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INTERACTION OF MANGANESE(II) WITH METHYL SALICYLATE, ETHYL SALICYLATE AND PHENYL SALICYLATE

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ABSTRACT

The proton ligand stability constants of methyl salicylate, ethyl salicylate and phenyl salicylate and the stepwise stability constants of manganese(II) complexes with these have been determined potentiometrically in aqueous ethanol system 50/50 (v/v) at 25°C at different ionic strengths, viz. 0.050 M, 0.075 M, 0.100 M and at 35 and 45°C at an ionic strength of 0.05 M. The thermodynamic stability constants of the complexes have been evaluated from the various values by extrapolating to zero ionic strength at 25°C. The thermodynamic parameters such as free energy changes (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) involved have been calculated.

INTRODUCTION

Methyl salicylate, ethyl salicylate and phenyl salicylate are of immense importance on account of their medicinal activities. They are used as antiseptics and insecticides and also in perfumery and cosmetics and in the preparation of a number of dyes.

The manganese(II) ion plays an important role in a vast number of biological processes. Manganese is one of the elements essential for the growth of plants and animals. It is also an important catalyst. Therefore, the study of the interaction of manganese(II) with esters of salicylic acid is of great importance from the biological point of view. The clear picture can be obtained by studying the equilibrium between manganese(II) and the esters of salicylic acid such as methyl salicylate, ethyl salicylate and phenyl salicylate.

Perrin[1] determined the stability constants of the chelates of Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with methyl salicylate in aqueous solutions. Isreali[2] determined the stability constants of mixed ligand complexes of nickel(II) and copper(II) with nitrillotriacetate and methyl salicylate. The stability constants of Be^{2+}, Mg^{2+} and Al^{3+} with methyl salicylate have been reported in 50% dioxane–water medium by Charan Das and Rao[3]. Jabalpurwala et al.[4] reported the stability constants of the complexes of Cu(II), Ni(II), Zn(II) and Hg(II) with derivatives of salicylic acid including ethyl salicylate in dioxane–water medium by a potentiometric method.

No systematic work is available in the literature on the interaction of manganese (II) with esters of salicylic acid. Information regarding the thermodynamic stability constants and other thermodynamic functions of complexes of manganese(II) with methyl salicylate, ethyl salicylate and phenyl salicylate have not been reported so far.

The present work deals with the determination of the proton–ligand stability constants of methyl salicylate, ethyl salicylate and phenyl salicylate and the stepwise stability constants of the complexes of these with manganese(II) in 50/50 (v/v) aqueous alcohol at 25 °C and various ionic strengths (μ = 0.05 M, 0.075 M, 0.10 M). These constants have been studied at 35 and 45 °C at an ionic strength of 0.05 M. The Bjerrum–Calvin pH titration technique[5, 6] as adopted by Irving and Rossotti[7] was employed for the study. The proper ionic strengths were maintained by the addition of the requisite quantity of 1 M $NaClO_4$. The thermodynamic stability constants have been evaluated at 25 °C by extrapolation to zero ionic strength.

The free energy changes (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) involved in the formation of complexes of Mn(II) with methyl salicylate, ethyl salicylate and phenyl salicylate are reported at an ionic strength of 0.05 M $NaClO_4$ at 25, 35 and 45 °C.

EXPERIMENTAL

Materials

Standard carbonate-free potassium hydroxide solution was used for potentiometric titrations. All inorganic salts used were of "AnalaR" grade (BDH). The stock solution of Mn^{2+} was prepared from its chloride in double glass-distilled water and estimated by the standard methods. The standard solution (0.01 M) was obtained from it.

An aqueous solution of sodium perchlorate (1 M) was employed to maintain the ionic strengths constant during the titrations. The aqueous solution of perchloric acid (0.05 M) was standardized against a standard alkali solution. Methyl salicylate was obtained from Sarabhai M. Chemicals and purified by distillation. Purity was checked by its boiling point (223 °C). Ethyl salicylate was prepared by the reaction of absolute alcohol with salicylic acid in the presence of concentrated sulphuric acid. It was washed with sodium carbonate, dried over anhydrous calcium chloride, filtered and distilled to get it in the pure form (b.p. 234 °C). Phenylsalicylate was obtained from BDH and purified by crystallisation from ethanol. Purity was checked by its melting point (m.p. 43 °C). Solutions of the esters (0.05 M) were prepared in absolute alcohol.

