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Note

THERMODYNAMICS OF GROUP IIA METAL IONS COMPLEXES OF PHENETSAL

S. CHOPRA, R.P. SINGH * and B.S. PANNU

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

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Phenetsal possesses analgesic, anti-inflammatory and antipyretic activity. Some metal ions of group IIA like Mg^{2+}, Ca^{2+} play an important role in biological processes. Further to the previous work on metal complexes of phenetsal [1–3], the determination of thermodynamic functions of its complexes with group IIA metal ions was undertaken. The stability constants have been determined by the Bjerrum–Calvin pH titration technique [4,5] as modified by Irving and Rossotti [6,7].

EXPERIMENTAL

Phenetsal solution. Phenetsal was prepared by the method reported in the literature [8]. The purified sample (m.p. 187.5 °C) was dissolved in absolute alcohol to produce a 0.02 M solution.

Metal ion solutions. Metal nitrates were dissolved in double-distilled water and the solutions standardized to 0.01 M.

Other reagents. Aqueous solution of sodium perchlorate (1 M) was used to maintain the ionic strength. The standard solutions of $HClO_4$ (0.05 M) and carbonate free KOH (0.10 M) were prepared in double-distilled water.

pH measurements. A systronics model 322-1 pH meter, having a glass and calomel electrodes assembly, calibrated with buffer solutions was used to measure pH.

A water thermostat SICO (Calcutta) thermostat type TBS, was used to maintain constant temperature. The following three solutions were titrated against 0.1 M KOH solution: (i) 2.00 ml of 0.05 M $HClO_4$; (ii) 2.00 ml of 0.05 M $HClO_4$ + 5.00 ml of 0.02 M ligand; (iii) 2.00 ml of 0.05 M $HClO_4$ +

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* G.G.N. Khalsa College, Ludhiana, India.

5.00 ml of 0.02 M ligand + 2.00 ml of 0.01 M metal ion. The initial volume was 20.00 ml in alcohol : water 70 : 30 (v/v) in each case. The titrations were carried at 25 °C with ionic strengths 0.05, 0.10 and 0.20 M, and at 35 and 45 °C with ionic strength 0.05 M.

TABLE 1

The stability constants of metal phenetsal complexes in an alcohol : water system 70 : 30 (v/v) at different temperatures and ionic strengths

Metal ion	Temperature (°C)	Ionic strength (M)	log K_1	log K_2	log β_2
Be^{2+}	25	0.00	8.87	7.38	16.25
		0.05	8.68	7.23	15.91
		0.10	8.60	7.12	15.72
		0.20	8.49	7.02	15.51
	35	0.05	8.47	7.04	15.51
	45	0.05	8.28	6.87	15.15
Mg^{2+}	25	0.00	4.97	3.32	8.29
		0.05	4.80	2.95	7.75
		0.10	4.73	2.86	7.59
		0.20	4.62	2.68	7.30
	35	0.05	4.66	2.84	7.50
	45	0.05	4.53	2.75	7.28
Ca^{2+}	25	0.00	5.66	3.47	9.13
		0.05	5.48	3.28	8.76
		0.10	5.40	3.20	8.60
		0.20	5.30	3.10	8.40
	35	0.05	5.33	3.13	8.46
	45	0.05	5.19	2.99	8.18
Sr^{2+}	25	0.00	4.70	2.95	7.65
		0.05	4.48	2.82	7.30
		0.10	4.35	2.77	7.12
		0.20	4.25	2.72	6.97
	35	0.05	4.30	2.63	6.93
	45	0.05	4.14	2.46	6.60
Ba^{2+}	25	0.00	4.22	2.51	6.73
		0.05	3.98	2.29	6.27
		0.10	3.88	2.20	6.08
		0.20	3.75	2.05	5.80
	35	0.05	3.83	2.24	5.88
	45	0.05	3.69	2.10	5.61

RESULTS AND DISCUSSION

The corrected pH values were obtained by the Van Uitert and Haas method [9]. The values of average coordination number, $\bar{n}$ and free ligand

TABLE 2

The energy changes ΔG, involved in the formation of metal phenetsal complexes in the alcohol : water system 70 : 30 (v/v)

