

## **THERMODYNAMIC AND PHYSICOCHEMICAL STUDIES OF SOME TRANSITION METAL IONS WITH VIOLURIC ACID AND SOME OF ITS HOMOLOGS**

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### **ABSTRACT**

Thermodynamic proton ligand stability constants of violuric acid ( $H_2VA$ ), methyl violuric acid ( $H_2MVA$ ) and phenyl violuric acid ( $H_2PVA$ ) and thermodynamic metal ligand stability constants of the complexes of  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$  and  $Mn^{2+}$  with these acids have been determined in 50% ethanol–water medium by potentiometric measurements. The thermodynamic functions  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  corresponding to the stepwise complexation processes have been calculated at 31°C. The stepwise complexation is found to be predominantly an enthalpy driven process. The composition of the complexes determined potentiometrically was confirmed by elemental analysis of isolated samples.

### **INTRODUCTION**

Violuric acid, the 5-oxime of alloxan, is known to exist as a mixture of keto–enol tautomers [1]. It is blue in the presence of many organic bases [2] and many of its salts are yellow or red [3]. Since the behaviour of heterocyclic imines and enols are of current interest in biopolymers and in the physical chemistry of drug action, it is desirable that more information is gathered about similar model systems. Violuric acid containing enolic and imine groups in a benzenoid heterocyclic ring system has been selected as one of these. This paper presents detailed potentiometric studies on some transition metal chelates of violuric acid and some of its homologs. The composition of the complexes determined potentiometrically was confirmed by elemental analysis of isolated complexes.

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## EXPERIMENTAL

*Materials used*

Samples of violuric acid of chromatographic grade (E. Merck) were used without further treatment. All other violuric acids were synthesised by the method described in the literature [4–6].

All the metal ion solutions were prepared using AR grade samples of metal nitrates or sulphates (BDH) and were standardised by the conventional gravimetric procedures. Sodium perchlorate (Riedel) was used to keep the ionic strength constant. A 0.2 M sodium hydroxide solution in 50 vol% ethanol–water was used as the titrant. All other chemicals used were of reagent grade.

*Apparatus*

pH values were measured with an expanded scale pH-meter (Elico Model No. pH 821, Hyderabad, India), equipped with glass and saturated calomel electrodes and were corrected from calibration curves to obtain the true pH values.

*Procedure*

For each metal–ligand combination, the following mixtures: (1) 25 ml  $\text{HClO}_4$  (0.005 M) + 5 ml  $\text{NaClO}_4$  (1.0 M) + 20 ml ethanol–water; (2) 25 ml  $\text{HClO}_4$  (0.005 M) + 5 ml  $\text{NaClO}_4$  (1.0 M) + 5 ml ligand (0.01 M) + 15 ml ethanol–water; (3) 25 ml  $\text{HClO}_4$  (0.005 M) + 5 ml  $\text{NaClO}_4$  (1.0 M) + 5 ml ligand (0.01 M) + 10 ml metal (0.001 M) + 5 ml ethanol–water were titrated with carbonate-free 0.2 M NaOH solution using the pH meter. In this set the metal–ligand ratio was kept at 1 : 5 and two other sets with metal–ligand ratios of 1 : 3 and 1 : 4 were also used for all ligands. Titrations were carried out in a sealed vessel with a water-jacket at a fixed temperature.

The experimentation and calculations are essentially based on the method of Bjerrum [7] and Calvin [8], as modified by Irving and Rossotti [9]. By applying various computational methods, i.e. interpolation at half  $n^-$  values, interpolation at various  $n^-$  values and the midpoint slope method, the stepwise metal–ligand stability constants were determined. The values obtained by different methods were in fair agreement. Similar titrations and calculations were carried out at 18°C, 31°C and 42°C.

## RESULTS AND DISCUSSION

The pH titration curves at different metal–ligand ratios (1 : 3, 1 : 4 and 1 : 5) revealed that in all cases  $n^-$  values approach a maximum value of 2.0.

TABLE 1

Stepwise stability constants of transition metal ions with ligands at different temperatures

