Thermochimica Acta, 62 (1983) 369–373
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

COMPLEXATION OF ZINC GROUP METAL IONS WITH PHENETSAL

V.K. JAITLY, H.S. HOTHI and B.S. PANNU

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

(Received 6 September 1982)

Phenetsal (*p*-acetylaminophenylsalicylate) was synthesised by Sterwin [1]. This compound possesses analgesic, anti-inflammatory, antipyretic and tuberculostatic properties. Therefore, the interaction of phenetsal with metal ions was considered desirable and its complexes with Fe(III) have already been reported [2]. In the present paper the stabilities and other thermodynamic functions of phenetsal complexes with Zn^{2+}, Cd^{2+} and Hg^{2+} are reported. The Bjerrum–Calvin [3,4] pH titration technique as extended by Irving and Rossotti [5] has been used for study.

EXPERIMENTAL

Phenetsal solution

Phenetsal (*p*-acetylaminophenylsalicylate) was synthesised by the method already reported [1]. It was dissolved in absolute alcohol to give a 0.02 M solution.

Metal salt solution

The metal salts used were of BDH AnalaR grade. These were dissolved in double distilled water and standardised to 0.01 M solution.

Carbonate-free KOH solution (0.1 M) was used for the potentiometric titrations. A one molar aqueous solution of $NaClO_4$ was used to maintain the required ionic strength. The aqueous 0.05 M $HClO_4$ was standardised against standard alkali.

Water thermostat

A SISCO (Calcutta) water thermostat type TBS was used to regulate the temperature during titration. It was fitted with an electric stirrer, heater and toluene regulator. The accuracy of temperature was maintained within $\pm 0.1°C$.

0040-6031/83/0000–0000/$03.00

pH meter

A systronics model 322-1 pH meter fitted with a glass and calomel electrode assembly reading up to 0.05 units was used for pH measurements. It was calibrated with standard buffers. Three titrations were performed with a standard alkali: (i) mineral acid alone; (ii) mineral acid + ligand solution; and (iii) mineral acid + ligand solution + metal ion solution.

The total initial volume in all titrations was 20.00 ml in a 70 : 30 (v/v) alcohol water system. The pH of the solution was noted after each addition of KOH. As the titrations were carried out in an alcohol water system, the correct values of pH were obtained by appropriate correction [6]. Curves were plotted between the volumes of alkali added and the pH reached.

RESULTS AND DISCUSSION

The values of $\bar{n}_A$, $\bar{n}$ and pL were calculated from the titration curves. The values of log k_1^H already reported [2] were used in the present calculations. Values of the stability constants of complexes were calculated by the half $\bar{n}$ method and the linear extrapolation method [7]. The values obtained by both methods are in good agreement and the average values of the stability constants are given in Table 1. The values of stability constants are in the order

$$Hg^{2+} > Zn^{2+} > Cd^{2+}$$

The second ionization potential values are 17.96, 16.91 and 18.75 eV and the electronegativity values, according to the Pauling scale, are 1.6, 1.7 and 1.9 for Zn, Cd and Hg, respectively. The ionic radii for Zn^{2+}, Cd^{2+} and Hg^{2+} are 0.74, 0.97 and 1.10 Å, respectively. The stability of a complex is directly related to the ionization potential and electronegativity of the metal, but it bears an inverse relation to the ionic radius of the ion. Values of the stability constant decrease with rise of temperature and ionic strength of the medium.

THERMODYNAMIC FUNCTIONS

Thermodynamic stability constants at 25°C were obtained by plotting log k_n against $\sqrt{\mu}$ and extrapolating to zero ionic strength. These values are given in Table 1. Values of the free energy changes (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS), associated with complexation, were derived using

$$\Delta G = -2.303\, RT \log k$$

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

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

TABLE 1

Stability constants and free energy change data of complexes of zinc group metal ions with *p*-acetylaminophenylsalicylate in a 70:30 (v/v) alcohol water system

