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THERMODYNAMIC STUDIES ON THE CHELATION BEHAVIOUR OF BIVALENT METAL COMPLEXES OF 2-HYDROXY-1,4-NAPHTHOQUINONE MONOSEMICARBAZONE (HNQS)

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ABSTRACT

Thermodynamic studies on bivalent metal complexes have been made potentiometrically in 75% (v/v) aqueous dioxan medium at various temperatures. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used to find out the values of $\bar{n}$ and pL. The stability constants have been calculated on an IBM 360 computer using a weighted least-squares method. The values of $S_{\min}$ have also been calculated. The order of stability constants was found to be Cu > Pb > Zn > Ni > Co > Cd > Mn > Mg. The other thermodynamic functions (ΔG, ΔH and ΔS) have been calculated from the stability constants obtained for different temperatures at constant ionic strength.

INTRODUCTION

The semicarbazones and thiosemicarbazones of certain ketones and aldehydes have significant antimicrobial activities [1–5]. Domagk et al. [6] reported for the first time the anti-tubercular activities of metal thiosemicarbazones and semicarbazones. Since then a number of papers have appeared on the pharmacology of these compounds. The activity of semicarbazones is thought to be due to their power of chelation with traces of metal ions present in biological systems.

As a part of an intense study undertaken in our laboratories on the thermal behaviour of metal complexes of biologically active *O*-hydroxy naphthoquinones, we describe here the thermal stability results of bivalent metal complexes with 2-hydroxy-1,4-naphthoquinone monosemicarbazone at different temperatures in 75% dioxan medium.

EXPERIMENTAL

Chemicals

2-Hydroxy-1,4-naphthoquinone monosemicarbazone (HNQS) was prepared by dissolving the requisite amount of 2-hydroxy-1,4-naphthoquinone

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in a minimum amount of alcohol and adding to it an aqueous solution containing semicarbazide hydrochloride and an equal amount of anhydrous sodium acetate. The mixture was refluxed for 1 h and the HNQS was precipitated by adding dilute hydrochloric acid to the solution. The HNQS thus obtained was recrystallised from ethanol. HNQS solution was prepared in freshly distilled dioxan.

The solutions of bivalent metal ions, viz. Mg(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), were standardised by conventional methods.

Me_4NOH (TMAH) (Merck) in 75% dioxan (aqueous) was used as titrant. This solution was standardised with $(CO_2H)_2$.

$HClO_4$ was standardised with Na_2CO_3 and diluted to the required molarity (0.05 M); conductivity $H_2O \cdot NaClO_4$ (Riedel) was used to maintain the ionic strength.

Dioxan AR (BDH) was purified by the method given by Vogel [7].

Apparatus

A digital pH meter (ECIL, model PH 5651) in conjunction with a glass electrode was used for pH measurements. The pH meter was standardised with potassium hydrogen phthalate and phosphate buffers before performing the titration. All measurements were made at a definite temperature maintained constant by using an MLW (West Germany) (NBE type) thermostat. An IBM 360 computer was used for most of the calculations.

Titration technique

Investigations were carried out at four temperatures, viz. 20, 30, 40 and 50°C, at 0.1 M $NaClO_4$ ionic strength. For each set of experiments, the final volume was made up to 20 cm^3, maintaining the 75% aqueous dioxan medium. Each set was titrated against 0.05 M TMAH in 75% aqueous dioxan.

The titrations were carried out in a covered, double-walled glass cell in an atmosphere of N_2, which was presaturated with the solvent (75% dioxan in H_2O) before being passed into the reaction solution.

