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Potentiometric and Thermodynamic Studies of Some Metal Complexes with Carboxymethyl Mercapto Succinic Acid

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ABSTRACT

The metal ligand stability constants of carboxy methyl mercapto succinic acid with some transition metals ions have been determined in 40%(v/v) methanol –water mixture at ionic strength
μ= 0.1M (KNO_3) at three different temperature (25°,35° and 45°C) employing Bjerrum-Calvin pH titration technique. The stability of complexes follows the order- $Cu^{2+} > Ni^{2+} > Mn^{2+}$
The free energy, enthalpy and entropy changes involved in the complexation have also been evaluated at 35°C in 40%(v/v) methanol – water mixture.

Keywords: Potentiometry, Methanol, Stability constant, Free energy,Enthalpy.

INTRODUCTION

Mercapto compounds have several applications in biological, pharmaceutical and other chemical fields and are well known to form complexes with various metals. Gupta and coworker have carried out significant investigation on the electrochemical behavior of several biologically active organo-sulphur compounds and their complexation behavior with metals [8,9,10].
Carboxy methyl mercapto succinic acid has coolant additive with corrosion inhibitor and scale preventive property [4]. The complex ester of CMMSA may be used directly as lubricants or may be blended with other mineral or synthetic lubricants and various additive and it is also used as adhesive,oxidation inhibitor, detergents and corrosion resisting agents[1,14,5].In view of wide pharmaceutical and analytical applications of CMMSA, it seems interesting to study the complexation equilibria of CMMSA with some transition metals in 40%(v/v) methanol – water mixture. This communication reports the formation, stability constants, and thermodynamic parameters of Ni^{2+}, Cu^{2+},Mn^{2+}, complexes with CMMSA employ potentiometric technique. The log K_{stab} values determined at 25°,35°,and 45°C by Calvin and Melchior's extension of Bjerrum's method [3,2].The stability constant have been further determined by correction term and Schroder's convergence formula[6,11].

MATERIAL AND METHODS

All the chemicals used for experiment, such as methanol, potassium nitrate, nitric acid and CMMSA. etc were of analytical grade, Double distilled water was used in preparation of various solutions. All the metal ion solutions were prepared in double distilled water and standardized by using conventional procedures[12].A carbonate free sodium hydroxide was used as a titrate and standardized against oxalic acid. The pH measurements were carried out with 335-Systronic pH meter (accuracy±0.05 units) using glass and calomel electrode. The electrode system was calibrated by using standard buffer solutions of pH 4.00, 7.00, 9.2. The empirical correction to pH meter reading in methanol medium was corrected according to Van-Uitert and Hass relation[13].The following sets of titrations were performed under nitrogen atmosphere at ionic strength μ = 0.1 M (KNO_3)at temperature 25°,35°,45°C in 40% methanol – water mixtures against 0.1 M NaOH .The temperature were controlled by an electrically maintained thermostat.

(i) Free HNO_3 (2.0×10^{-3} M)
(ii) Free HNO_3 (2.0×10^{-3} M) + Ligand (2.0×10^{-3} M)
(iii) Free HNO_3 (2.0×10^{-3} M) + Ligand (2.0×10^{-3} M) + metal ion solution (4.0×10^{-4}).

The log K_{stab} values determined at 25°,35°,and 45°C by Calvin and Melchior's extension of Bjerrum's method [3,2].The stability constant have been further determined by correction term and Schroder's convergence

formula[6,11].The thermodynamic parameter for binary complex systems were calculated by Gibb's Helmholtz and Isobar equation [15].

RESULTS AND DISCUSSION

Identical titration curves were obtained for the different binary system under investigation, according to the sequence described in experimental section. For the sake of brevity only. Figures (1,2,3) are representing formation curves of metal ions .

