

Note

THE CHELATION OF ESTERS OF SALICYLIC ACID WITH ZINC GROUP METALS

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Esters of salicylic acid behave as weak acids due to the presence of the phenolic group ($-\text{OH}$). Their ions can form chelates with metal ions due to the presence of carboxyl ($\text{C}=\text{O}$) and phenolate oxygen ($-\text{O}^-$). The complexity constants of methyl salicylate with metal ions of the first transition series and $\text{Cd}(\text{II})$ were reported by Perrin [1]. The stability constants of complexes of ethyl salicylate with $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ have been studied by Jabalpurwala et al. [2]. Studies on the stability constants of complexes of methyl salicylate, ethyl salicylate and phenyl salicylate with metal ions at different temperatures and ionic strengths were started in our laboratory. The determination of thermodynamic parameters was undertaken as these were not reported in the literature. The $\log k_1^{\text{H}}$ values of these esters and their interaction with $\text{Mn}(\text{II})$ have already been reported by Gupta and Pannu [3]. $\text{Zn}(\text{II})$ appears to be quite an important metal ion in biological systems [4]. $\text{Cd}(\text{II})$ competes efficiently with $\text{Zn}(\text{II})$ for protein binding sites. However, very little detailed information is known regarding this [5]. Complexes of $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$ are generally harmful to biological systems and the study of their interaction with biologically important compounds is of vital importance. With the study in continuation, the interaction of $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$ with methyl salicylate, ethyl salicylate and phenyl salicylate was investigated. The stability constants have been determined at 25°C at different ionic strengths, viz. 0.05, 0.075 and 0.10 M, and at 35 and 45°C at 0.10 M. The Bjerrum—Calvin [6,7] pH titration technique as adopted by Irving and Rossotti [8] was used for the study.

EXPERIMENTAL

Materials

Carbonate-free KOH solution (0.1 M) was used for the potentiometric titrations. Salt solutions were prepared by dissolving zinc chloride, cadmium acetate and mercuric chloride of BDH AnalaR grade in double-distilled water and standardizing to obtain 0.01 M solutions. The ester solutions (0.05 M) were prepared in absolute alcohol. An aqueous solution of sodium perchlorate (1 M) was prepared by direct weighing and was employed to maintain

constant ionic strength throughout the titration. The aqueous solution of perchloric acid was standardized against a standard alkali to obtain 0.05 M HClO_4 . Absolute alcohol and double glass distilled water were used to obtain the alcohol–water medium, 50 : 50 (v/v).

Apparatus

A Systronix Model 322-1 pH meter with glass and calomel electrode assemblies was used for pH measurements, and was calibrated with solutions of standard buffers before use. The titrations were carried out at 25 ± 0.1 , 35 ± 0.1 and $45 \pm 0.1^\circ\text{C}$.

Procedure

In order to satisfy the maximum coordination number of the metal, the ratio of metal to ligand was kept at 1 : 5. The following three solutions were titrated against a standard alkali: (A) 2 ml 0.05 M HClO_4 ; (B) A + 2 ml 0.05 M ligand; (C) B + 2 ml 0.01 M metal. The total initial volume was 20 ml, in which the alcohol : water ratio was 50 : 50 (v/v). The ionic strength was adjusted by adding 1 M NaClO_4 . The titration curves were obtained by plotting pH vs. volume of alkali added.

RESULTS AND DISCUSSION

The following relationships were used for the calculations.

