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Note

INTERACTION OF Zn(II), Cd(II) AND Hg(II) WITH HYPOXANTHINE

SAVINDRA RANDHAWA, B.S. PANNU and S.L. CHOPRA

Department of Chemistry, Punjab Agricultural University, Ludhiana (India)

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The interaction of hypoxanthine with copper(II) has been studied potentiometrically by Reinert and Weiss [1]. No systematic work on the complexes of hypoxanthine with metal ions appears to have been done. The systematic investigation was initiated in our laboratory by the authors and the interaction of transition metals with hypoxanthine has been previously communicated [2]. It was thought desirable to study the complexes of zinc(II), cadmium(II) and mercury(II) with hypoxanthine in aqueous solution, keeping in view the importance of zinc(II) in most of the biological processes involving enzymatic reactions and the involvement of mercury in poisoning resulting in increased excretion of copper and zinc. The important factor which influences these processes is the stability of the metal ion complexes.

EXPERIMENTAL

All the metal ion reagents used were of Analar grade. The solutions were prepared in double glass-distilled carbon dioxide-free water. Solutions of chlorides of zinc, cadmium and mercury were prepared and standardised. Suitable volumes of these solutions were diluted to get 0.01 M concentration. A solution of hypoxanthine (0.05 M) was prepared by direct weighing from a pure sample (Readel A.R.). A standardised solution of potassium perchlorate (1 M) was used to maintain the required ionic strength. Solutions of perchloric acid and carbonate free potassium hydroxide were prepared and standardised. These were used to prepare 0.05 M $HClO_4$ and 0.1 M KOH solutions.

Apparatus

A systronic pH meter T 331 fitted with a glass and calomel electrode assembly was used for recording pH readings.

The Bjerrum—Calvin [3,4] pH titration technique as modified by Irving and Rossotti [5,6] was used for the study. The following three solutions (total initial volume 20 ml) were titrated against a standard alkali (0.1 M KOH) after adjusting their ionic strengths and temperature in a water thermostat: (A) 20 ml of 0.05 M $HClO_4$, (B) 18 ml A + 2.0 ml of 0.05 M ligand, (C) 18 ml B + 2.0 ml of 0.01 M metal. The ratio of metal to ligand concentration was kept at 1 : 5 in order to satisfy the highest coordination number of the metal. The plots of pH versus the volume of the standard alkali added to reach a corresponding reading were prepared.

RESULTS AND DISCUSSION

The values of $\bar{n}_A$, $\bar{n}$ and pL were calculated from the pH titration curves by the Irving and Rossotti method [5,6]. The values of log K_1^H, already reported at different temperatures and ionic strengths, have been used here. The formation curves between $\bar{n}$ and pL were plotted and are shown in Fig. 1. The formation curves show that for Hg(II), $\bar{n}$ attains a maximum value which is less than one but in the case of Zn(II) and Cd(II) it approaches two. The occurrence of precipitation in the case of Hg(II) did not permit the $\bar{n}$ value to go above one. This clearly indicates the formation of only one complex ML of mercury whereas there is a stepwise formation of two complexes ML_1 and ML_2 in the case of Zn(II) and Cd(II) in solution. The values of the stability constants were obtained from the formation curves by the half $\bar{n}$ and linear extrapolation methods [5,6]. The values of stability constants (log k_1, log k_2, log β_2) obtained at 25, 35 and 45°C and at different ionic strengths

