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ELECTROCHEMICAL AND THERMODYNAMIC STUDIES OF COMPLEXES OF VO (II) AND UO_2(II) WITH ORTHO-MERCAPTOBENZOIC ACID

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ABSTRACT

The interaction of UO_2(II) and VO(II) ions with orthomercoptobenzoic acid have been investigated pH metrically at constant ionic strength μ = 0.1M (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 thermodynamic parameters have been calculated only for 40% (v/v) methanol-water mixture.

Keywords : Potentiometry, Stability constant, free energy, entropy, enthalpy ortho-mercaptobenzoic acid.

INTRODUCTION

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]. Inspite of the extremely rapid development of co-ordination chemistry, the equilibrium studies of thioacids with metal ions have not yet reached maturity and in view of wide pharmaceutical and analytical applications of OMBA[7]. 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, 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 μ = 0.1 M (KNO_3) at temperature 25°C, 35°C, 45°C in 40% (v/v) methanol-water mixtures and at 25°C temperature in 60% (v/v) methanol-water system against 0.1M *NaOH*. Temperature were controlled by electrically maintained thermostat.

(i) Free HNO_3(2.0 x 10^{-3}M); (ii) Free HNO_3(2.0 x 10^{-3}M)+ligand(2.0 x 10^{-3}M); (iii) Free HNO_3(2.0 x 10^{-3}M)+ligand(2.0 x 10^{-3}M)+metal ion soln.(4.0 x 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 representative curves of $\overline{n}$ as a function of –log [A] and log β as a function of 1/T for the complexes of VO(II) and UO_2(II) have been given.