Apparatus

A "Systronic" pH meter with a glass and calomel electrode assembly was used to follow the change in pH during the titrations which were carried at 25 ± 0.1 °C, 35 ± 0.1 °C and 45 ± 0.1 °C in a constant temperature water bath.

Procedure

The mole ratio of metal to ligand was kept at 1 : 5 in order to fulfil the maximum co-ordination number of metal. The following solutions (total initial volume 20 ml) were titrated against a standard alkali. (A) 2 ml of $HClO_4$ (0.05 M); (B) A + 2 ml of ligand (0.05 M); and (C) B + 2 ml of metal ion (0.01 M).

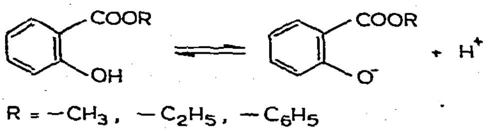
The ionic strength (0.05, 0.075 and 0.10 M) was maintained by the addition of a calculated amount of sodium perchlorate solution. The plots of pH against the volume of the alkali added to reach the corresponding pH changes were made. The shapes of the titration curves were as usual.

RESULTS AND DISCUSSION

Proton–ligand stability constant

Methyl salicylate, ethyl salicylate and phenyl salicylate behave as weak acids owing to the presence of the phenolic group.

The dissociation of these can be as



The average number of protons ($\bar{n}_A$) associated with the ligand is defined as

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

where y is the number of dissociable protons, v' and v'' are the volumes of alkali in acid and ligand titrations to reach the same pH, V^0, N^0 and E^0 are the initial total volume of the titration mixture, the total concentration of alkali and the total concentration of acid, respectively, and T_L is the total ligand concentration.

The formation curves were plotted between $\bar{n}_A$ and pH. The values of log K_1^H were calculated from the relationship

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

To obtain the value of the proton–ligand stability constant (log K_1^H), the pH was plotted against log $[(1 - \bar{n}_A)/\bar{n}_A]$ in the region $\bar{n}_A < 1$.

The values of the proton–ligand stability constants at various ionic strengths and different temperatures are given in Table 1.

The value of log K_1^H depends upon the nature of the alkyl or aryl group present and decreases in the order methyl salicylate > ethyl salicylate > phenyl salicylate.

TABLE 1

PROTON–LIGAND STABILITY CONSTANTS OF THE ESTERS USED IN 50:50(v/v) ALCOHOL:WATER MIXTURE

Temperature ($^\circ C$)	*Ionic strength (μ)*	*log K_1^H*		
		Methyl salicylate	*Ethyl salicylate*	*Phenyl salicylate*
25	0.05	9.75	9.70	9.35
	0.075	9.64	9.50	9.30
	0.10	9.55	9.30	9.25
35	0.05	9.60	9.35	9.30
45	0.05	9.45	9.30	9.15

The ionic strength also has a pronounced effect on the value of log K_1^H which shows a decrease with the increase of ionic strength for all the esters taken. Increase in temperature resulted in decrease of the value of log K_1^H.

Metal–ligand stability constants

The average number of ligands ($\bar{n}$) bound to each metal ion was calculated by

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

The free ligand concentration defined by pL was calculated from the equation

$$\mathrm{pL} = \log_{10}\left[\frac{\sum_{n=0}^{n=j} \beta_n^H \left(\frac{1}{\text{antilog } B}\right)^n}{T_L - \bar{n}T_M} \cdot \frac{V^0 + v''}{V^0}\right]$$

where T_M is the total concentration of metal ion present in the solution, β_n^H is the overall proton–ligand stability constant and other terms have their usual meanings.

The value of $\bar{n}$ approaches 2 but it does not go above 2 in any case. This indicates the formation of 1:1 and 1:2 complexes of manganese(II) with methyl salicylate, ethyl salicylate and phenyl salicylate in the pH range 5.00–7.50. The formation curves between $\bar{n}$ and pL for the manganese(II) ligand system at 25°C and different ionic strengths are shown in Fig. 1. There is no sharp change in the shape of the formation curves suggesting that the various species coexist in solution.