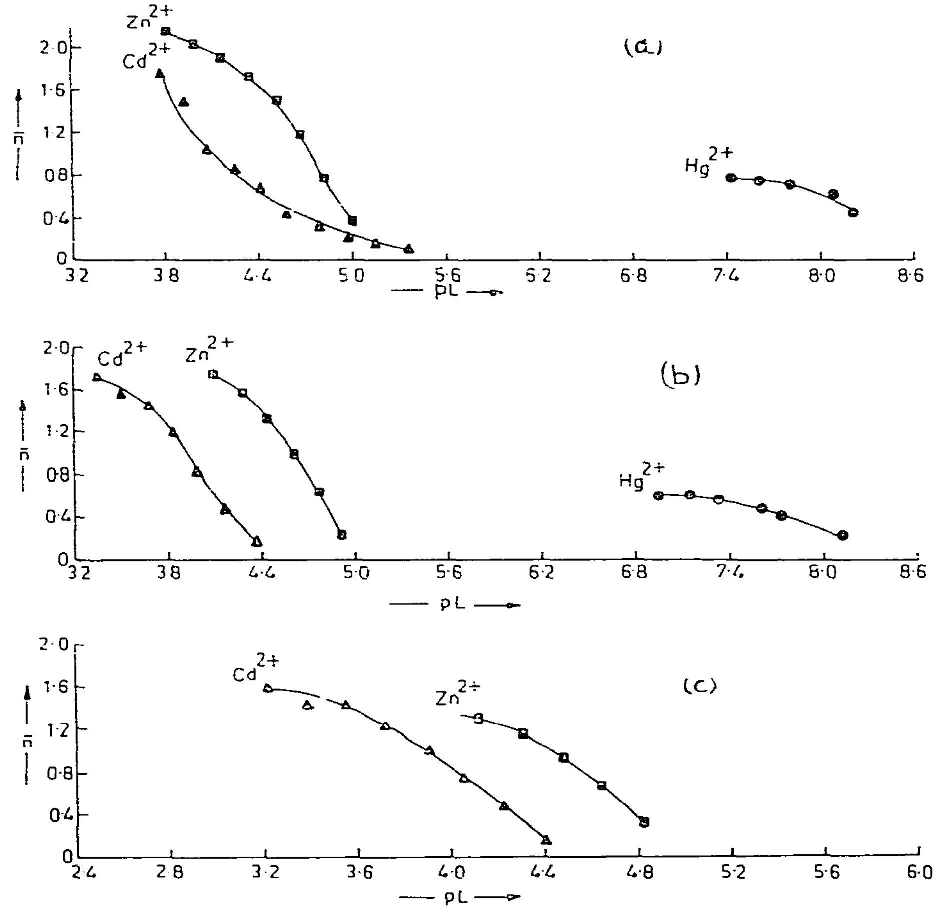

Fig. 1. Formation curves for metal—hypoxanthine complexes at 35°C and at (a) μ = 0.05 M; (b) μ = 0.10 M; (c) μ = 0.20 M.

TABLE 1

Stability constants of metal—hypoxanthine complexes at different temperatures and ionic strengths

Metal ion	Constant	$T = 25^\circ C$	$T = 35^\circ C$			$T = 45^\circ C$
		$\mu = 0.10$	$\mu = 0.05$	$\mu = 0.10$	$\mu = 0.20$	$\mu = 0.10$
Zn(II)	$\log k_1$	5.20	4.97	4.76	4.55	4.57
	$\log k_2$	4.92	4.60	4.44	4.30	4.29
	$\log \beta_2$	10.12	9.57	9.20	8.85	8.86
Cd(II)	$\log k_1$	4.44	4.61	4.45	4.23	4.17
	$\log k_2$	3.88	3.67	3.37	2.97	3.34
	$\log \beta_2$	8.32	8.28	7.82	7.20	7.51
Hg(II)	$\log k_1$	7.32	8.08	7.37		7.46
	$\log k_2$					
	$\log \beta_2$					

are given in Table 1. These values show that $\log k_1$ in the case of the Hg(II) complex is higher than those of the Zn(II), and Cd(II) complexes. The values of $\log k_1$, $\log k_2$ and $\log \beta_2$ for the Zn(II) complexes are higher than those of the Cd(II) complexes. These observations can be explained on the basis of electronegativity values and ionization potentials for Zn(II), Cd(II) and Hg(II). The electronegativity values on the Pauling scale for Zn(II), Cd(II) and Hg(II) are 1.6, 1.7 and 1.9, respectively. The second ionization potentials for Zn(II), Cd(II) and Hg(II) are 17.89, 16.84 and 18.65 eV, respectively. The electronegativity and ionization potential can be regarded as a direct measure of the tendency for a metal ion to accept electrons from other groups or ions. There exists a correlation between the stability of the complex and these properties of the metal ion. Van Panthaleon [7] has correlated the stability of a complex with the ionization potential by the relationship

$$\log K = P(I - q)$$

where I is the ionization potential. P and q are constants depending on the ligand and other conditions independent of the metal ion. This clearly supports the stability order Hg(II) > Zn(II) > Cd(II) for the complexes of these ions.

The comparison of the stability constants at 25, 35 and 45°C at $\mu = 0.1$ M (Table 1) shows that the stability of the complexes in the case of Zn(II) and Cd(II) decreases with the rise in temperature. In the case of values of $\log k_1$ for Hg(II), it is seen that the stability increases with rise in temperature.

The values of $\log \beta_n$ at 35°C and at different ionic strengths of the complexes, namely $\mu = 0.05$, 0.10, 0.20 M (Table 1), decrease with the increase in the ionic strength of the medium. This is due to the decreased tendency of the metal ion to interact with the ligand. The negatively charged atmosphere around the cation is denser in salt solutions and it screens the interaction of metal ions with the ligands which reduces the rate of combination.