Plots of $\bar{n}$ as a function of – log C

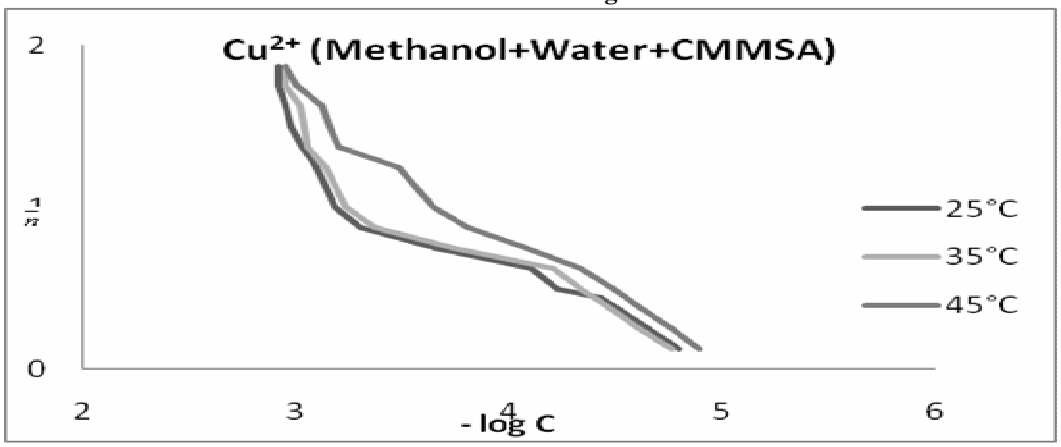

Fig.-1

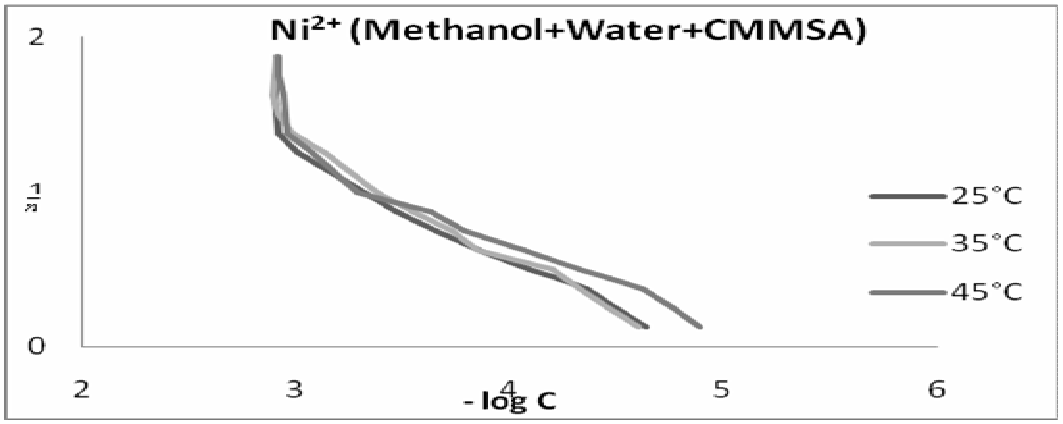

Fig.-2

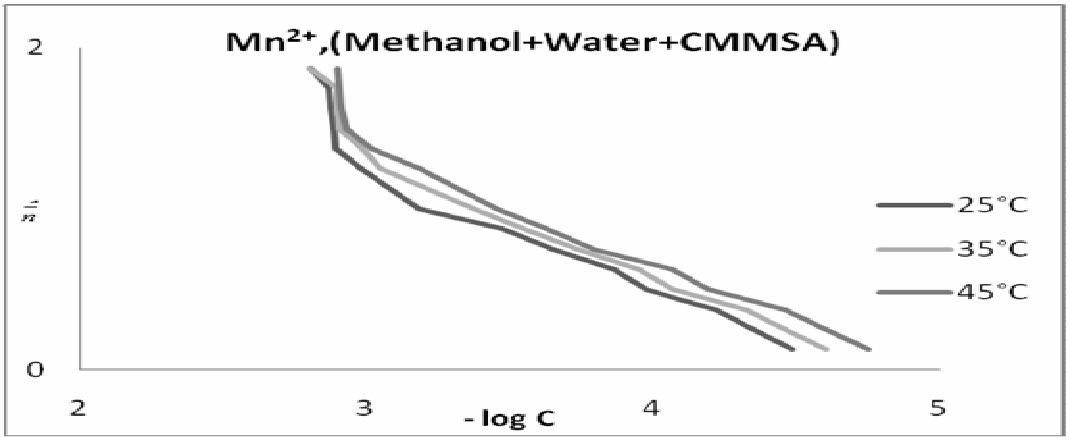

Fig.-3

Metal-ligand stability constant

Calvin and Melchior's extension of Bjerrum's method was used for determining stability constant of the complexes from potentiometric titration data and their values were further determined by Schroder's Convergence formula and Correction term method the values of stability constants are given in Table-1 [2,11,7].

