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POTENTIOMETRIC AND THERMODYNAMIC STUDIES OF SOME TRANSITION METAL COMPLEXES WITH ORTHO-MERCAPTOBENZOIC ACID IN METHANOL-WATER MEDIUM

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ABSTRACT

The complex formation equilibria of some metal ions [Zn (II), Co (II), Ni (II), Cu (II)] with ortho mercaptobenzoic acid were determined by pH-titration method at constant ionic strength $\mu = 0.1$ M (KNO_3) at three different temperatures (25°C, 35°C, 45°C) in 40% (v/v) methanol-water and in 60% (v/v) methanol-water mixture at 25°C. The stability constants of various complexes were determined by various computational methods. The stability constants are in fair agreement with Irving-Williams order. The thermodynamic parameters have been calculated only for 40% (v/v) methanol-water mixture.

Key words: Potentiometry, Stability constant, Free energy, Entropy, Enthalpy, ortho-Mercaptobenzoic acid.

INTRODUCTION

Co-ordination compounds play an important role in numerous chemical and biological systems like water softening, ion exchange resin, electroplating dyeing, antioxidants, removal of undesirable and harmful metals from living organisms. Thiols and thioacids containing an active-SH group have been reported to form complexes with some metals[1-3]. Ortho-mercaptobenzoic acid (OMBA) is an organo sulphur compound containing carboxylic and sulfhydryl functional groups. Both functional groups participate in binding[4]. It forms chelate complexes with variety of metal ions[5]. OMBA is a moiety of thiomersal (an organomercurial) and used as an antiseptic, antifungal and bacteriostatic. It is also used as a precursor to the dyestuff thioindigo. Thiol based redox buffers are used to enhance the folding rate of disulfides containing protein *in vitro* folding rates of scrumbled ribonuclease at pH ≈ 6 – 7.8 with ortho and meta-substituted aromatic thiols were upto ten times greater than those with glutathione[6]. In view of wide pharmaceutical and analytical applications[7] of

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OMBA, it seems interesting to study the complexation equilibria of OMBA with various metal ions in methanol-water mixtures.

EXPERIMENTAL

All the chemicals used for experiment, such as methanol, potassium nitrate and nitric acid etc. were of analytical grade. OMBA (Evan chemicals USA) was commercial product and was used as such. Double distilled water was used in preparation of various solution. All the metal ion solutions were prepared in double distilled water and standardized by using conventional procedures[8]. A carbonate free sodium hydroxide was used as a titrant and standardized against oxalic acid. The pH-measurements were carried out with 335 – systronic pH meter (accuracy ± 0.05) using glass and calomel electrode.

The electrode system was calibrated by using standard buffer solution of pH 4.00, 7.00 and 9.20. The empirical correction to pH meter reading in methanol medium was corrected according to Van-Uitert and Hass relation[9]. The following sets of titration were performed under nitrogen atmosphere at ionic strength $\mu = 0.1$ M (KNO_3) at temperature 25°C, 35°C and 45°C in 40% (v/v) methanol-water mixtures and at 25°C temperature in 60% (v/v) methanol-water system against 0.1 M NaOH. Temperature were controlled by 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 soln. (4.0×10^{-4} M)

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 representing formation curves of metal ions have been given.

Proton ligand stability constants : OMBA has two protons pKa_1, corresponds to release of proton from carboxylic group, pKa_2 corresponds to release of proton from sulfhydryl group. The pKa values were calculated by Albert and Seargent method[10].

The values of proton-ligand stability constant of OMBA in methanol-water have been given in Table 1.

Table 1: Proton-ligand stability constant of OMBA in methanol-water

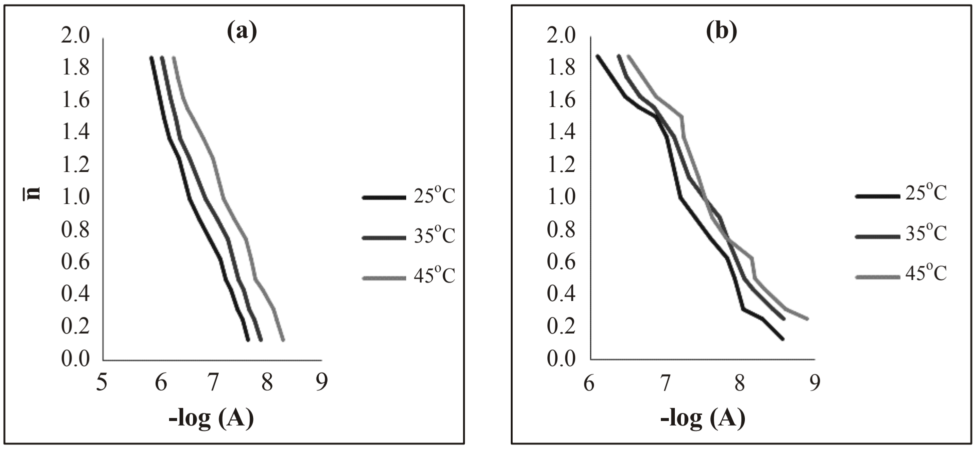
S. No.	% of Methanol	pKa$_1$			pKa$_2$		
		25°C	35°C	45°C	25°C	35°C	45°C
1	40% Methanol	4.77	4.65	4.56	9.39	9.27	9.18
2	60% Methanol	5.02	-	-	9.66	-	-

