



## Potentiometric and Thermodynamic Studies of Some Metal Complexes with Carboxy Methyl Mercapto Succinic Acid

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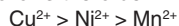
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### ABSTRACT

The metal ligand stability constants of carboxy methyl mercapto succinic acid with some transition metals ions have been determined in dioxane –water mixture at ionic strength  $\mu=0.1\text{M}(\text{KNO}_3)$  at three different temperature (25°, 35° and 45°C) employing Bjerrum-Calvin pH titration technique. The stability of complexes follows the order.



The free energy, enthalpy and entropy changes involved in the complexation have also been evaluated at 35°C in 40%(v/v) dioxane – water mixture.

**Key words:** Free energy, Dioxane, Potentiometry, Stability constant.

### 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<sup>1-4</sup> have carried out significant investigation on the electrochemical behavior of several biologically active organo-sulphur compounds and their complexation behavior with metals.

Carboxy methyl mercapto succinic acid has coolant additive with corrosion inhibitor and scale preventive<sup>5</sup> property. The complex ester of c.m.m.s.a. may be used directly as lubricants<sup>6</sup>, or

may be blended with other mineral or synthetic lubricants and various additive and it is also used as adhesive<sup>7</sup>, biodegradable, bleach –stabilizers for detergents<sup>8</sup>. In view of wide pharmaceutical and analytical applications of c.m.m.s.a., it seems interesting to study the complexation equilibria of c.m.m.s.a. with some transition metals in dioxane – water mixture. This communication reports the formation, stability constants, and thermodynamic parameters of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ , complexes with c.m.m.s.a. by employing potentiometric technique. The  $\log K_{\text{stab}}$  values determined at 25°, 35°, and 45°C by Calvin and Melchior's extension<sup>9</sup> of Bjerrum's method<sup>10</sup>. The stability constant have been further determined by correction term<sup>11</sup> and Schroder's convergence formula<sup>12</sup>.

### MATERIALS AND METHOD

All the chemicals used for experiment, such as dioxane, potassium nitrate, nitric acid and c.m.m.s.a. 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<sup>13</sup>. 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 $\pm$ 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 dioxane medium was corrected according to Van-Uitert and Hass relation<sup>14</sup>. The following sets of titrations were performed under nitrogen atmosphere at ionic strength  $\mu = 0.1$  M ( $\text{KNO}_3$ ) at temperature 25°, 35°, 45°C in 40%(v/v) dioxane – water mixtures against 0.1 M NaOH. The temperature were controlled by an electrically maintained thermostat.

- (i) Free  $\text{HNO}_3$  ( $2.0 \times 10^{-3}$  M)
- (ii) Free  $\text{HNO}_3$  ( $2.0 \times 10^{-3}$  M) + Ligand ( $2.0 \times 10^{-3}$  M)
- (iii) Free  $\text{HNO}_3$  ( $2.0 \times 10^{-3}$  M) + Ligand ( $2.0 \times 10^{-3}$  M) + metal ion solution ( $4.0 \times 10^{-4}$ ).

The  $\log K_{\text{stab}}$  were values determined at 25°, 35°, and 45°C by Calvin and Melchior's extension<sup>9</sup> of Bjerrum's method<sup>10</sup>. The stability constant have been further determined by correction term<sup>11</sup> and Schroder's convergence formula<sup>12</sup>. The thermodynamic parameter for binary complex systems were calculated by Gibb's Helmholtz and Iso-bar equation<sup>16</sup>.

### 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 fig (1,2,3) representing formation curves of metal ions have been given.

**Table 1: Metal ligand stability constant of complexes of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  with C.M.M.S.A. In 40%(v/v) dioxane-water mixture at different temperature and ionic strength  $\mu = 0.1$  m ( $\text{kno}_3$ )**