$$\bar{n}_A = Y - \frac{(V'' - V')(N^0 + E^0)}{(V^0 + V')T_L}$$

$$\log K_1^H = \text{pH} + \log \frac{\bar{n}_A}{1 - \bar{n}_A}$$

$$\bar{n} = \frac{(V''' - V'')(N^0 + E^0)}{(V^0 + V'')\bar{n}_A T_M}$$

$$\text{pL} = \log \left[\frac{\sum_{n=0}^{n=j} \beta_n^H \left(\frac{1}{\text{antilog } \beta} \right)^n}{T_L - \bar{n}T_M} \times \frac{V^0 + V''}{V^0} \right]$$

where Y is the number of dissociable protons, N^0 , E^0 , T_L and V^0 are the normality of alkali, normality of acid, concentration of ligand and initial total volume, respectively, V' , V'' and V''' are the volumes of alkali used in the acid, ligand and metal ion titrations, respectively, to reach the same pH, K_1^H is the proton–ligand stability constant, \bar{n}_A and \bar{n} are the average number of protons associated with the ligand and the average number of ligands associated with the metal ion, respectively, T_M is the total concentration of metal ion, and the other terms have their usual meaning:

The formation curves at 25°C and various ionic strengths are shown in Fig. 1. The maximum value of \bar{n} approaches 2 in the case of Zn(II) and Cd(II), whereas it does not exceed 1 in the case of Hg(II). This clearly indicates the formation of 1 : 1 and 1 : 2 complexes in the case of Zn(II) and Cd(II), but formation of 1 : 1 complexes in the case of Hg(II).

The values of the $\log K_1^H$ were determined and were found to be in agreement with those published previously by Gupta and Pannu [3]. The stability constants of metal complexes were calculated by half \bar{n} , least square and elimination methods [9]. The average log values of the stability constants are given in Table 1.

Comparison of stability constants at 25, 35 and 45°C (Table 1) clearly shows that the stability of complexes of Zn(II) and Cd(II) with all ligands decreases with rise in temperature. But for Hg(II) complexes the trend is reversed in the case of all the ligands, where the stability of the complexes increases with the rise in temperature. Therefore, low temperature is favourable for the formation of Zn(II) and Cd(II) complexes of these esters, while high temperature favours the formation of Hg(II) complexes.