The proton ligand stability constants of OMBA (Table 1) increases (become less acidic) with increasing composition of methanol in methanol-water mixture. It should be noted that as predicted by Born-equation, the creation of charge in media of low dielectric constant is an unfavourable process hence resulting in higher pKa values which were higher in 60% (v/v) melthanol water mixture.

Metal-ligand stability constant

Calvin and Melchior's[11] Extension of Bjerrum[12] method was used for determining stability constants of the complexes from potentiometric titration data and their values were further determined by Schroder's convergence formula[13] and correction term method[14]. The values of stability constants are given in Table 2.

The values of log K_1 and log K_2 were read directly from the formation curves at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ (Fig. 1). These values increases with temperature, which shows that higher temperature is favourable for the formation of stable complexes and follow the order Cu (II) > Zn (II) > Ni (II) > Co (II), which is in agreement with Irving williams order of stability[15]. The values of metal ligand stability constants are greater in 60% (v/v) as compared to 40% (v/v) methanol water mixtures at the same temperature.



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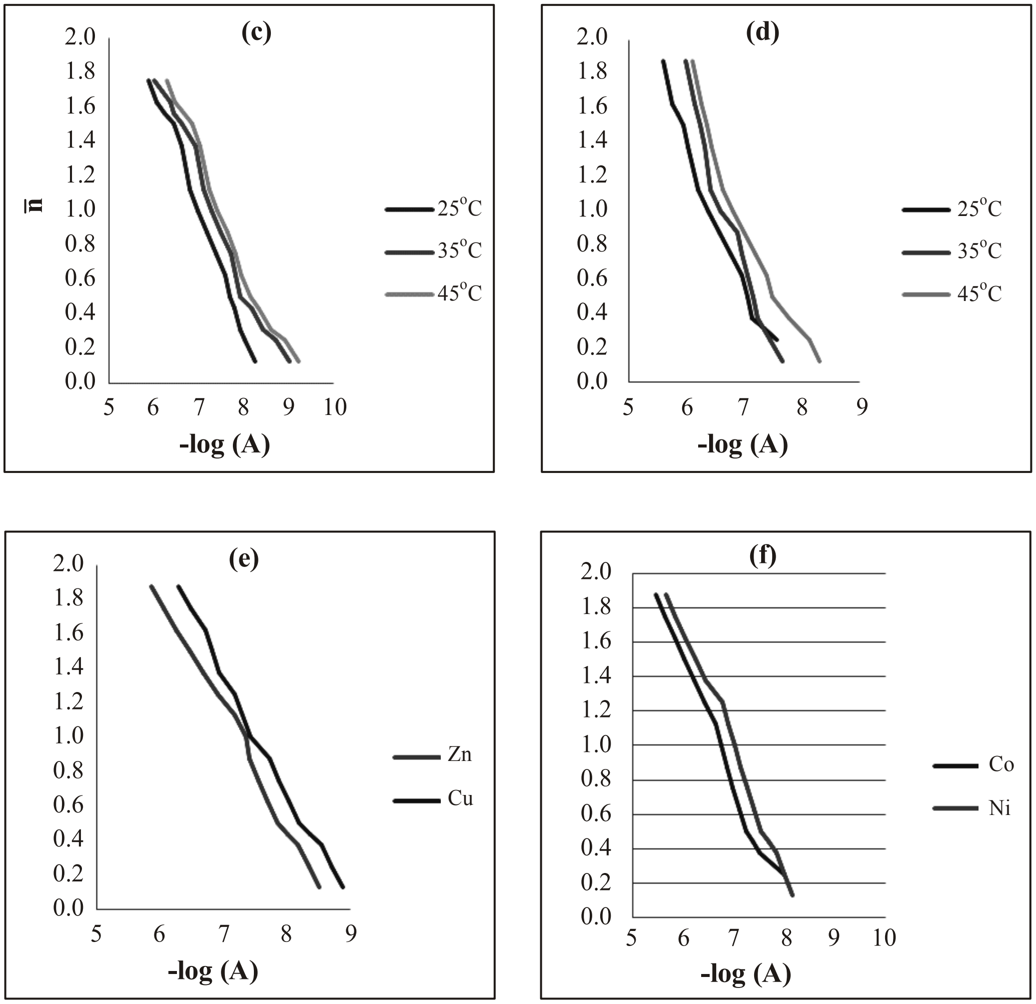

