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Note

THERMODYNAMICS OF Fe(III) COMPLEXES OF *p*-ACETYLAMINOPHENYL SALICYLATE AND *p*-ACETYLAMINOPHENYL 3,5-DINITROSALICYLATE

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Phenetsal (*p*-acetylaminophenyl salicylate) has biological importance on account of its antipyretic, anti-inflamatory and analgesic activity. Iron(III) has a vital role to play in life processes. A literature survey shows no work on the stability of metal ion complexes of phenetsal and *p*-acetylaminophenyl 3,5-dinitrosalicylate. Therefore, the stability constants of the Fe(III) complexes of these ligands are studied. The Bjerrum–Calvin [1,2] pH titration technique as extended by Irving and Rossotti [3,4] has been used for the study.

EXPERIMENTAL

Phenetsal was prepared by the method reported by Sterwin [5] and its purity was checked by its melting point (187.5°C). Its 0.02 M solution was prepared in absolute alcohol.

p-Acetylaminophenyl 3.5-dinitrosalicylate was prepared by the reaction of 3,5-dinitrosalicyloyl chloride with *p*-acetyl-aminophenol in dry solvent ether. The mixture was refluxed under a water condenser for about an hour. The mixture on cooling gave colourless crystals with melting point 228°C. The nitrogen content was checked in an autoanalyser. Its 0.05 M solution was prepared in absolute alcohol.

Ferric chloride of BDH AnalaR Grade was dissolved in double distilled water and standardized to 0.01 M $FeCl_3$.

The standard solution (0.05 M) of $HClO_4$ was prepared in double distilled water.

A 1 M solution of sodium perchlorate was prepared in double distilled water. It was used to maintain the required ionic strength.

A Systronics model 322-1 pH meter having a glass and calomel electrode assembly and calibrated with buffer solution was used to measure pH during titration. The following three solutions were titrated against 0.1 M KOH: (A) 2.00 ml of 0.05 M $HClO_4$; (B) A + 2.00 ml of 0.05 M ligand or 5.00 ml of

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0.02 M ligand; and (C) B + 2.00 ml of 0.01 M Fe^{3+}.

The initial total volume was 20.00 ml in alcohol–water 70:30 (v/v) in all cases. The titrations were carried at 25°C with ionic strength 0.05 M, 0.10 M and 0.20 M; at 35°C and 45°C with ionic strength 0.10 M. The temperature was maintained at 25 ± 0.1, 35 ± 0.1 and 45 ± 0.1°C in a water thermostat.

RESULTS AND DISCUSSION

As the titrations were carried out in an alcohol–water system, the correct pH values were obtained by the Van Uitert and Haas method [6]. The titration curves were drawn between the volumes of alkali added and pH of the solution reached. The separation of the titration curves of acid + ligand and acid + ligand + Fe(III) suggests the formation of complexes. The values of average protonation number, $\bar{n}_A$, the average number of ligands bound per metal ion, $\bar{n}$, and the free ligand concentration pL ($-\log$ [L]) were calculated from the titration curves. The values of the protonation constant $\log k_1^H$ were obtained from the plot of the equation

$$\mathrm{pH} = \log k_1^H + \log\left(\frac{1-\bar{n}_A}{\bar{n}_A}\right)$$

The value of $\log k_1^H$ was obtained as the intercept. These values are given in Table 1. It can be seen that they decrease with rise of temperature and ionic strength. The value of $\log k_1^H$ for phenetsal is higher than that of *p*-acetylaminophenyl 3,5-dinitrosalicylate. This is due to the presence of two nitro groups. These electron-withdrawing groups facilitate the release of a proton and hence lower the $\log k_1^H$ value.

The values of the stability constants of the ferric complexes were calculated by interpolation at half $\bar{n}$ and linear extrapolation method [3]. The

TABLE 1

The proton–ligand stability constants of phenetsal and *p*-acetylaminophenyl 3,5-dinitrosalicylate

Temperature (°C)	Ionic strength (M)	$\log k_1^H$	
		Phenetsal	*p*-Acetylaminophenyl 3,5-dinitrosalicylate
25	0.05	8.93	8.65
	0.10	8.80	8.50
	0.20	8.70	8.20
35	0.10	8.60	8.05
45	0.10	8.45	7.80

TABLE 2

The stability constants of Fe(III) complexes in a 70:30 (v/v) alcohol water system