The stability constants at 25°C and different ionic strengths (0.05, 0.075

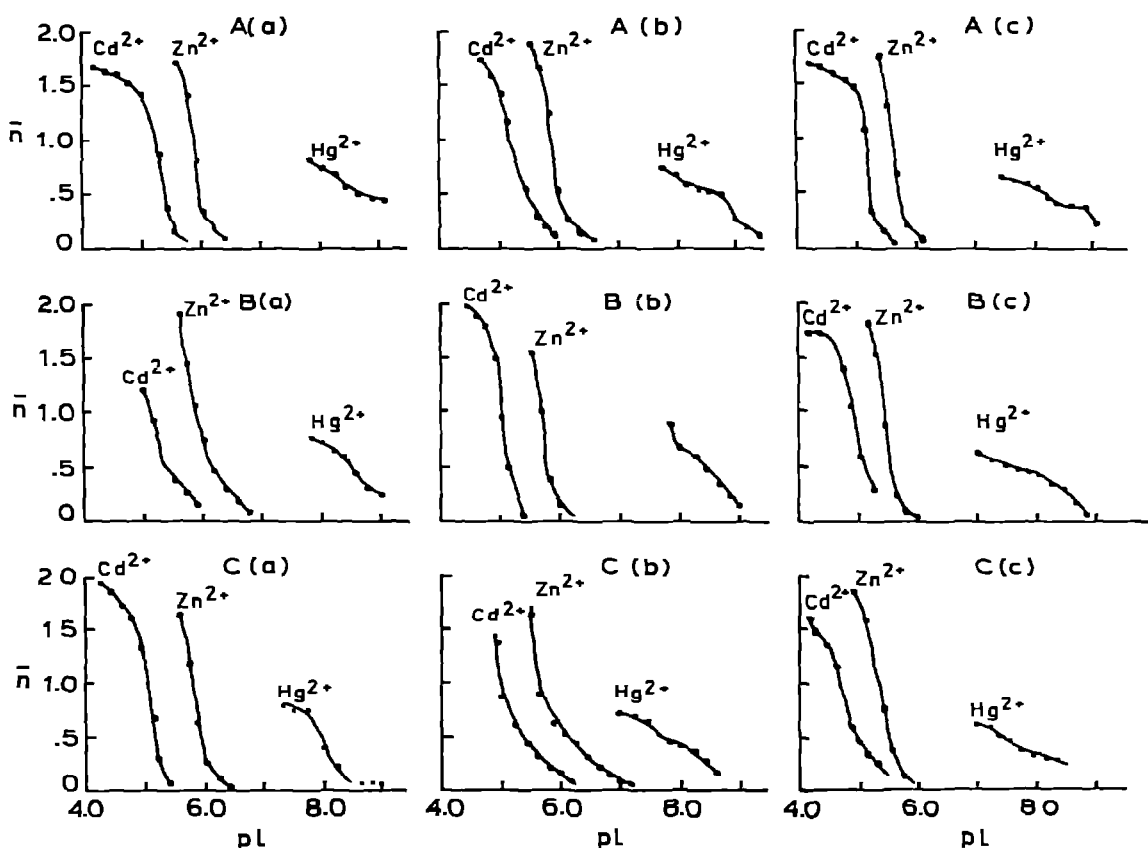


Fig. 1. Formation curves of metal-ester complexes at 25°C at three ionic strengths. A, Methyl salicylate; B, ethyl salicylate; C, phenyl salicylate. (a) $\mu = 0.05$; (b) $\mu = 0.075$; (c) $\mu = 0.10$.

TABLE 1

Stability constants of metal complexes with esters of salicylic acid at different temperatures and different ionic strengths in an alcohol—water system (50:50 v/v)

Ligand	Metal ion	Constant ^a	$\mu =$	$\mu =$	$\mu =$			
			0.05 M	0.075 M	0.10 M			
			$T =$	$T =$	$T =$	$T =$	$T =$	
			25°C	25°C	25°C	35°C	35°C	
Methyl salicylate	Zn(II)	$\log k_1$	6.02	5.91	5.82	5.80	5.76	
		$\log k_2$	5.78	5.76	5.74	5.60	5.47	
		$\log \beta_2$	11.80	11.67	11.56	11.40	11.23	
	Cd(II)	$\log k_1$	5.47	5.42	5.38	5.15	4.97	
		$\log k_2$	5.13	5.06	5.01	4.89	4.57	
		$\log \beta_2$	10.60	10.48	10.39	10.04	9.54	
	Hg(II)	$\log k_1$	8.75	8.65	8.55	8.95	9.05	
		Zn(II)	$\log k_1$	5.89	5.78	5.69	5.65	5.50
			$\log k_2$	5.65	5.62	5.59	5.45	5.22
$\log \beta_2$	11.54		11.40	11.28	11.10	10.72		
Ethyl salicylate	Cd(II)	$\log k_1$	5.38	5.33	5.29	5.07	4.75	
		$\log k_2$	5.02	4.97	4.90	4.63	4.51	
		$\log \beta_2$	10.40	10.30	10.19	9.70	9.26	
	Hg(II)	$\log k_1$	8.55	8.43	8.35	8.70	8.80	
		Zn(II)	$\log k_1$	5.82	5.72	5.62	5.54	5.47
			$\log k_2$	5.55	5.46	5.43	5.20	5.17
$\log \beta_2$	11.37		11.18	11.05	10.74	10.64		
Phenyl salicylate	Cd(II)	$\log k_1$	5.20	5.15	4.95	4.87	4.72	
		$\log k_2$	5.00	4.95	4.90	4.57	4.48	
		$\log \beta_2$	10.20	10.10	9.85	9.44	9.20	
	Hg(II)	$\log k_1$	8.00	7.76	7.55	8.05	8.55	

^a In the case of Hg(II), only the $\log k_1$ values could be reported.

and 0.10 M) show that the stability of the complexes decreases with increase in ionic strength. This shows that the activity of the metal ions to interact with ligands decreases with increase in ionic strength. It is self evident that the metal ion is screened from the ligand in the salt solution and the rate of combination is reduced. This is also in accordance with earlier findings by Debye [10].