Ion	Temperature	H <sub>2</sub> VA		H <sub>2</sub> MVA		H <sub>2</sub> PVA	
		log K <sub>1</sub>	log K <sub>2</sub>	log K <sub>1</sub>	log K <sub>2</sub>	log K <sub>1</sub>	log K <sub>2</sub>
H(I)	18	10.25	4.30	10.34	4.40	10.86	5.02
	31	9.95	4.21	10.14	4.28	10.62	4.76
	42	9.85	4.15	9.95	4.18	10.40	4.52
Co(II)	18	7.82	5.60	7.88	5.68	8.25	6.02
	31	6.95	5.28	7.02	5.35	7.35	5.68
	42	6.08	5.00	6.18	5.09	6.60	5.40
Cu(II)	18	7.35	5.26	7.42	5.35	7.86	5.68
	31	6.60	4.90	6.67	4.98	7.12	5.32
	42	5.90	4.58	5.98	4.65	6.43	5.00
Zn(II)	18	6.12	4.62	6.18	4.68	6.68	5.23
	31	5.54	4.38	5.61	4.45	6.28	4.92
	42	5.04	4.17	5.10	4.23	5.56	4.67
Fe(II)	18	6.00	4.53	6.05	4.63	6.60	5.02
	31	5.48	4.26	5.52	4.30	6.10	4.66
	42	5.00	3.98	5.08	4.00	5.60	4.35
Ni(II)	18	5.88	4.28	5.96	4.37	6.55	4.83
	31	5.40	4.00	5.45	4.06	6.08	4.52
	42	4.96	3.70	5.02	3.86	5.65	4.30
Mn(II)	18	4.85	3.88	4.88	3.96	5.30	4.48
	31	4.52	3.78	4.56	3.83	4.95	4.21
	42	4.22	3.66	4.28	3.72	4.65	3.97

The values of log K<sub>1</sub> and log K<sub>2</sub> are accurate to 0.02 log K unit.

It is therefore concluded that there are only two complexes viz. 1 : 1 and 1 : 2 present in the system. The pK<sub>a</sub> values of ligands are given in Table 1 with the stability constants of various complexes at different temperature. The thermodynamic parameters of complexes at 31°C are summarised in Table 2.

In the case of the acids H<sub>2</sub>VA, H<sub>2</sub>PVA, H<sub>2</sub>MVA examined here a linear relationship between pK<sub>a</sub> and log K<sub>1</sub> for any metal system were observed with a pK<sub>a</sub> order of H<sub>2</sub>PVA > H<sub>2</sub>MVA > H<sub>2</sub>VA and a log K order of H<sub>2</sub>PVA > H<sub>2</sub>MVA > H<sub>2</sub>VA.

Stability of metal complexes with these acids was observed to be in the order Co(II) > Cu(II) > Zn(II) > Fe(II) > Ni(II) > Mn(II). Except for the Co(II) complex, this sequence is in agreement with that found by Irving and Williams [10]. The abnormally high stability of Co(II) complexes indicates that in solution the Co(II) is transformed to the Co(III) complex. Moratal et al. [11], studying the Co(II) complexes of violuric acid have proved this point.

As the tendency of a metal ion to take up a ligand is proportional to the number of vacant sites, the ratio between consecutive constants, to a certain

extent, is determined statistically [7]. For an anionic ligand, coulombic attraction is more for the  $M^{2+}$  ion compared with the  $MA^+$  ion. As such,  $\log(K_1/K_2)$  is positive. In systems described here values of  $\log(K_1/K_2)$  are positive and lie between 0.85 and 2.23 log units against the statistically determined unity values.

The stability constants shown in Table 1 have been further corrected for activity coefficients with the help of the Davies equation [12] to obtain the thermodynamic stability constants ( $K_T$ ).  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  values were calculated from the relationships

$$-\Delta G = 2.303 RT \log(K_T), \frac{d \log K_T}{d(1/T)} = \frac{-\Delta H}{4.57} \text{ and } \Delta G = \Delta H - \Delta ST$$

TABLE 2

Thermodynamic parameters of complexation at 31°C

Ion	H <sub>2</sub> VA					
	-ΔG(kcal mol <sup>-1</sup> )		-ΔH(kcal mol <sup>-1</sup> )		-ΔS(cal mol <sup>-1</sup> deg <sup>-1</sup> )	
	-G <sub>1</sub>	-G <sub>2</sub>	-H <sub>1</sub>	-H <sub>2</sub>	-S <sub>1</sub>	-S <sub>2</sub>
Co(II)	10.20	7.59	31.85	11.47	71.21	12.76
Cu(II)	9.71	7.06	29.85	10.88	66.25	12.56
Zn(II)	8.24	6.34	20.47	10.02	40.23	12.10
Fe(II)	8.16	6.18	18.20	9.80	33.02	11.90
Ni(II)	8.05	5.82	16.76	9.10	28.65	10.78
Mn(II)	6.83	5.51	10.77	3.65	12.96	6.11
Ion	H <sub>2</sub> MVA					
	-ΔG(kcal mol <sup>-1</sup> )		-ΔH(kcal mol <sup>-1</sup> )		-ΔS(cal mol <sup>-1</sup> deg <sup>-1</sup> )	
	-G <sub>1</sub>	-G <sub>2</sub>	-H <sub>1</sub>	-H <sub>2</sub>	-S <sub>1</sub>	-S <sub>2</sub>
Co(II)	10.29	7.69	30.78	11.97	67.40	14.07
Cu(II)	9.81	7.18	28.91	11.38	62.82	13.81
Zn(II)	8.34	6.44	19.61	10.48	37.07	13.28
Fe(II)	8.22	6.23	18.76	10.20	34.67	13.05
Ni(II)	8.12	5.90	17.29	9.72	30.16	12.56
Mn(II)	6.88	5.58	13.65	3.70	22.26	6.18
Ion	H <sub>2</sub> PVA					
	-ΔG(kcal mol <sup>-1</sup> )		-ΔH(kcal mol <sup>-1</sup> )		-ΔS(cal mol <sup>-1</sup> deg <sup>-1</sup> )	
	-G <sub>1</sub>	-G <sub>2</sub>	-H <sub>1</sub>	-H <sub>2</sub>	-S <sub>1</sub>	-S <sub>2</sub>
Co(II)	10.79	8.15	32.49	11.77	71.38	11.90
Cu(II)	10.43	7.65	24.81	10.95	47.30	11.85
Zn(II)	9.27	7.09	22.75	10.20	44.30	10.23
Fe(II)	9.02	6.73	19.49	9.72	34.44	9.83
Ni(II)	8.99	6.54	17.06	9.20	26.54	8.75
Mn(II)	7.43	6.11	12.13	8.64	15.46	8.32