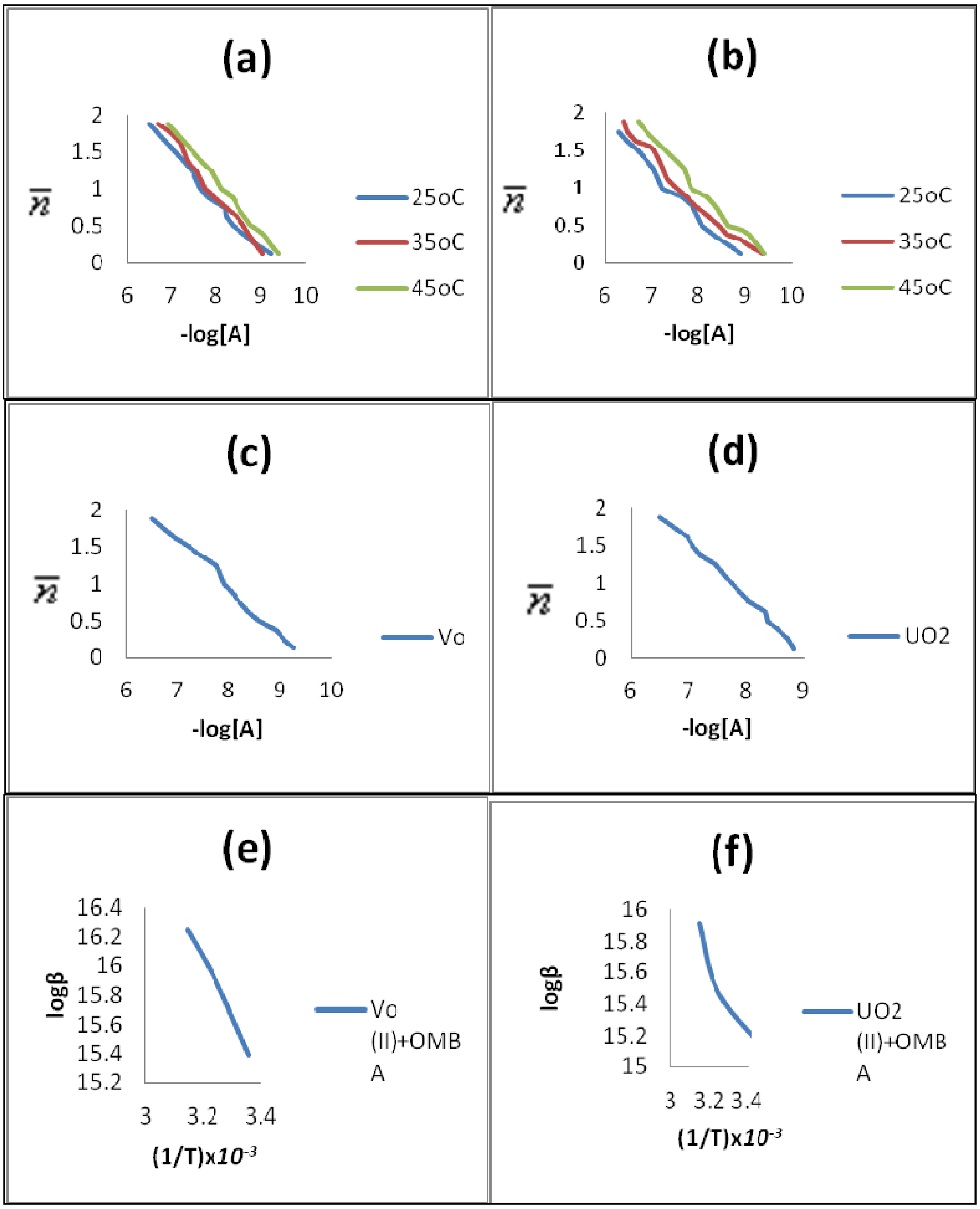

Fig.-1: plots of $\overline{n}$ as a function of -log[A] in 40% MeOH -water mixture for complexes of (a) VO(II) (b) UO_2(II) at 25°C, 35°C and 45°C and in 60% MeOH-Water mixture for complexes of (c) VO(II) and (d)UO_2 at 25°C and plots of logβ as a function of (1/T)x10-3 for (e) VO(II) (f) UO_2(II)

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 are 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

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 higher pKa values which were higher in 60% (v/v) melthanol water mixture.

Table-2: Metal Ligand Stability Constant of Complexes of VO(II), UO_2(II) with OMBA in methanol - Water mixture at different temperature and μ = 0.1M (KNO_3)

% of Methanol	Temperature	METHOD	40% Methanol - Water Mixture					
			VO(II)			UO2(II)		
			log K_1	log K_2	log β	log K_1	log K_2	log β
40%	25°C	A	8.34	6.96	15.30	8.19	6.84	15.03
		B	8.36	7.12	15.48	8.12	6.91	15.03
		C	8.33	7.06	15.39	8.23	6.78	15.01
		Mean value	8.34	7.05	15.39	8.18	6.84	15.02
40%	35°C	A	8.60	7.26	15.86	8.45	7.04	15.49
		B	8.59	7.34	15.93	8.39	7.09	15.48
		C	8.54	7.31	15.85	8.41	7.03	15.44
		Mean value	8.58	7.30	15.88	8.42	7.05	15.47
40%	45°C	A	8.76	7.47	16.23	8.62	7.27	15.89
		B	8.76	7.54	16.30	8.51	7.33	15.89
		C	8.68	7.55	16.23	8.65	7.30	15.95
		Mean value	8.73	7.52	16.25	8.59	7.30	15.91
60%	25°C	A	8.55	7.20	15.75	8.36	7.06	15.42
		B	8.54	7.21	15.75	8.29	7.13	15.42
		C	8.49	7.26	15.75	8.29	7.05	15.34
		Mean value	8.53	7.22	15.75	8.31	7.08	15.39

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

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 and correction term method[13,14].The values of stability constants have been 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. At the same temperature and composition, the values of metal ligand stability constant of VO(II) complex is greater than UO_2(II) complex. The higher stability of VO(II) complex may be attributed to the participation of 3d orbital in co-ordination, in contrast to behaviour of 5f orbitals in UO_2(II) complex. 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.

Table-3: Thermodynamic Parameters (ΔG), (ΔH), and (ΔS) for Complexes of VO(II), UO2(II) with OMBA at 35°C

Metal Complexes	ΔG KJmol^{-1}	ΔH KJmol^{-1}	ΔS Jmol^{-1}K^{-1}
VO(II)	-93.65	-79.13	47.14
UO_2(II)	-91.23	-78.10	42.63

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

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 positive values of entropy changes confirming that the complex formation is entropically favourable.

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