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Note

THERMODYNAMICS OF ZINC GROUP COMPLEXES OF *p*-ACETYLAMINOPHENYL 3,5-DINITRO SALICYLATE

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In continuation with the study of metal complexes of *p*-acetylaminophenyl 3,5-dinitrosalicylate [1,2] the interaction of zinc group ions with it was thought to be valuable. The stability constants and the related thermodynamic functions are reported in this communication.

EXPERIMENTAL

The ligand solution (pure *p*-acetylaminophenyl 3,5-dinitrosalicylate) was prepared by the method previously reported [1] and a 0.05 M solution was prepared in absolute alcohol.

The salts of BDH AnalaR Grade were used to prepare 0.05 M $HClO_4$, 1.0 M $NaClO_4$, 0.10 M KOH and 0.01 M metal ion solutions in double-distilled water.

The buffer solutions of pH 4.0 and 9.2 were prepared in a 70 : 30 (v/v) alcohol–water system for calibration of the pH meter. A Sico (Calcutta) water thermostat (type TBS) was used to regulate the temperature. A systronic pH meter (model 322-1) with a glass and calomel electrodes assembly was used for the pH measurement. A modified method [3] of the Bjerrum–Calvin [4,5] pH titration technique was used. The following three solutions were titrated against standard alkali:

(A) mineral acid alone;
(B) mineral acid + ligand solution;
(C) mineral acid + ligand solution + metal ion solution.

The total initial volume was 20 ml in alcohol–water (70 : 30, v/v) in each case. The ionic strength was adjusted with 1 M $NaClO_4$ solution.

RESULTS AND DISCUSSION

The titration curves were plotted between the volume of alkali added and the corresponding *B* value (*B* is pH meter reading). The shapes of the

TABLE 1

Stability constants of zinc group complexes of *p*-acetylaminophenyl 3,5-dinitrosalicylate in the system alcohol–water (70 : 30, v/v)

Metal ion	Temp. (°C)	Ionic strength (M)	Log K_1	Log K_2	Log β_2
Zn^{2+}	25	0.00	4.55	4.10	8.65
		0.05	4.15	3.60	7.75
		0.10	3.82	3.30	7.12
		0.20	3.65	3.12	6.77
	35	0.10	3.58	3.08	6.66
	45	0.10	3.40	2.90	6.30
Cd^{2+}	25	0.00	3.80	3.15	6.95
		0.05	3.47	2.92	6.39
		0.10	3.22	2.62	5.84
		0.20	3.03	2.60	5.63
	35	0.10	2.90	2.57	5.47
	45	0.10	2.80	2.52	5.32
Hg^{2+}	25	0.00	5.55	5.00	10.55
		0.05	5.10	4.52	9.62
		0.10	4.93	4.12	9.02
		0.20	4.52	3.85	8.37
	35	0.10	4.43	3.65	8.08
	45	0.10	4.23	3.40	7.63

TABLE 2

Free energy changes (ΔG) associated with zinc group complexes of *p*-acetylaminophenyl 3,5-dinitrosalicylate in the system alcohol–water (70 : 30, v/v)

Metal ion	Temp. (°C)	Ionic strength	$-\Delta G_1$ (kcal mol^{-1})	$-\Delta G_2$ (kcal mol^{-1})	$-\Delta G^{*}$ [a] (kcal mol^{-1})
Zn^{2+}	25	0.00	6.20	5.59	11.79
		0.05	5.66	4.91	10.57
		0.10	5.21	4.50	9.71
		0.20	4.98	4.25	9.23
	35	0.10	5.05	4.34	9.39
	45	0.10	4.95	4.22	9.17
Cd^{2+}	25	0.00	5.18	4.30	9.48
		0.05	4.73	3.98	8.71
		0.10	4.39	3.57	7.96
		0.20	4.13	3.53	7.66
	35	0.10	4.09	3.62	7.71
	45	0.10	4.07	3.67	7.74
Hg^{2+}	25	0.00	7.57	6.81	14.38
		0.05	6.95	6.16	13.11
		0.10	6.72	5.61	12.33
		0.20	6.16	5.25	11.41
	35	0.10	6.24	5.14	11.38
	45	0.10	6.16	4.95	11.11

[a] $\Delta G^{*} = \Delta G_1 + \Delta G_2$.

TABLE 3

Enthalpy changes (ΔH) associated with zinc group complexes of *p*-acetylaminophenyl 3,5-dinitrosalicylate in the system alcohol–water (70:30, v/v) with $\mu = 0.10$ M

Metal ion	$-\Delta H_1$ (kcal mol^{-1})	$-\Delta H_2$ (kcal mol^{-1})	$-\Delta H^*$ (kcal mol^{-1})
Zn^{2+}	9.81	8.58	18.39
Cd^{2+}	9.15	4.87	14.02
Hg^{2+}	12.71	11.90	24.61

titration curves indicate the formation of complexes. It has been observed that the formation of all the complexes starts around pH 1.5 and becomes appreciable at above pH 5. The values of $\bar{n}_A$, $\bar{n}$ and pL were calculated from the titration curves by the Irving and Rossotti method [3]. The values of $\bar{n}$ do not go beyond 2. This suggests the formation of 1:1 and 1:2 complexes. The formation curves were plotted of $\bar{n}$ vs. pL. The values of stability constants were obtained by half $\bar{n}$ and linear extrapolation methods [6]. The thermodynamic stability constants were obtained by plotting log K_n vs. $\sqrt{\mu}$ and extrapolating to zero ionic strength. These values are given in Table 1. The stability constants decrease with the rise in temperature and increase in ionic strength. The stabilities of the complexes are in the order $Hg^{2+} > Zn^{2+} > Cd^{2+}$. This shows that the stabilities increase with the increase in ionization potential and decrease in ionic radius. The high values of stability constants suggest a chelate nature for these complexes. The values of free energy changes, ΔG, enthalpy changes, ΔH, and entropy changes, ΔS, associated with complexation are given in Tables 2–4. All the complexes are enthalpy stabilized. The negative values of ΔH suggest that the formation of complexes is exothermic. However, these complexes are not entropy stabilized as these values are negative.

TABLE 4

Entropy changes (ΔS) associated with zinc group complexes of *p*-acetylaminophenyl 3,5-dinitrosalicylate in the system alcohol–water (70:30, v/v) with $\mu = 0.10$ M

Metal ion	Temp. (°C)	$-\Delta S_1$ (cal K^{-1} mol^{-1})	$-\Delta S_2$ (cal K^{-1} mol^{-1})	$-\Delta S^*$ (cal K^{-1} mol^{-1})
Zn^{2+}	25	15.44	13.70	29.14
	35	15.45	13.77	29.22
	45	15.29	13.71	29.00
Cd^{2+}	25	15.97	4.36	20.33
	35	16.43	4.38	21.81
	45	15.98	3.77	19.75
Hg^{2+}	25	20.10	21.11	41.21
	35	21.00	21.95	42.95
	45	20.60	21.86	42.46

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