Thermochimica Acta, 46 (1981) 61—63
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

STEPWISE STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF 4-(2-HYDROXYPHENYL) HYDRAZONO-*N*-BENZYLSULPHONYL-3-METHYL-2-PYRAZOLIN-5-ONE (HBSP) AND ITS METAL COMPLEXES

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(Received 5 November 1980)

Pyrazolin-5-ones have been of interest because of their medicinal [1,2], analytical [3,4] and commercial importance [5]. Because of this, the metal complexes of pyrazolin-5-ones have been studied by various workers [6,7]. A literature survey reveals that HBSP, a potential antidiabetic compound [8], has not been studied from the viewpoint of coordination, so it was considered interesting to extend our study to determine the stability constants and thermodynamic functions of the complexes of UO_2^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+} and Mn^{2+} with HBSP in a 75 : 25 (v/v) methanol—water mixture employing the Bjerrum—Calvin titration technique as modified by Irving and Rossotti [9,10].

EXPERIMENTAL

Metal salt solutions were prepared in double-distilled water and standardised. The reagent (HBSP) was prepared following the method described by Garg and Prakash [8]. Since HBSP is insoluble in water its stock solution (0.002 M) was prepared in methanol. pH values of the solutions were measured using an ECIL expanded scale pH meter with a glass and calomel electrode combination.

The experimental procedure involved the titration of the following carbonate-free solutions against standard sodium hydroxide (0.1 M).

(i) 4 ml 0.04 M $HClO_4$ + 4 ml 1.0 M $NaClO_4$ + 30 ml methanol + 2 ml water;

(ii) 4 ml 0.04 M $HClO_4$ + 4 ml 1.0 M $NaClO_4$ + 20 ml 0.002 M ligand + 10 ml methanol + 2 ml water;

(iii) 4 ml 0.04 M $HClO_4$ + 4 ml 1.0 M $NaClO_4$ + 20 ml 0.002 M ligand + 10 ml methanol + 1 ml 0.01 M metal salt solution + 1 ml water.

All the solutions were thermostated at 25, 30 and 35 ± 0.1°C. The ligand : metal ratio was 4 : 1 in all the titrations.

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0040-6031/81/0000—0000/$02.50

RESULTS AND DISCUSSION

The average number of protons associated with the ligand was determined from the acid—ligand titration curve employing the equation of Irving and Rossotti. The $\bar{n}_A$ values were always found to be less than one. The value of log K^H was obtained at half integral value. The proton ligand stability constants and their thermodynamic functions are given in Tables 1 and 2, respectively, which show that log K^H decreases with increase in temperature.

Values of $\bar{n}$ of the metal complexes at various pH values were determined from the titration curves of solutions (ii) and (iii). From a knowledge of practical K^H values and $\bar{n}$ values at a particular pH, the corresponding pL value was then calculated. The $\bar{n}$ values are plotted against the corresponding pL values to give the formation curves of the metal complexation equilibria. K_1 and K_2 can be read directly from the formation curves using Bjerrum's half $\bar{n}$ method. The least squares method [10] was used to correct the stability constants.

The metal ligand stability data, log K_1 (±0.04), log K_2 (±0.05) and log β_2 (±0.09), at various temperatures are reported in Table 1. In all the cases studied the values of $\bar{n}$ were always less than two, showing the formation of only two complexes, viz. 1 : 1 and 1 : 2 complexes. The order of stability of bivalent and trivalent metal complexes at 25°C is found to be $Fe^{3+} > UO_2^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Fe^{2+} > Mn^{2+}$. The higher stability of the Co^{2+} complex as compared to that Ni^{2+} may be attributed to Jahn–Teller distortion present in the former case. At 30 and 35°C the order of stability is in accordance with the Irving—Williams rule [11].

The higher stability of the Fe(III) complex as compared to that of bivalent metal complexes is justified on the basis of the charge and ionisation potential of ions [12]. The overall changes in free energy, enthalpy and entropy have also been evaluated using standard expressions [10]. The values of log β_2 obtained at different temperatures were plotted as a function of $1/T$. The gradient was taken to $-H/4.57$; wherever a linear plot was not obtained a tangent was drawn to obtain the slope. The values of thermo-

TABLE 1

Stability constants of metal complexes with HBSP at different temperatures (at μ = 0.1 M ($NaClO_4$)

Cations	25°C			30°C			35°C		
	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2
H^+			8.60			8.40			8.10
Fe^{3+}	7.90	5.80	13.70	7.55	5.70	13.25	7.40	5.35	12.75
UO^{2+}	7.55	5.65	13.20	7.30	5.45	12.75	7.10	5.24	12.30
Cu^{2+}	7.30	5.56	12.86	7.15	5.30	12.45	6.85	5.15	12.00
Ni^{2+}	6.75	5.00	11.75	6.65	4.80	11.45	6.40	4.65	11.05
Co^{2+}	6.90	4.95	11.85	6.48	4.65	11.13	6.30	4.45	10.75
Fe^{2+}	6.35	4.85	11.20	6.15	4.55	10.70	5.95	4.15	10.10
Mn^{2+}	5.65	4.66	10.31	5.40	4.25	9.65	5.25	4.00	9.25

TABLE 2

Values of thermodynamic functions of metal complexes with HBSP at 30°C

Cations	$-\Delta G$ (kcal mole^{-1})			$-\Delta H$ (kcal mole^{-1})			$-\Delta S$ (cal mole^{-1})		
	ΔG_1	ΔG_2	ΔG^0	ΔH_1	ΔH_2	ΔH^0	ΔS_1	ΔS_2	ΔS^0
H^+			11.65			21.76			33.37
Fe^{3+}	10.45	7.90	18.37	19.04	20.77	41.54	28.29	42.48	76.48
UO_2^{2+}	10.12	7.56	17.68	19.87	17.58	39.81	32.18	33.07	73.04
Cu^{2+}	9.91	7.35	17.26	15.76	17.58	38.08	19.36	33.76	68.70
Ni^{2+}	9.22	6.66	15.88	15.23	15.87	31.56	26.45	30.39	51.75
Co^{2+}	8.98	6.45	15.43	21.76	21.76	48.21	42.16	50.53	108.18
Fe^{2+}	8.53	6.31	14.84	17.58	26.88	45.70	29.87	67.89	101.85
Mn^{2+}	7.49	5.89	13.38	15.76	27.73	45.70	27.29	72.08	106.67

dynamic functions are summarised in Table 2. It is seen that ΔG values are negative, showing that complex formation is spontaneous. The negative values of ΔH and ΔS also indicate that complex formation is accompanied by liberation of energy and is an enthalpy directed process.

Potentiometric studies suggest the formation of 1 : 1 and 1 : 2 complexes and thermodynamic studies point towards an enthalpy-directed process.

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