Since violurate ions and bivalent metal cations behave as soft donor and soft acceptor respectively, the complexation reactions must be exothermic. If in the consecutive complexation processes there is no significant change in the type of bonding, then the enthalpy values are likely to be of the same magnitude, as is evident from Table 2.

The entropy changes associated with consecutive complexation processes are as follows: (1) charge neutralisation, (2) liberation of ordered water molecules from the hydration shell, (3) loss of vibrational and rotational degrees of freedom of the ligand by chelation phenomena. Only process (2) gives a small positive contribution to entropy because for soft-soft interaction, a very weak hydration shell occurs. The weak hydration implies that no large increase of entropy can occur. The coordination may actually involve a considerable net loss of entropy owing to the rotational and conformational constraints to which the ligands are subjected in the complex. Therefore, the contributions of processes (1) and (3) together more than offset that due to process (2) and hence all steps have negative  $\Delta S$  values. The complexation of violuric and other acids with these bivalent metal ions then appears to be an enthalpy-driven process. Since a favourable enthalpy change is associated with the covalent nature of the metal-ligand bond, it may be concluded that the metal-ligand bonds in these complexes are sufficiently covalent.

### *Solid state*

The metal chelates of  $H_2VA$ ,  $H_2MVA$  and  $H_2PVA$  were prepared similarly in the solid state by the method reported previously [13]. These complexes are highly coloured and are insoluble in water but soluble in organic solvents such as acetone, ethyl alcohol, dioxan etc. The elemental analysis of these compounds indicates 1:2 (metal-ligand) stoichiometry. They do not possess sharp melting points but decompose on heating above  $210^\circ C$ .

### *IR spectra*

A comparison of the IR spectra of  $H_2VA$ ,  $H_2MVA$  and  $H_2PVA$  with those of their chelates shows the formation of chelates through the OH and C-N=O groups of the nitroso-enolic form of the ligands. In the IR spectra of the ligands the main bands are observed at 3450, 1720, 1650, 1580 and  $1420\text{ cm}^{-1}$  for  $H_2VA$ ; 3440, 1715, 1655, 1575 and  $1405\text{ cm}^{-1}$  for  $H_2MVA$ ; 3420, 1710, 1645, 1560 and  $1395\text{ cm}^{-1}$  for  $H_2PVA$  which correspond to  $\gamma NH$ ,  $\gamma C=O$ ,  $\gamma C=NOH$ ,  $\gamma C-N=O$  and  $\gamma OH$  respectively. The disappearance of  $\gamma C=NOH$  and shifting of  $\gamma C-N=O$  to lower frequency in the spectra of metal chelates indicates that the oximino-ketonic form of the ligands has been completely converted into the nitroso-enolic form during complex formation. Furthermore, the appearance of bands in the narrow

range 410–415  $\text{cm}^{-1}$  suggest metal–nitrogen bonding in the chelates and thus that coordination probably occurs through the nitrogen of the nitroso group. The bands due to  $\gamma\text{OH}$  disappeared in the metal chelates suggesting the involvement of this group in complexation. The formation of (M–O) bonds due to the deprotonation of the –OH group of these ligands is evidenced by the appearance of bands in the ranges 505–525  $\text{cm}^{-1}$ . All the metal chelates gave one broad bands in the region 3320–3160  $\text{cm}^{-1}$  and other sharp bands in the narrow range 800–810  $\text{cm}^{-1}$  due to  $\gamma\text{OH}$  of water. The loss of water at relatively high temperatures (170–210°C) suggests that these molecules are coordinated and not lattice-held.

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