.1°C. The experimental procedure as described earlier [2,3] involved a series of pH and conductometric titrations of MBTAA with standard 0.1M NaOH in the absence and presence of metal ion at various ligand to metal ratios.

The values of log K_1 and log K_2 were read directly from the formation curves at n values of 0.5 and 1.5 respectively.

Results and Discussion

Stiochiometry

To establish the stoichiometry of the complex species formed during the interaction of M^{+2} (Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}) and methylenebis (thioacetic acid), the magnitude of proton displacement was determined by pH titration of solutions containing 4 x 10^{-3} MBTAA (Fig.1; curve 1) and 4 x 10^{-3} MBTAA with different concentrations of M^{+2} ions viz. 1.33 x 10^{-3}M, 2 x 10^{-3}M, 4 x 10^{-3}M (fig.1; curve 2, 3 & 4) against 0.1M.NaOH. For the sake of brevity only figure 1 representing titrations with Cu^{+2} ions has been given.

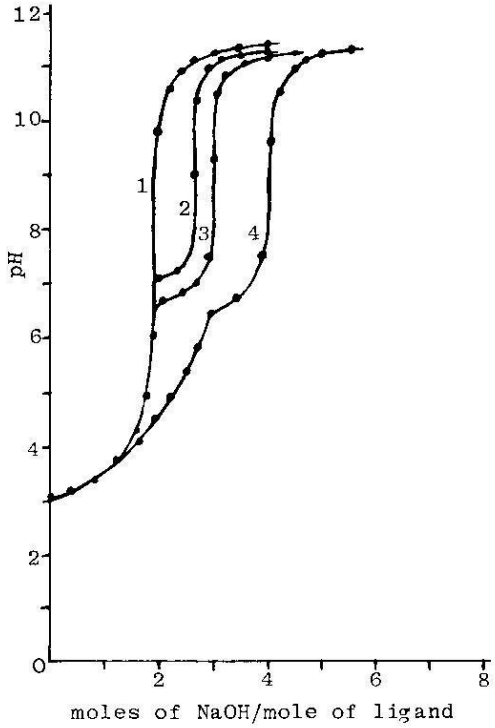

Fig.1: pH meteric titration of the solution

Curve (1) 4 x 10^{-3}M MBTAA

(2) 4x10^{-3}M MBTAA+1.33 M Cu^{+2}

(3) 4x10^{-3}M MBTAA+2x10^{-3}M Cu^{+2}

(4) 4x10^{-3}M MBTAA+4x10^{-3}M Cu^{+2}

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

$$A = \begin{array}{l} S\text{-}CH_2COO^- \\ | \\ CH_2 \\ | \\ S\text{-}CH_2.COO^- \end{array}$$

the reaction between 'm' interval of 0-2 may be represented in a single step by the equation

$$H_2A + 2OH^- \longrightarrow A^{-2} + 2H_2O \quad (1)$$

The absence of an inflection at 1 mole 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 Cu^{+2}, Ni^{+2}, Co^{+2} and Mn^{+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 expressed as

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

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

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

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

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

When two moles of ligand are added to M^{+2} (Fig.1, curve 3), two inflections at 2 and 3 moles of NaOH per mole of ligand are observed which correspond to the formation of 1:2 chelate and its decomposition into disodium salt of acid and hydroxide.

$$1/2M^{+2} + H_2A + 2OH^{-} \rightleftharpoons 1/2[M(A)_2]^{-2} + 2H_2O \quad (5)$$

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

which is further confirmed by the inflection at 2 and 2.66 moles of NaOH per mole of ligand (Fig.1, curve 2) when the ratio of metal to ligand has decreased to 1:3.

Conductometric studies

Conductometric titrations of solutions containing metal ions and the ligand mixed in different ratios against O.1M NaOH were also performed and the breaks in titration curves revealed the formation of 1:1 and 1:2 [M:L] complexes as obtained from pH titration data.

Computation of Stability Constants

Calvin and Melchior's [4] extension of Bjerrum's [5] method was used for determining the stability constants of the complexes from potentiometric titration data and their values were further refined by 1) Least square treatment [6], 2) convergence formula [6], and the correction term method [7].

The values of log K_1 and log K_2 at 20°, 30° and 40°C were read directly from the formation curves at $\bar{n}$ = 0.5 and $\bar{n}$ = 1.5 (not given for the sake of brevity). These values increase with temperature which shows that higher temperature is favourable for the formation of stable complexes and follow the order

$Cu^{+2} > Ni^{+2} > Co^{+2} > Mn^{+2}$ (Table 1)

Thermodynamic Functions

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complexation reaction have been determined at 30°C with the help of Gibbs Helmholtz and isobar equations [8].

The value of the ΔG is obtained from the expression

$$\Delta G = - RT\ In\beta$$

ΔH is determined with the help of an isobar $(d\ In\ \beta)/dt = \Delta H/RT^2$,

Table-1: Log K_{stab} values of Cu^{+2}, Ni^{+2}, Co^{+2} and Mn^{+2} complexes with MBTAA at 20°, 30° and 40°C

Method	Log K_{stab}	20°C				30°C				40°C			
		Cu^{+2}	Ni^{+2}	Co^{+2}	Mn^{+2}	Cu^{+2}	Ni^{+2}	Co^{+2}	Mn^{+2}	Cu^{+2}	Ni^{+2}	Co^{+2}	Mn^{+2}
[A]	log K_1	3.29	3.19	2.92	2.72	3.76	3.62	3.27	2.99	4.12	4.12	3.70	3.34
	log K_2	2.74	2.65	2.68	2.63	2.94	2.78	2.83	2.71	3.25	3.01	3.00	2.83
	log β	6.03	5.84	5.60	5.35	6.70	6.40	6.10	5.70	7.37	7.13	6.70	6.17
[B]	log K_1	3.30	3.16	2.90	2.73	3.75	3.60	3.25	2.96	4.10	4.11	3.68	3.35
	log K_2	2.67	2.65	2.66	2.52	2.88	2.83	2.71	2.78	3.22	2.98	3.05	2.72
	log β	5.97	5.81	5.56	5.25	6.63	6.43	5.96	5.75	7.32	7.09	6.73	6.07

[A] and [B] represent Bjerrum and the least square methods respectively. The log K_{stab} values obtained by correction term and Schrodingers convergence formulas are in close proximity with those obtained from [A] and [B] but they are not recorded for the sake of brevity.

which may be written as

$$\frac{d(\log \beta)}{d(1/T)} = \frac{-\Delta H}{4.57}$$

The values of log β obtained at different temperatures are plotted as a function of 1/T. The gradient of the tangent drawn at the point corresponding at 30°C is determined and equated to $\frac{-\Delta H}{4.57}$, S is then evalutated from the relation

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

Metal Complexes	(-) ΔG (K cal/mol)	(-) ΔH (K cal/mole)	- ΔS (cal/deg/mol)
Cu^{+2}	9.23	27.42	60.00
Ni^{+2}	8.89	26.90	58.20
Co^{+2}	8.35	24.35	52.83
Mn^{+2}	7.92	17.36	31.27

The negative values of Δ G show that the reaction tends to proceed spontaneously. The values of enthalpy changes are negative indicating the exothermic nature of the reaction and the entropy changes are related to the decrease in the number of particles on complex formation.

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