Metal Complexes	Method	Temperature								
		25°			35°			45°		
		$\log K_1$	$\log K_2$	$\log \beta$	$\log K_1$	$\log K_2$	$\log \beta$	$\log K_1$	$\log K$	$\log \beta$
$\text{Cu}^{2+}$	a	4.46	3.17	7.63	4.64	3.32	7.96	4.78	3.47	8.25
	b	4.39	3.25	7.64	4.57	3.39	7.96	4.72	3.54	8.26
	c	4.39	3.26	7.65	4.57	3.37	7.94	4.73	3.54	8.27
Mean Value		4.41	3.23	7.64	4.59	3.36	7.95	4.74	3.52	8.26
$\text{Ni}^{2+}$	a	4.32	3.08	7.40	4.46	3.12	7.58	4.60	3.24	7.84
	b	4.24	3.16	7.40	4.40	3.19	7.59	4.59	3.24	7.83
	c	4.34	3.11	7.45	4.47	3.14	7.61	4.63	3.25	7.88
Mean Value		4.30	3.12	7.42	4.44	3.15	7.59	4.59	3.26	7.85
$\text{Mn}^{2+}$	a	4.06	2.94	7.00	4.18	2.98	7.16	4.32	3.12	7.44
	b	3.95	3.05	7.00	4.09	3.07	7.16	4.22	3.18	7.40
	c	3.94	3.04	6.98	4.08	3.07	7.15	4.21	3.19	7.40
Mean Value		3.98	3.01	6.99	4.12	3.04	7.16	4.25	3.16	7.41

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

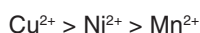
**Table 2: Thermodynamic parameter ( $\Delta G$ ), ( $\Delta H$ ) and ( $\Delta S$ ) of complexes of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  with C.M.M.S.A. AT 35°C**

Metal Complexes	$\Delta G = \text{KJ MOL}^{-1}$ (-ve)	$\Delta H = \text{KJ MOL}^{-1}$ (-ve)	$\Delta S = \text{J MOL}^{-1} \text{K}^{-1}$ (+ve)
$\text{Cu}^{2+}$	46.88	40.40	21.04
$\text{Ni}^{2+}$	44.76	39.63	16.65
$\text{Mn}^{2+}$	42.22	38.29	12.76

**Metal-ligand stability constant**

Calvin and Melchior's extension of Bjerrum's<sup>9</sup> 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<sup>11</sup> and Correction term method<sup>14</sup> the values of stability constants are given in Table 1.

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-1,2,3). These values increases with temperature which shows that higher temperature is favorable for the formation of stable complexes and follow the order



Which is in agreement with Irving-Williams order of stability<sup>14</sup>

**Thermodynamic Functions**

The values of overall changes in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) accompanying complex reactions have been determined at 35°C with the help of Gibbs – Helmholtz and Isobar equation<sup>15</sup> the values of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  in 40% (v/v) dioxane -water mixture are given in Table -2. The negative value of free energy ( $\Delta G$ ) shows that the reaction tends to proceed spontaneously. The values of enthalpy changes are negative indicating the exothermic nature of the reaction and the positive values of the entropy changes confirming that the complex formation is entropically favorable.

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

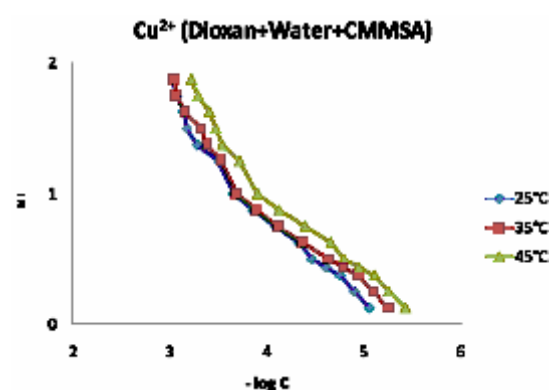


Fig. 1:

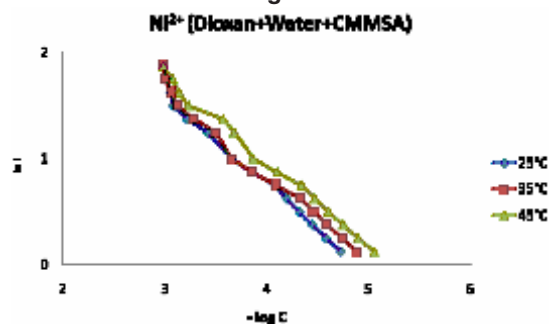


Fig. 2:

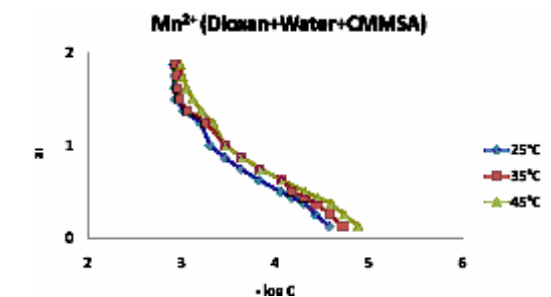


Fig. 3:

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