



Thermodynamics of the Interaction of Some Transition Metal Ions with some N-substituted Thiovioluric Acids

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(Received: October 10, 2012; Accepted: November 15, 2012)

ABSTRACT

Thermodynamic protonation constants of N-ortho xylyl thiovioluric acid [NOXTVA], N-para xylyl thiovioluric acid [NPXTVA], N- meta xylyl thiovioluric acid [NMXTVA] and N- α -naphtyl thiovioluric acid [NANTVA] and thermodynamic formation constants of the complexes of Cu (II), Co(II), Ni (II), Pb (II) and Zn (II) with these compounds have been determined at three different temperatures in 80% v/v water dioxane mixture by potentiometric measurements. The thermodynamic functions corresponding to stepwise complexation processes have been calculated at 30°C. The stepwise complexation is found to be predominantly as enthalpy driven process.

Key words: Transition metal ions, Thiovioluric acids, Thermodynamics.

INTRODUCTION

The studies on the behaviour of the 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. Thiovioluric acids containing enolic and imine groups in benzenoid heterocyclic ring system have been selected as one such model compounds. Thiovioluric acid and its derivatives also have varied analytical¹⁻² medicinal³⁻⁴ and industrial⁵⁻⁶ applications. The stabilities of thiovioluric acid and some of its derivatives with various metal ions have been studied by various workers⁷⁻¹³ but so far the chosen N-substituted thiovioluric acid have not been explored. We present here the results of the potentiometric determination of the formation

constants of some bivalent transition metal ions with the chosen compound in 80% v/v water-dioxane medium at 20, 30 and 40°C.

EXPERIMENTAL

The N-substituted thiovioluric acids were obtained by action of HNO₂ on the corresponding N-substituted thiobarbituric acids which have been synthesised by the method reported in literature¹⁴. All these thiovioluric acids were used after further purification. The solutions of metal ions were prepared using A.R. grade B.D.H. samples of metal nitrate or sulphate and were standardized by the conventional gravimetric procedures. Dioxane was purified using method of Weissberger *et al.*,¹⁵. The carbonate free sodium hydroxide was prepared by the electrolytic method of Vogel¹⁶.

The experimental procedure consisted of pH-metric titrations performed using a pre-calibrated expanded-scale pH-meter [Elico 821, India] equipped with a glass electrode and a saturated calomel electrode. Titrations were carried out in a sealed water-jacketed vessel at a fixed temperature. The titrating solution was made up of metal ion (1.25×10^{-3} M), ligand (1.25×10^{-2} M) and HClO_4 (6.00×10^{-3} M) and the carbonate free sodium hydroxide was used as titrant. The ionic strength of the titrating solution was maintained at 0.1 M with NaClO_4 .

The average number of proton (n_{H^+}) associated with H_2A , the average number of ligand molecules attached per metal ion (n) and the free ligand exponent (PL) were calculated adopting the Irving-Rossotti technique¹⁷. By applying various computational methods (e.g., Interpolation at half n values, interpolation at various n values, the mid-point slope method and the correction term method), the stepwise metal-ligand stability constants were determined. The values obtained by different methods are in fair agreement. Bjerrum's half integral method¹⁸ has been applied to evaluate the protonation constants.

RESULTS AND DISCUSSION

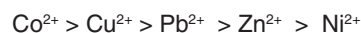
The titrations were carried out in triplicate and a ratio of 10:1 of the ligand to metal ion concentration was invariably maintained in order to satisfy the highest possible coordination number of metal ion under investigation. In all metal-ligand titrations, the n values steadily increase with pH from <0.20 to >1.5 to ≤ 2.10 before precipitation occurs, indicating the formation of 1:2 metal-ligand complexes as the highest complexes in these systems. There is no evidence of polynuclear complexes, or influence of Cl^- , ClO_4^- , NO_3^- , SO_4^{2-} , Na^+ , on the values of pK_a , K_1 and K_2 under the experimental condition employed here. The stepwise protonation constants of chosen thiovioluric acids and the stepwise formation constants of corresponding metal-ligand complexes are given as logarithmic values in table 1. Since the activity coefficient corrections have been applied on the basis of Davies equation, pK_a and $\log K$ values given here are the thermodynamic constants. Formation constants, determined as above, were

reproducible to 0.05 log unit or less in replicate experiments, while variation in the initial concentration of metal and chelating agent gave result with a variation of ± 0.10 log units or less.