Metal ion	Temp. (°C)	Ionic strength, *M*	log k_1	log k_2	log β_2	$-\Delta G_1$ (kcal mole^{-1})	$-\Delta G_2$ (kcal mole^{-1})	$-\Delta G$ [a] (kcal mole^{-1})
Zn^{2+}	25	0.00	5.49	4.34	9.83	7.49	5.92	13.41
		0.05	5.06	4.17	9.23	6.90	5.69	12.59
		0.10	4.92	3.99	8.91	6.71	5.44	12.15
		0.20	4.65	3.81	8.46	6.34	5.20	11.54
	35	0.10	4.58	3.70	8.28	6.46	5.21	11.67
	45	0.10	4.31	3.47	7.78	6.27	5.05	11.32
Cd^{2+}	25	0.00	5.03	3.90	8.93	6.86	5.32	12.18
		0.05	4.60	3.64	8.24	6.27	4.96	11.23
		0.10	4.36	3.54	7.90	5.95	4.83	10.78
		0.20	4.17	3.40	7.57	5.69	4.64	10.33
	35	0.10	4.05	3.10	7.15	5.71	4.37	10.08
	45	0.10	3.82	2.83	6.65	5.56	4.12	9.68
Hg^{2+}	25	0.00	6.67	4.65	11.32	9.10	6.34	15.44
		0.05	6.26	4.32	10.58	8.54	5.89	14.43
		0.10	6.01	4.15	10.25	8.20	5.66	13.86
		0.20	5.84	4.00	9.84	7.96	5.45	13.41
	35	0.10	5.75	3.84	9.59	8.10	5.41	13.51
	45	0.10	5.54	3.60	9.14	8.06	5.24	13.30

[a] $\Delta G = \Delta G_1 + \Delta G_2$

TABLE 2

Enthalpy data of complexes of zinc group metal ions with *p*-acetylaminophenylsalicylate in a 70 : 30 (v/v) alcohol water system

Metal ion	$-\Delta H_1$ (kcal mole^{-1})	$-\Delta H_2$ (kcal mole^{-1})	$-\Delta H = -(\Delta H_1 + \Delta H_2)$ (kcal mole^{-1})
Zn^{2+}	13.66	11.44	25.00
Cd^{2+}	12.00	11.20	23.20
Hg^{2+}	12.30	11.97	24.27

TABLE 3

Entropy data of complexes of zinc group metal ions with *p*-acetylaminophenylsalicylate in a 70 : 30 (v/v) alcohol water system

Metal Ion	Temp. (°C)	Ionic strength *M*	$-\Delta S_1$ (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})
Zn^{2+}	25	0.00	20.70	18.52	39.22
		0.05	22.68	19.30	41.98
		0.10	23.32	20.14	43.46
		0.20	24.56	20.93	45.49
	35	0.10	23.38	20.23	43.61
	45	0.10	23.24	20.09	43.33
Cd^{2+}	25	0.00	17.24	19.73	36.97
		0.05	19.22	20.93	40.15
		0.10	20.30	21.38	41.68
		0.20	21.17	22.10	43.27
	35	0.10	18.53	22.92	41.45
	45	0.10	20.25	23.75	44.00
Hg^{2+}	25	0.00	10.74	18.89	29.63
		0.05	12.62	20.40	33.02
		0.10	13.76	21.17	34.93
		0.20	14.56	21.87	36.43
	35	0.10	13.64	21.30	34.94
	45	0.10	13.33	21.16	34.49

Log k_n was plotted against $1/T$ and the slope, s, of the curve was obtained.

The value of ΔH was calculated using

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

The values of ΔG, ΔH and ΔS are given in Tables 1, 2 and 3, respectively. Both ΔH and ΔS are negative. The enthalpy changes show that complexation is favourable at low temperature.

REFERENCES

1 A.G. Sterwin, Neth. Pat. Appl., 6 (1965) 517, 605.
2 V.K. Jaitly and B.S. Pannu, Thermochim. Acta, 60 (1983) 109.
3 J. Bjerrum, Metal Ammine Formation in Aqueous Solution, Haase, Copenhagen, 1941.
4 M. Calvin and K.W. Wilson, J. Am. Chem. Soc., 67 (1945) 2003.
5 H. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.
6 L.G. Van Uitert and C.G. Haas, J. Am. Chem. Soc., 75 (1953) 451.
7 H. Irving and H.S. Rossotti, J. Chem. Soc., (1953) 3397.