

Potentiometric and thermodynamic studies of VO(II), UO₂(II) complexes with carboxy methyl mercapto succinic acid

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Abstract

The metal ligand stability constants of carboxy methyl mercapto succinic acid with VO(II), UO₂(II) metals ions have been determined in 40 % (v/v) methanol – water and 40% (v/v) dioxane- water mixtures at ionic strength $\mu = 0.1 \text{ M}(\text{KNO}_3)$ at three different temperatures (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) methanol – water and 40% (v/v) dioxane- water mixtures.

Key words: Potentiometry, Methanol, Stability constant, Free energy, thermodynamic parameters.

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 coworker¹⁻³ 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 preventive⁴ property. The complex ester of CMMSA may be used directly as lubricants⁵, or may be blended with other mineral or synthetic lubricants and various additives and it is also used as adhesive⁶, oxidation inhibitor, detergents⁷ and corrosion resisting agents. In view of wide pharmaceutical and analytical applications of CMMSA, it seems interesting to study the complexation equilibria of CMMSA with VO(II), UO₂(II) in 40 % (v/v) methanol – water and 40% (v/v) dioxane-

water mixtures. This communication reports the formation, stability constants, and thermodynamic parameters of VO(II), UO₂(II) complexes with CMMSA employing potentiometric technique. The log K_{stab} values have been determined at 25°, 35°, and 45°C by Calvin and Melchior's extension⁸ of Bjerrum's method⁹. The stability constant have been further determined by correction term¹⁰ and Schroder's convergence formula¹¹. Thermodynamic parameters for binary complex systems were calculated by Van't hoff isotherm and Gibb's Helmholtz equation.

Experimental

All the chemicals used for experiment, such as methanol, dioxane, vanadyl sulphate, uranyl nitrate, potassium nitrate, nitric acid etc were of analytical grade and CMMSA (Evan's chemicals USA) was commercial product and used as such, 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 procedures¹². 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 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 relation¹³. The following sets of titrations were performed under nitrogen atmosphere at ionic strength $\mu = 0.1$ M (KNO₃) at temperature 25°, 35°, 45°C in 40% (v/v)

methanol – water and 40% (v/v) dioxane-water mixtures against carbonate free 0.1 M NaOH solution. The temperature were controlled by an electrically maintained thermostat.

- (i) Free HNO₃ (2.0 X 10⁻³ M) + KNO₃ (0.1 M)
- (ii) Free HNO₃ (2.0 X 10⁻³ M) + Ligand (2.0 X 10⁻³ M) + KNO₃ (0.1 M)
- (iii) Free HNO₃ (2.0 X 10⁻³ M) + Ligand (2.0 X 10⁻³ M) + metal ion solution (4.0 X 10⁻⁴) + KNO₃ (0.1 M).

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

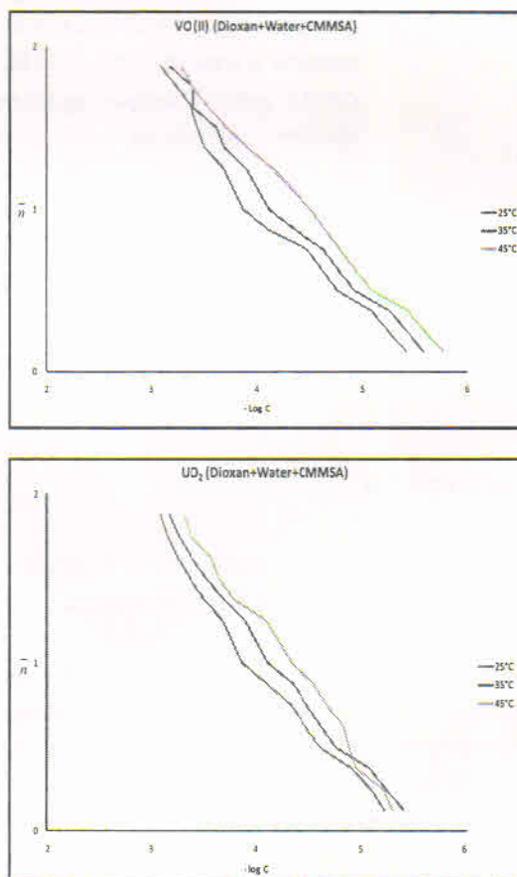


Figure 1

Observation

Table 1. Metal ligand stability constant of complexes of VO(II) and UO₂ (II) with CMMSA in 40% (V/V) methanol-water and 40% (V/V) dioxane-water mixture at different temperature and ionic strength $\mu = 0.1$ M (KNO₃)