It is evident from Table 1 that the introduction of a (ortho, para, or meta) xylyl and α -naphthyl groups into N-position of thiovioluric acid molecule has a parallel effect on the proton-ligand and metal ligand stability constants: for example, the pK_a order is N- α -naphthyl thiovioluric acid [NANTVA] > N-para xylyl thiovioluric acid [NPXTVA] > N-meta xylyl thiovioluric acid [NMXTVA] > N-ortho xylyl thiovioluric acid [NOXTVA] and identical to the order of $\log K$.

The small variation in pK_a and $\log K$ values in case of α -naphthyl and xylyl derivatives indicates that the steric effects of these substituent groups can not be transmitted to the coordination centre located far from it. But there does exist an unmistakable gradation, albeit small, as shown above. The substituent effect in interactions of α -naphthyl and xylyl groups then operates through the N-heterobenzenoid ring and affects the electron demand of the bonding site. The parallel orders of $\log K$ and pK_a also emphasise the fact that the not electron demand in metal association remains the same as in protonation in spite of a chelate ring, most probably non-coplanar with thioviolurate ring, being produced.

The order of the stability of metal complexes with all the chosen thiovioluric acids is -



Except for the Co(II) complex, this sequence is in agreement with that found by Irving and William. The abnormal high stability of Co(II) complexes indicates that in the solution the Co(II) is transferred to the Co(III) complex. The study of Moratal and Faus¹⁵ on the Co(II) complexes of thiovioluric acids has conclusively proved this point. The greater stability of Cu(II) complexes is produced by the well known Jahn-Teller effect. The relatively low values of Ni^{2+} can be attributed to steric hindrance preventing the formation of square planar structure¹⁶.

Table 1: Thermodynamic Stability Constants of Complexes of N-substituted thiovioluric acids at different temperatures and other thermodynamic functions at 30°C

Cations	Log K ₁			Log K ₂			Thermodynamic Functions at 30°C			
	20°C	30°C	40°C	20°C	30°C	40°C	-ΔH° ₁ Kcal Mole ⁻¹	-ΔS° ₁ cal Mole ⁻¹ deg ⁻¹	-ΔH° ₁ Kcal Mole ⁻¹	-ΔS° ₁ cal Mole ⁻¹ deg ⁻¹
N-o-xylyl thiovioluric acid (NOXTVA)										
H ⁺	10.57	10.40	10.23	4.64	4.64	4.29	11.40	1.05	9.42	2.27
Cu ²⁺	8.07	7.82	7.62	6.32	6.12	5.88	10.75	0.82	8.80	2.04
Zn ²⁺	7.62	7.40	7.14	5.90	5.72	5.42	11.77	1.12	9.72	2.37
Co ²⁺	8.33	8.08	7.86	6.23	6.32	6.02	11.07	0.99	9.16	2.20
Pb ²⁺	7.84	7.60	7.30	6.14	5.95	5.70	10.39	0.66	8.58	1.92
Ni ²⁺	7.40	7.18	6.93	5.72	5.55	5.30				
N-m-xylyl thiovioluric acid (NIMXTVA)										
H ⁺	10.69	10.58	10.33	4.73	4.54	4.35	11.52	0.99	9.78	3.10
Cu ²⁺	8.17	7.92	7.68	6.40	6.20	5.95	10.84	0.85	9.15	2.80
Zn ²⁺	7.73	7.50	7.25	6.02	5.80	5.58	11.89	1.05	9.85	3.23
Co ²⁺	8.42	8.18	8.00	6.62	6.42	6.17	11.18	0.89	9.45	2.94
Pb ²⁺	7.94	7.70	7.40	6.22	6.00	5.80	10.62	0.79	8.82	2.64
Ni ²⁺	7.55	7.32	7.04	5.80	5.60	5.42				
N-pxylyl thiovioluric acid (NPXTVA)										
H ⁺	10.81	10.70	10.50	4.92	4.74	4.56	12.32	2.47	10.27	3.82
Cu ²⁺	8.44	8.18	7.92	6.60	6.40	6.17	11.50	1.98	9.69	3.62
Zn ²⁺	7.92	7.70	7.48	6.22	6.02	5.72	12.78	2.97	10.60	3.61
Co ²⁺	8.68	8.40	8.12	6.85	6.62	6.45	11.87	2.17	9.96	3.49
Pb ²⁺	8.20	7.92	7.67	6.40	6.20	6.02	11.18	1.88	9.40	3.36
Ni ²⁺	7.73	7.48	7.23	6.02	5.82	5.57				
N-a-naphthyl thiovioluric acid [NANTVA]										
H ⁺	10.98	10.76	10.56	4.96	4.76	4.58	12.40	2.55	10.37	3.22
Cu ²⁺	8.58	8.38	8.13	6.68	6.46	6.25	11.58	2.05	9.78	3.98
Zn ²⁺	8.08	7.86	7.64	6.28	6.07	5.95	12.57	3.08	10.80	3.72
Co ²⁺	8.88	8.68	8.43	7.05	6.83	6.60	11.92	2.33	10.05	3.57
Pb ²⁺	8.50	8.25	8.02	6.52	6.30	6.08	11.25	1.95	9.66	3.44
Ni ²⁺	7.88	7.65	7.40	6.18	5.92	5.68				