The metal–ligand stability constants were calculated from the formation curves by interpolation at half $\bar{n}$ value and the other computational methods[8]. The values obtained by different methods are in good agreement. These values, which are accurate to 0.05 log units in terms of log β_n, at different temperatures and ionic strengths are given in Table 2.

The values of the stability constants (log β_2) of the complexes of manganese(II) with all the three ligands decrease with an increase of ionic strength. This is due to the decreased activity of the metal ion for its interaction with other species present in the solution at higher ionic strength. This is in accordance with the earlier findings of Debye[9].

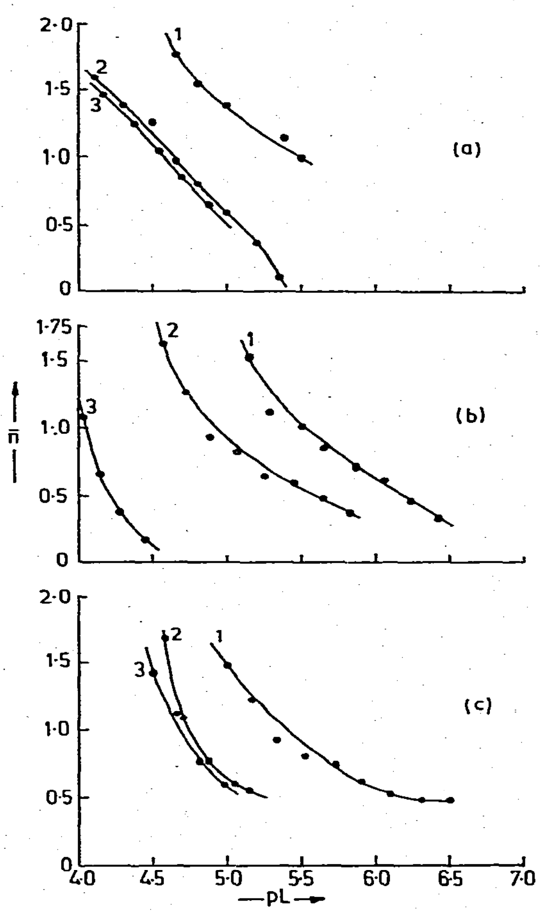


Fig. 1. Formation curves for manganese(II) complexes with (a) methyl salicylate, (b) ethyl salicylate and (c) phenyl salicylate at 25°C. 1, μ = 0.05 M; 2, μ = 0.075 M; 3, μ = 0.1 M.

TABLE 2

STABILITY CONSTANTS OF Mn(II) COMPLEX OF ESTERS OF SALICYLIC ACID IN 50 : 50(V/V) ALCOHOL : WATER SYSTEM

Temperature (°C)	*Ionic strength (μ)*	*Methyl salicylate*			*Ethyl salicylate*			*Phenyl salicylate*		
		logK_1	*logK_2*	*logβ_2*	*logK_1*	*logK_2*	*logβ_2*	*logK_1*	*logK_2*	*logβ_2*
25	0.05	6.75	4.98	11.73	6.15	4.85	11.00	6.04	4.61	10.65
	0.075	5.75	4.20	9.95	5.40	4.04	9.44	5.40	4.00	9.40
	0.10	4.92	3.80	8.72	4.60	3.65	8.25	4.55	3.60	8.15
35	0.05	5.20	4.20	9.40	4.72	4.08	8.80	4.50	3.60	8.10
45	0.05	4.74	4.10	8.84	4.57	3.97	8.54	4.00	2.90	6.90

The stabilities of the complexes decrease with increase in temperature (Table 2). This shows that the formation of these complexes is favoured at lower temperatures.

The comparison of the stability constants of the complexes of manganese(II) with methyl salicylate, ethyl salicylate and phenyl salicylate at the same temperature and ionic strength shows that these decrease in the order methyl salicylate > ethyl salicylate > phenyl salicylate.