Table-1: Metal Ligand Stability Constant of Complexes of Cu^{2+}, Ni^{2+} AND Mn^{2+} with CMMSA in 40% (V/V) Methanol- Water Mixture at Different temperature and Ionic Strength μ = 0.1 M (KNO_3)

Metal Complexes	Method	Temperature								
		25°			35°			45°		
		$logK_1$	$logK_2$	$log\,\beta$	$logK_1$	$logK_2$	$log\,\beta$	$logK_1$	$logK_1$	$log\,\beta$
Cu^{2+}	a	4.23	2.98	7.21	4.34	3.04	7.38	4.47	3.16	7.63
	b	4.16	3.06	7.22	4.27	3.11	7.38	4.41	3.23	7.64
	c	4.23	2.97	7.20	4.38	3.00	7.38	4.52	3.16	7.68
	Mean value	4.21	3.00	7.21	4.33	3.05	7.38	4.47	3.18	7.65
Ni^{2+}	a	4.10	2.91	7.01	4.20	2.92	7.12	4.07	2.91	6.98
	b	4.03	3.00	7.03	4.12	2.99	7.11	3.97	3.03	7.00
	c	4.14	2.91	7.05	4.19	2.96	7.15	4.08	2.93	7.01
	Mean value	4.09	2.94	7.03	4.17	2.96	7.13	4.04	2.96	7.00
Mn^{2+}	a	3.97	2.87	6.84	4.07	3.91	6.98	4.19	2.93	7.12
	b	3.85	2.99	6.84	3.97	3.03	7.00	4.11	3.01	7.12
	c	3.99	2.85	6.84	4.08	2.93	7.01	4.19	2.94	7.13
	Mean value	3.94	2.90	6.84	4.04	2.96	7.00	4.16	2.96	7.12

Method a,b and c represent Bjerrum's Method, Schroder's convergence formula and Correction Term Method respectively.

The values of log K_1 and log K_2 at 25°,35°,and 45°C were read directly from the formation curves at $\bar{n}$= 0.5 and $\bar{n}$=1.5 (fig-i,ii,iii). These values increases with temperature which shows that higher temperature is favorable for the formation of stable complexes and follow the order

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

Which is in agreement with Irving-Williams order of stability [7].

THERMODYNAMIC FUNCTIONS-

The values of overall changes in free energy (ΔG),enthalpy (ΔH) and entropy (ΔS) accompanying complex reactions have been determined at 35°C with the help of Gibbs –Helmholtz and Isobar equation the values of ΔG, ΔH and ΔS in 40%(V/V) methanol -water mixture are given in Table-2[15].

Table-2:Termodynamic Parameters (ΔG),(ΔH) and (ΔS) of Complexes of Cu^{2+}, Ni^{2+} and Mn^{2+} with CMMSA at 35°C

Metal Complexes	ΔG =$KJMOL^{-1}$ (-ve)	ΔH= $KJMOL^{-1}$ (-ve)	ΔS =$JMOL^{-1}K^{-1}$ (+ve)
Cu^{2+}	43.52	40.02	11.36
Ni^{2+}	42.05	38.87	10.32
Mn^{2+}	41.28	38.29	9.71

The negative value of free energy (ΔG) shows that the reaction tends to proceed spontaneously. The values of enthalpy changes are negative indication the exothermic nature of the reaction and the positive values of the entropy changes confirming that the complex formation is entropically favorable.

CONCLUSION

An examination of the Tables-1 and 2 shows that –

1. The decrease in pH for metal ligand titration curves relative to ligand titration point to formation of metal complexes.
2. The maximum value of $\bar{n}$ was ≈ 2 indicating the formation of 1:1 and 1:2 (metal -ligand) complexes only.
3. The stability constant (log $K_1$and log K_2) for the ligand complexes increases with the increasing temperature i.e. the stability constants increase with increasing temperature.
4. At constant temperature the stability constant of the complexes follows the order-

$$Mn^{2+} < Ni^{2+} < Cu^{2+}$$

Which is in agreement with Irving-Williams order of stability [7].

5. The negative value of free energy change (ΔG) for the complexation process suggest the spontaneous nature of the process.
6. The negative values of enthalpy change suggest that formation of these complexes is an exothermic process.
7. Positive values of the entropy changes confirming that the complex formation is entropically favorable.

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