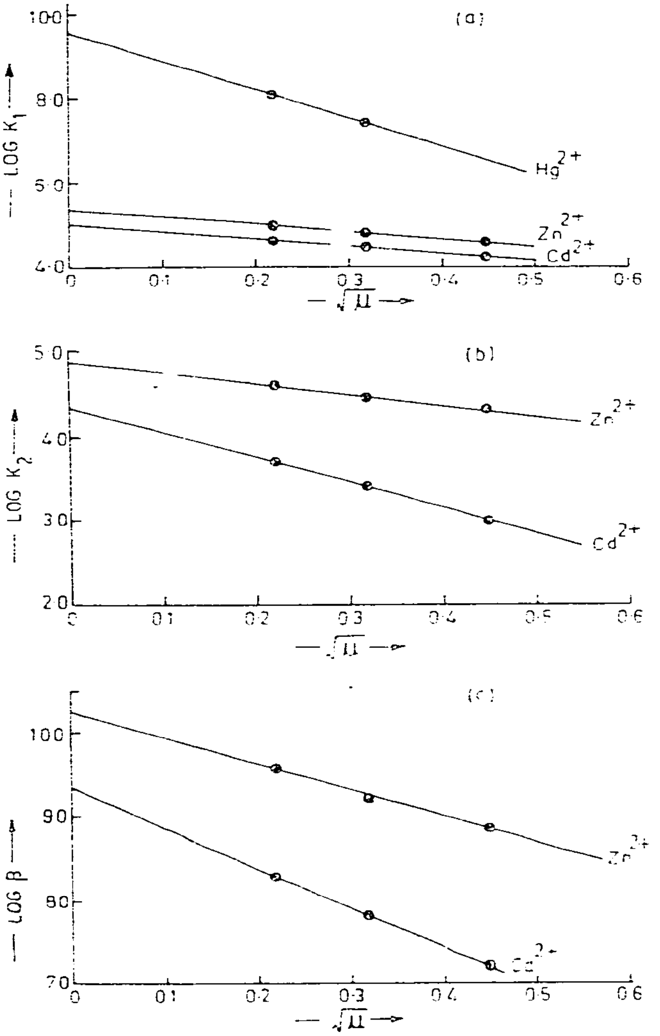

Fig. 2. Plots of (a) log K_1, (b) log K_2, (c) log β vs. $\sqrt{\mu}$ for metal hypoxanthine complexes at 35°C.

This is in accordance with the similar findings reported by Hückel [8] that the stability decreases with increase in the ionic strength of the medium.

The curves were obtained by plotting log k_1, log k_2 and log β_2 versus $\sqrt{\mu}$ for Zn(II) and Cd(II) complexes and log k_1 versus $\sqrt{\mu}$ for Hg(II) complexes. These curves were extrapolated to zero ionic strength in order to obtain the thermodynamic stability constants shown in Fig. 2. These values are given in Table 2.

TABLE 2

Thermodynamic stability constants of metal—hypoxanthine complexes at 35°C

Metal ion	log k_1	log k_2	log β_2
Zn(II)	5.36	4.88	10.24
Cd(II)	5.00	4.35	9.35
Hg(II)	9.55		

TABLE 3

Free energy of metal—hypoxanthine at ionic strength = 0.10 M

Metal ion	Free energy (kcal mole^{-1})	T (°C)		
		25	35	45
Zn(II)	$-\Delta G_1$	7.09	6.71	6.65
	$-\Delta G_2$	6.71	6.26	6.24
	$-\Delta G$	13.80	12.97	12.89
Cd(II)	$-\Delta G_1$	6.06	6.27	6.07
	$-\Delta G_2$	5.29	4.75	4.86
	$-\Delta G$	11.35	11.02	10.93
Hg(II)	$-\Delta G_1$	9.98	10.38	10.85
	$-\Delta G_2$			
	$-\Delta G$			

The free energy changes (ΔG) associated with the formation of the complexes were calculated from the equation

$$\Delta G = -2.303\ RT \log K$$

The data at 25, 35 and 45° C and at ionic strength of 0.1 M are given in Table 3. From a perusal of the results, it is seen that the changes (ΔG) are all negative which means that the complexation processes are spontaneous. By comparing the values of ΔG for Hg(II), Zn(II) and Cd(II), it is seen that this value is lowest for Hg(II). This suggests that Hg(II) has the highest tendency

TABLE 4

Enthalpy changes of metal—hypoxanthine at ionic strengths of 0.1 M (kcal mole^{-1})

Metal ion	ΔH_1	ΔH_2	ΔH *
Zn(II)	−18.48	−20.16	−38.64
Cd(II)	0.420	−21.40	−20.98
Hg(II)	−2.241		

TABLE 5

Entropy of metal—hypoxanthine complexes at ionic strengths of 0.1 M (cal deg^{-1} mole^{-1})

Metal ion	T (°C)	ΔS_1	ΔS_2	ΔS
Zn(II)	25	−38.89	−45.13	−84.02
	35	−38.21	−45.12	−83.33
Cd(II)	25	21.74	−54.06	−32.32
	35	21.72	−54.05	−32.33
Hg(II)	25	25.96		
	35	26.46		

for interaction with hypoxanthine and also it confirms the stability order Hg(II) > Zn(II) > Cd(II).

In the present case, it is further observed that the values of ΔH and ΔS are negative for Zn(II) and Cd(II) (Tables 4 and 5) which indicates that only ΔH is favourable for complexation and that the complexes are enthalpy stabilized. The negative values of ΔS suggest that a primary hydration sphere is retained and the complexes are of outer sphere, ion pair type.

The value of ΔH_1 in the case of the Hg(II) complex is negative, but ΔS is positive, showing thereby that both the enthalpy and entropy terms are favourable for the reaction under study.

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