Ligand	Temperature (°C)	Ionic strength (M)	log k_1	log k_2	log β_2
p-Acetylaminophenyl salicylate					
	25	0.00	10.07	6.02	16.09
		0.05	8.88	5.23	14.11
		0.10	8.68	5.08	13.76
		0.20	8.00	4.86	12.86
	35	0.10	8.10	4.60	12.70
	45	0.10	7.72	4.30	12.02
p-Acetylaminophenyl 3,5-dinitrosalicylate					
	25	0.00	7.38	5.92	13.30
		0.05	6.80	5.50	12.30
		0.10	6.50	5.37	11.87
		0.20	6.25	5.20	11.45
	35	0.10	6.22	5.15	11.37
	45	0.10	6.00	5.07	11.07

values obtained by both the methods are in good agreement. The thermodynamic stability constants were obtained at 25°C by plotting log k_n against $\sqrt{\mu}$ and extrapolating to zero ionic strength. The values of the stability constants are given in Table 2. They show that log $k_1 >$ log k_2 at all temperatures and ionic strengths. The stabilities of the phenetsal complexes are higher than those of *p*-acetylaminophenyl 3,5-dinitrosalicylate under similar conditions. This accords with the log k_1^H value of phenetsal being higher than that of *p*-acetylaminophenyl 3,5-dinitrosalicylate. The ligands having higher values of log k_1^H form more stable complexes [7]. The stabilities of complexes record a decrease with rise of temperature and ionic strength. The values of the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) associated with complexation are calculated by the relationships

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

$$\frac{\Delta H}{RT^2} = \frac{\mathrm{d} \ln k}{\mathrm{d}T}$$

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

In order to obtain ΔH values, log k_n was plotted against $1/T$. The slope of the curve was calculated and used to calculate ΔH from

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

where s is the slope of the curve.

TABLE 3

The free energy changes (ΔG) associated with the formation of Fe(III) complexes at different temperatures and ionic strength 0.10 M

Ligand	Temperature (°C)	$-\Delta G_1$ (kcal mole^{-1})	$-\Delta G_2$ (kcal mole^{-1})	$-\Delta G = -(\Delta G_1 + \Delta G_2)$ (kcal mole^{-1})
p-Acetylaminophenyl salicylate				
	25	11.84	6.93	18.77
	35	11.42	6.48	17.90
	45	11.23	6.27	17.50
p-Acetylaminophenyl 3,5-dinitrosalicylate				
	25	8.86	7.32	16.18
	35	8.77	7.26	16.03
	45	8.73	7.29	16.02

TABLE 4

The enthalpy changes (ΔH) associated with the formation Fe(III) complexes in 70:30 (v/v) alcohol–water

Ligand	$-\Delta H_1$ (kcal mole^{-1})	$-\Delta H_2$ (kcal mole^{-1})	$-\Delta H = -(\Delta H_1 + \Delta H_2)$ (kcal mole^{-1})
p-Acetylaminophenyl salicylate			
	19.90	15.60	35.50
p-Acetylaminophenyl 3,5-dinitrosalicylate			
	11.46	9.80	21.26

TABLE 5

The entropy changes (ΔS) associated with the formation of Fe(III) complexes at ionic strength 0.01 M in 70:30 (v/v) alcohol–water

Ligand	Temperature (°C)	$-\Delta S_1$ (cal deg^{-1} mole^{-1})	$-\Delta S_2$ (cal deg^{-1} mole^{-1})	$-\Delta S = -(\Delta S_1 + \Delta S_2)$ (cal deg^{-1} mole^{-1})
p-Acetylaminophenyl salicylate				
	25	27.04	29.00	56.04
	35	27.53	29.60	57.13
	45	27.26	29.33	56.59
p-Acetylaminophenyl 3,5-dinitrosalicylate				
	25	8.72	8.32	17.04
	35	8.67	8.25	16.92
	45	8.58	7.89	16.47

The values of ΔG, ΔH and ΔS involved are given in Tables 3–5. The values of all these functions suggest that complexation in the present case is favourable at low temperature. The higher values of log k_n may be due to chelate formation.

REFERENCES

1 J. Bjerrum, Metal Ammine Formation in Aqueous Solution, Hasse, Copenhagen, 1941.
2 M. Calvin and K.W. Wilson, J. Am. Chem. Soc., 67 (1945) 2003.
3 H. Irving and H.S. Rossotti, J. Chem. Soc., (1953) 3397.
4 H. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.
5 A.G. Sterwin, Neth. Pat. Appl. 6,605,517 (1965).
6 L.G. Van Uitert and C.G. Haas, J. Am. Chem. Soc., 75 (1953) 451.
7 R.G. Pearson, J. Am. Chem. Soc., 85 (1963) 3533.