Metal ion	Temperature (°C)	Ionic strength (M)	$-\Delta G_1$ (kcal mol^{-1})	$-\Delta G_2$ (kcal mol^{-1})	$-\Delta G$ [a] (kcal mol^{-1})
Be^{2+}	25	0.00	12.09	10.06	22.15
		0.05	11.84	9.86	21.70
		0.10	11.73	9.71	21.44
		0.20	11.58	9.57	21.15
	35	0.05	11.93	9.92	21.71
	45	0.05	12.04	10.00	22.04
Mg^{2+}	25	0.00	6.78	4.53	11.31
		0.05	6.55	4.02	10.57
		0.10	6.45	3.90	10.35
		0.20	6.30	3.66	9.96
	35	0.05	6.56	4.00	10.56
	45	0.05	6.59	4.00	10.59
Ca^{2+}	25	0.00	7.72	4.73	12.45
		0.05	7.47	4.47	11.94
		0.10	7.36	4.36	11.72
		0.20	7.32	4.23	11.55
	35	0.05	7.51	4.41	11.92
	45	0.05	7.55	4.35	11.90
Sr^{2+}	25	0.00	6.41	4.02	10.43
		0.05	6.11	3.85	9.96
		0.10	5.94	3.78	9.72
		0.20	5.80	3.71	9.51
	35	0.05	6.06	3.71	9.72
	45	0.05	6.02	3.58	9.51
Ba^{2+}	25	0.00	5.76	3.42	9.18
		0.05	5.43	3.12	8.55
		0.10	5.30	3.00	8.30
		0.20	5.12	2.80	7.92
	35	0.05	5.40	3.16	8.29
	45	0.05	5.37	3.05	8.16

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

TABLE 3

The enthalpy changes ΔH associated with the formation of metal–phenetsal complexes in the alcohol : water system 70 : 30 (v/v)

Metal ion	$-\Delta H_1$ (kcal mol^{-1})	$-\Delta H_2$ (kcal mol^{-1})	$-\Delta H$ [a] (kcal mol^{-1})
Be^{2+}	8.55	7.89	16.44
Mg^{2+}	5.93	4.45	10.38
Ca^{2+}	6.08	6.00	12.08
Sr^{2+}	7.26	7.62	14.88
Ba^{2+}	6.57	6.28	12.85

[a] $\Delta H = \Delta H_1 + \Delta H_2$.

concentration pL ($-\log$ [L]) were calculated from the titration curves drawn for each titration by plotting the volumes of alkali added against pH reached. The formation curves were plotted between $\bar{n}$ and pL values. These curves were used to calculate the stability constants. The thermodynamic stability constants at 25 °C were obtained by plotting log K versus $\sqrt{\mu}$ and extrapolating to zero ionic strength. The values of the stability constants at different temperatures and ionic strengths are given as log K_n or log β_2 in Table 1.

The values of the free energy change ΔG and enthalpy change ΔH associated with the formation of complexes were calculated by the relationships $\Delta G = -RT \ln K$ and $\Delta H/RT^2 = \mathrm{d} \ln k/\mathrm{d}T$.

The values of enthalpy changes ΔH, were obtained by making a plot of log K vs. $1/T$ and getting the slope S of the curve. Then the values of ΔH were calculated using the relationship $\Delta H = -2.303\ RS$, where $R = 1.987$ cal K^{-1} mol^{-1}. The values of ΔG and ΔH obtained are given in Tables 2 and 3, respectively.

The stability order for these complexes is $Be^{2+} > Mg^{2+} < Ca^{2+} > Sr^{2+} > Ba^{2+}$. The observed order of stabilities except Mg^{2+} can be explained on the basis of ionic radii, ionization potential and electronegativity values [9,10]. However, in some other cases also the stability of Mg^{2+} complexes has been reported to be less than that of Ca^{2+} [10,11]. This may be due to chelate formation where the small size of Mg^{2+} compared with Ca^{2+} may not be favourable for ring formation.

The values of stabilities of Be^{2+} complexes are very large compared with those of other ions. Be^{2+} exhibits different behaviour from the other metal ions. Beryllium and oxygen each being the first member of respective families in the periodic table, these should interact to give highly stable complexes according to the classification of metal ions into class (a) and class (b) or hard and soft acids and bases [12,13]. Beryllium behaves as a metal ion of class (a) or hard acid. This is why it forms very stable complexes with phenetsal which contains oxygen as a coordinating site. The stabilities record a decreasing trend with increase of ionic strength of the medium and rise of temperature.

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