The ratio of successive stability constants, $\log(k_1/k_2)$, is found to be positive in all the systems. Further more, it is observed that the values of $\log k_2$ are lower than $\log k_1$, by nearly 1.50-1.95 units. This implies that in these systems not only the statistical affect which gives $\log k_1 - \log k_2 = 0.80$ units, is to be considered of but the electrostatic effect and the steric hindrance to be considered of but the electrostatic effect and the steric hindrance to the addition of the second cheelate group are also significant. In the case of chelating agents containing bulky substituent¹⁷ near the donor atoms, steric hindrance to the addition of the second group causes $\log K_1/K_2$ to be unusually high.

The values of pKa and logK at higher temperatures indicate that the temperature increases the acidity of ligands and reduces the stabilities of the complexes, but to a smaller degree. Since $\log K$ values vary linearly with $1/T$, the enthalpy $[\Delta H^\circ]$ of complexation was determined by the Van't Hoff equation.

$$\frac{d \log K}{dT} = \frac{\Delta H^\circ}{2.303RT^2}$$

The free energy change $[\Delta G^\circ]$ and entropy change $[\Delta S^\circ]$ were calculated from the following relationships.

$$-\Delta G^\circ = 2.303 RT \log K_T$$

and

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T$$

The values of changes in free energy, enthalpy and entropy accompanying complexation reactions have been calculated at 30°C with the help above equations. The error in $[\Delta H^\circ]$ values lies in the range 0.2 - 0.4 Kcal Mole⁻¹ and that for $[\Delta S^\circ]$ is 0.20 cal k⁻¹, mol⁻¹.

The negative values of $[\Delta G^\circ]$ show that the teaction tends to proceed spontaneously. The negative values of $[\Delta H^\circ]$ suggest that the formatio of complexes between these thiovioluric acids and metals are enthalpy characterized reactions and this also explains the decrease in the value of $\log K$ with the rise of temperature. In the consecutive complexation process no significant change in the type of bonding is expected, this exhibiting enthalpy values which are of nearly the same magnitude. Being soft acceptors, thioviolurates are expected to be weakly solvated and the extent of charge neutralisation on associating with metal ions in solution is such that a positive entropy change is not predicted. On the other hand, restrictions imposed on the rotation and vibration of the ligand upon association will produce a considerable loss of entropy. Thus the complexation of chosen thiovioluric acids with these bivalent metals in solutions appears to be an enthalpy driven process.

ACKNOWLEDGMENTS

Grateful acknowledgement is made to the Department of chemistry Sahu Jain (P.G.) College, Najibabad for providing the necessary facilities and also to the I.I.T. Roorkee for providing Library facilities.

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