A perusal of the stability constants (Table 1) shows that $\log K_1$ of the Hg(II) complex is higher than those of Zn(II) and Cd(II) complexes with the same ligand. The values of $\log k_1$, $\log k_2$ and $\log \beta_2$ of Zn(II) complexes are higher than those of Cd(II) complexes. These observations can be explained on the basis of electronegativity values and ionization potentials for Zn, Cd and Hg. The electronegativity values on the Pauling scale for Zn, Cd and Hg are 1.6, 1.7 and 1.9, respectively. The second ionization potentials for Zn, Cd and Hg are 17.89, 16.84 and 18.45 eV, respectively. The electronegativity and ionization potential can be regarded as direct measurement of the tendency of a metal ion to accept electrons from ligands. A correlation

between the stability of the complexes and the ionization potential was given by Van Panthaleon Van Eck [11] as below

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

where I is the ionization potential, and P and q are constants depending on the ligand and other conditions independent of the nature of the metal ion. This clearly supports the stability order $\text{Hg(II)} > \text{Zn(II)} > \text{Cd(II)}$.

When the stability constants of the same metal ion with different ligands at the same temperature and ionic strength (Table 1) are compared, the following stability order is observed: methyl salicylate $>$ ethyl salicylate $>$ phenyl salicylate.

In general, the extent of complexation of a ligand with a metal ion depends on its basic strength; the greater the basic strength, the higher the stability of its complexes with metal ions. The basic strength of these ligands decreases from methyl salicylate, through ethyl salicylate to phenyl salicylate, which agrees with the values reported by Gupta and Pannu [3]. This supports the stability order given above.

The thermodynamic stability constants were obtained at 25°C by plotting $\log k_n$ or $\log \beta_n$ against $\sqrt{\mu}$ and extrapolating to zero ionic strength; these values are given in Table 2.

The free energy changes (ΔG^0) associated with the formation of chelates have been calculated according to the relationship

$$\Delta G^0 = -2.303 RT \log k_{\mu=0}$$

where $k_{\mu=0}$ is the stability constant at zero ionic strength; these values are given in Table 3.

The stability order of the chelates of salicylic acid esters is $\text{Hg(II)} > \text{Zn(II)} > \text{Cd(II)}$ and methyl salicylate $>$ ethyl salicylate $>$ phenyl salicylate at different temperatures and ionic strengths.

TABLE 2

Thermodynamic stability constants of metal-ester complexes at 25°C in an alcohol-water system (50:50 v/v)

Ligand	Metal ion	$\log k_1$	$\log k_2$	$\log \beta_2$
Methyl salicylate	Zn(II)	6.52	5.90	12.42
	Cd(II)	5.71	5.42	11.13
	Hg(II)	9.24		
Ethyl salicylate	Zn(II)	6.38	5.78	12.16
	Cd(II)	5.59	5.25	10.84
	Hg(II)	9.17		
Phenyl salicylate	Zn(II)	6.30	5.65	11.95
	Cd(II)	5.40	5.23	10.63
	Hg(II)	9.05		

TABLE 3

Change in free energies of metal—ester complexes at 25°C and zero ionic strength ($\mu=0$)

Ligand	Metal ion	ΔG_1^0 (kcal mole ⁻¹)	ΔG_2^0 (kcal mole ⁻¹)	$\Delta G^0 =$ $\Delta G_1^0 + \Delta G_2^0$ (kcal mole ⁻¹)
Methyl salicylate	Zn(II)	-8.89	-8.03	-16.92
	Cd(II)	-7.77	-7.39	-15.16
	Hg(II)	-12.60		-12.60
Ethyl salicylate	Zn(II)	-8.69	-7.88	-16.57
	Cd(II)	-7.62	-7.17	-14.79
	Hg(II)	-12.50		-12.50
Phenyl salicylate	Zn(II)	-8.59	-7.70	-16.29
	Cd(II)	-7.36	-7.13	-14.49
	Hg(II)	-12.34		-12.34

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