Metal complexes	Method	TEMPERATURE								
		25°			35°			45°		
		$\log K_1$	$\log K_2$	$\log \beta$	$\log K_1$	$\log K_2$	$\log \beta$	$\log K_1$	$\log K_2$	$\log \beta$
(Methanol-water) VO(II)	a	4.68	3.38	8.06	4.80	3.52	8.32	4.92	3.70	8.62
	b	4.61	3.44	8.05	4.72	3.60	8.32	4.83	3.78	8.61
	c	4.62	3.42	8.04	4.72	3.59	8.31	4.84	3.76	8.60
	Mean value	4.64	3.41	8.05	4.75	3.57	8.32	4.86	3.75	8.61
UO ₂ (II)	a	4.52	3.30	7.82	4.64	3.44	8.08	4.78	3.61	8.39
	b	4.43	3.39	7.82	4.55	3.53	8.08	4.69	3.71	8.40
	c	4.55	3.32	7.87	4.68	3.45	8.13	4.81	3.61	8.42
	Mean value	4.50	3.34	7.84	4.62	3.47	8.09	4.76	3.64	8.40
(Dioxane-water) VO(II)	a	4.76	3.44	8.20	4.92	3.61	8.54	5.09	3.71	8.80
	b	4.76	3.51	8.27	4.86	3.68	8.54	5.03	3.77	8.80
	c	4.73	3.46	8.19	4.96	3.60	8.50	5.11	3.73	8.84
	Mean value	4.75	3.47	8.22	4.89	3.63	8.52	5.07	3.74	8.81
UO ₂ (II)	a	4.61	3.36	7.97	4.75	3.52	8.27	4.89	3.65	8.54
	b	4.53	3.45	7.98	4.68	3.60	8.28	4.81	3.73	8.54
	c	4.59	3.39	7.98	4.72	3.53	8.25	4.83	3.71	8.54
	Mean value	4.58	3.40	7.98	4.72	3.55	8.27	4.84	3.70	8.54

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

Table 2. Thermodynamic parameter (ΔG), (ΔH) and (ΔS) of complexes of VO(II) and UO₂(II) with cmmsa 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)
(Methanol- water)			
VO(II)	49.06	44.42	15.06
U O ₂ (II)	47.71	43.96	12.75
(Dioxane-water)			
VO(II)	50.24	42.44	25.32
U O ₂ (II)	48.77	41.28	24.32

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

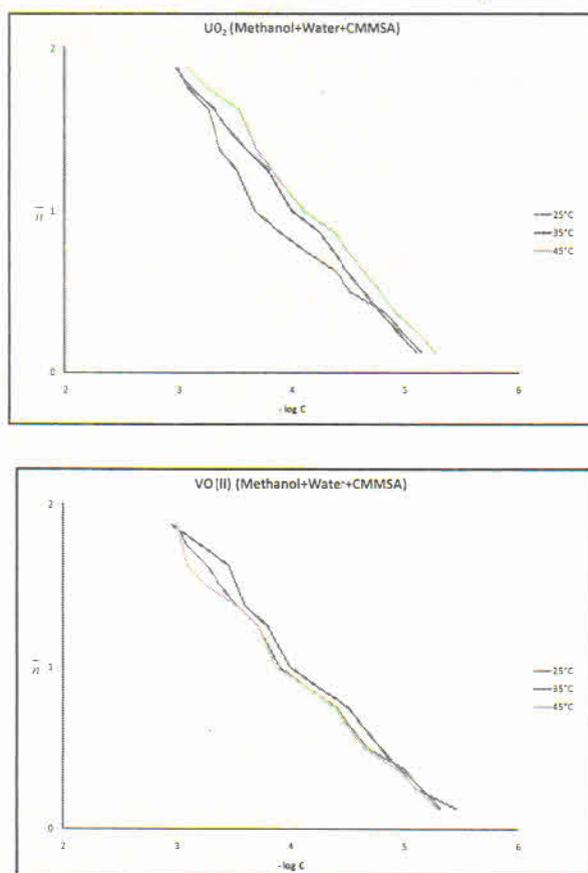


Figure 2

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) representing formation curves of VO(II), UO₂ (II) ions have been given.

Metal-ligand stability constant :

Calvin and Melchior's extension of Bjerrum's⁹ method was used for determining stability constant of the complexes from potentiometric titration data and their values were further determined by Schroder's Convergence formula¹¹ and Correction term method¹⁴ 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 $\bar{n} = 1.5$. The \bar{n} values lie in the range 0-2 in each case for both solvent systems, indicating the formation of 1:1 and 1:2 metal ligand complexes only. The metal -ligand stability constants ($\log K_1$ and $\log K_2$) values (table 1) were higher in 40% (v/v) dioxane -water as compared to 40% (v/v) methanol-water mixtures. This suggests that coordinate bond formed between metal and ligand has more covalent character in case of 40% (v/v) dioxane-water having (lower dielectric constant) as compared to 40% (v/v) methanol-water mixtures. The stability of VO(II) complexes may be attributed to the participation of 3d orbitals in coordination in contrast to 5f orbitals in UO₂ (II) (fig. 1 & 2). The values of $\log K_1$ and $\log K_2$ increases with

temperature which shows that higher temperature is favourable for the formation of stable complexes and follow the order- VO(II) > UO₂ (II)

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 equation¹⁵ the values of ΔG , ΔH and ΔS in 40%(V/V) methanol -water mixture are given in Table 2. 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 favourable.

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. At constant temperature the stability constant of the complexes follow the order- VO(II) < UO₂ (II)
4. 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.

ature.

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 favourable.

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