Fig. 1: $\bar{n}$ Plots of as a functiion of log [A] in 40% MeOH-water mixture for complexes of (a) Ni (II), (b) Cu (II), (c) Zn (II), (d) Co (II) at 25°C, 35°C, 45°C and in 60% methanol-water mixture for complexes of (e) Zn (II) Cu (II) (f) Co (II) Ni (II) at 25°C temp.

Thermodynamic functions

The values of overall change 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[16]. The values of ΔG, ΔH and ΔS in 40% v/v methanol water mixture are given in Table 3.

Table 2: Metal ligand stability constant of complexes of Cu (II), Zn (II), Ni (II) and Co (II) with OMBA in methanol - water mixture at different temperature and $\mu = 0.1$ M (KNO_3)

Metal complexes	Method	40% v/v Methanol - water mixture									60% Methanol - water mixture		
		25°C			35°C			45°C			25°C		
		log K_1	log K_2	log β	log K_1	log K_2	log β	log K_1	log K_2	log β	log K_1	log K_2	log β
Cu (II)	A	7.93	6.64	14.57	8.05	6.84	14.89	8.20	7.06	15.26	8.19	6.81	15.00
	B	7.86	6.71	14.57	8.11	6.93	15.04	8.09	7.16	15.25	8.13	6.86	14.99
	C	7.89	6.63	14.52	8.07	6.87	14.94	8.17	7.06	15.25	8.16	6.85	15.01
	Mean value	**7.89**	**6.66**	**14.55**	**8.08**	**6.88**	**14.96**	**8.16**	**7.09**	**15.25**	**8.16**	**6.84**	**15.00**
Zn (II)	A	7.70	6.44	14.14	7.93	6.64	14.57	6.85	6.85	15.00	7.85	6.45	14.30
	B	7.62	6.51	14.13	7.85	6.71	14.56	6.93	6.93	15.00	7.79	6.51	14.30
	C	7.62	6.50	14.12	7.92	6.73	14.65	6.93	6.93	15.03	7.78	6.48	14.26
	Mean value	**7.65**	**6.48**	**14.13**	**7.90**	**6.69**	**14.59**	**6.90**	**6.90**	**15.04**	**7.81**	**6.48**	**14.29**
Ni (II)	A	7.25	6.13	13.38	7.58	6.33	13.91	7.79	6.65	14.44	7.53	6.23	13.76
	B	7.25	6.14	13.39	7.47	6.54	14.01	7.75	6.63	14.38	7.45	6.31	13.76
	C	7.29	6.13	13.42	7.60	6.33	13.93	7.76	6.63	14.39	7.45	6.27	13.72
	Mean value	**7.26**	**6.13**	**13.40**	**7.55**	**6.40**	**13.95**	**7.77**	**6.64**	**14.41**	**7.48**	**6.27**	**13.75**
Co (II)	A	7.04	5.93	12.97	7.14	6.23	13.37	7.48	6.35	13.83	7.23	6.02	13.25
	B	6.93	6.05	12.98	7.12	6.25	13.37	7.37	6.45	13.82	7.22	6.03	13.25
	C	7.09	5.93	13.02	7.09	6.27	13.36	7.42	6.46	13.88	7.17	6.08	13.25
	Mean value	**7.02**	**5.97**	**12.99**	**7.12**	**6.25**	**13.37**	**7.42**	**6.42**	**13.84**	**7.21**	**6.04**	**13.25**

Methods A, B and C represent Bjerrum's Method, Correction Term method and Schroder Concergence formula respectively

Table 3: Thermodynamic parameters ΔG, ΔH and ΔS for Cu (II), Zn (II), Ni (II) and Co (II) with OMBA at 35°C

Metal complexes	ΔG KJ mol^{-1}	ΔH KJ mol^{-1}	ΔS $Jmol^{-1} K^{-1}$
Cu (II)	93.65	79.13	47.14
Zn (II)	86.04	74.79	36.53
Ni (II)	82.27	73.64	27.99
Co (II)	78.85	72.11	21.88

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

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