The stabilities of the complexes decrease with the increase in the bulk of R in the ligand ($ROOC \cdot C_6H_4O)^-$. This is in agreement with the previous results reported in the case of complexes of metal ions with $(R'COC_6H_4O)^-$ (where R' = $-NH_2$, $-NH-C_6H_5$) by Pannu et al.[10]. The complexes of metal ions with salicylamide were found to be more stable than those of salicylanilide. This supports the present findings.

Thermodynamic stability constants

The thermodynamic stability constants of the complexes were obtained at 25°C by plotting log K_n or log β_n versus $\mu^{\frac{1}{2}}$ and extrapolating log K_n or log β_n to zero ionic strength. These values are shown in Table 3.

TABLE 3

THERMODYNAMIC STABILITY CONSTANTS OF Mn(II) COMPLEXES OF ESTERS OF SALICYLIC ACID AT 25°C IN ALCOHOL:WATER SYSTEM 50;50 (v/v)

Ester	*log K_1*	*log K_2*	*log β_2*
Methyl salicylate	10.80	7.60	18.40
Ethyl salicylate	9.70	7.20	16.90
Phenyl salicylate	9.40	6.80	16.20

Thermodynamic functions

The different thermodynamic functions were calculated by the following relationships.

$$\Delta G = -RT \ln K$$

$$\frac{\Delta H}{RT^2} = -\frac{d\ln K}{dT}$$

$$\Delta G = \Delta H - T\Delta S$$

In order to obtain the enthalpy data, log K was plotted against $1/T$.

The values of ΔH were obtained from

$$\Delta H = -2.303\, Rs$$

where s is the slope of curve.

The free energy changes (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) associated with the formation of the complexes are given in Tables 4–6. The negative value of ΔG in the case of all the complexes suggest the spontaneous formation of complexes of high stability. The enthalpy changes (ΔH) have negative values for all the complexes whereas the entropy changes (ΔS) are also negative (Tables 5 and 6). So the enthalpy term is favourable while the entropy term is unfavourable for the formation of complexes. This can be due to the substitution of the solvent molecules attached to the metal ion by the ligands resulting in the release of solvent molecules.

TABLE 4

FREE ENERGY DATA OF Mn(II) COMPLEXES OF ESTERS OF SALICYLIC ACID AT $\mu = 0.05$ M

Ester	*Temperature (°C)*	$-\Delta G_1$ *(kcal mole^{-1})*	$-\Delta G_2$ *(kcal mole^{-1})*	$-\Delta G$ *(kcal mole^{-1})*
Methyl salicylate	25	9.20	6.79	15.99
	35	7.09	5.73	12.82
	45	6.47	5.59	12.06
Ethyl salicylate	25	8.39	6.61	15.00
	35	6.44	5.56	12.00
	45	6.20	5.40	11.60
Phenyl salicylate	25	8.20	6.29	14.49
	35	6.14	4.91	11.05
	45	5.45	3.96	9.41

TABLE 5

ENTHALPY DATA OF Mn(II) COMPLEXES OF ESTERS OF SALICYLIC ACID

Ester	$-\Delta H_1$ *(kcal mole^{-1})*	$-\Delta H_2$ *(kcal mole^{-1})*	$-\Delta H$ *(kcal mole^{-1})*
Methyl salicylate	64.48	32.44	96.92
Ethyl salicylate	59.48	32.03	91.51
Phenyl salicylate	64.06	42.98	107.04

TABLE 6

ENTROPY DATA OF Mn(II) COMPLEXES OF ESTERS OF SALICYLIC ACID

Ester	*Temperature (°C)*	ΔS_1 *(cal deg^{-1}mole^{-1})*	ΔS_2 *(cal deg^{-1}mole^{-1})*	ΔS *(cal deg^{-1}mole^{-1})*
Methyl salicylate	25	−184.90	− 89.13	−274.03
	35	−186.30	− 86.72	−273.03
	45	−182.40	− 84.12	−266.52
Ethyl salicylate	25	−171.50	− 85.29	−256.79
	35	−172.20	− 85.92	−258.12
	45	−167.50	− 83.73	−251.23
Phenyl salicylate	25	−187.50	−123.10	−310.60
	35	−188.10	−123.60	−311.70
	45	−184.30	−122.70	−307.00

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