RESULTS AND DISCUSSION

Values of $\bar{n}_H$ were calculated at various pH values from the titration curve. The pK value of the ligand was found by plotting $\log(\bar{n}_H/1-\bar{n}_H)$ vs. pH and the values thus obtained were: 7.40, 6.86, 6.48, 6.24 at 20, 30, 40 and 50°C, respectively, with $\mu = 0.1$ M $NaClO_4$. The stability constant order for the metal chelates of HNQS is: Cu > Pb > Zn > Ni > Co > Cd > Mn > Mg,

TABLE 1

Stability constants of bivalent metal complexes of 2-hydroxy-1,4-naphthoquinone monosemicarbazone

Metal ion	Weighted least-squares method			S_{min}
	log K_1	log K_2	log β_2	
μ = 0.1 M NaClO$_4$, temp. = 20 ± 0.5°C				
H^+	7.40	–	–	–
Cu(II)	5.68	5.00	10.68	0.0030
Pb(II)	5.27	4.67	9.94	0.0186
Zn(II)	4.82	3.75	8.57	0.0394
Ni(II)	4.55	3.74	8.29	0.0108
Co(II)	4.25	3.56	7.81	0.0080
Cd(II)	4.20	3.47	7.67	0.0315
Mn(II)	3.63	2.85	6.48	0.0000
Mg(II)	3.41	2.98	6.39	0.0137
μ = 0.1 M NaClO$_4$, temp. = 30 ± 0.5°C				
H^+	6.86	–	–	–
Cu(II)	5.40	5.16	10.56	0.0508
Pb(II)	5.17	4.52	9.69	0.0027
Zn(II)	4.72	4.51	9.23	0.0043
Ni(II)	4.34	4.04	8.38	0.0048
Co(II)	4.13	3.07	7.20	0.0004
Cd(II)	4.13	3.32	7.45	0.0021
Mn(II)	3.58	3.15	6.75	0.0006
Mg(II)	3.11	2.65	5.76	0.0016
μ = 0.1 M NaClO$_4$, temp. = 40 ± 0.5°C				
H^+	6.48	–	–	–
Cu(II)	5.18	5.03	10.21	0.0256
Pb(II)	4.90	4.70	9.60	0.0125
Zn(II)	4.63	3.34	7.97	0.0012
Ni(II)	4.25	3.98	8.23	0.0357
Co(II)	4.10	4.01	8.11	0.0229
Cd(II)	4.05	3.82	7.87	0.0171
Mn(II)	3.46	2.43	5.89	0.0000
Mg(II)	2.88	2.64	5.52	0.0003
μ = 0.1 M NaClO$_4$, temp. = 50 ± 0.5°C				
H^+	6.24	–	–	–
Cu(II)	5.09	4.71	9.80	0.0039
Pb(II)	4.75	3.82	8.57	0.0044
Zn(II)	4.55	4.37	8.92	0.0201
Ni(II)	4.12	3.06	7.18	0.0016
Co(II)	4.08	4.02	8.10	0.0035
Cd(II)	3.99	2.82	6.81	0.0001
Mn(II)	3.35	3.11	6.46	0.0001
Mg(II)	2.70	2.42	5.12	0.0002

TABLE 2

Thermodynamic parameters of bivalent metal complexes of 2-hydroxy-1,4-naphthoquinone monosemicarbazone at $\mu = 0.1$ M $NaClO_4$ and temp. = 20 ± 0.5°C

Metal ion	$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	ΔS (kcal K^{-1} mol^{-1})
Cu(II)	7.61	6.85	0.0026
Pb(II)	7.07	6.85	0.0007
Zn(II)	6.47	3.42	0.0103
Ni(II)	6.11	5.71	0.0013
Co(II)	5.71	2.83	0.0098
Cd(II)	5.64	2.83	0.0095
Mn(II)	4.87	3.42	0.0049
Mg(II)	4.58	4.57	0.0000

which is in good agreement with the order found by Mellor and Maley [8] and Irving and Williams [9,10]. In these studies the stability constant decreases as the temperature increases along with the pK value. These results are in good agreement with those of Pitzer [11]. The log K_1, log K_2, log β_2 and S_{min} values at different temperatures ($\mu = 0.1$ M) are given in Table 1.

The results show that the stability of the metal chelates increases regularly from Mn to Cu and falls again at Zn. Furthermore, the stability order is independent of the ligand. Minor deviations can be predicted on theoretical grounds. The regularity of this stability sequence can be correlated with a monotonic decrease in the ionic radii, and a monotonic increase in the second ionisation potential which, in passing from Mn to Cu, may be taken to indicate that either coordination has not altered the electronic ground-state of the metal ions or that any modifications are of secondary importance. For these chelates $\bar{n}$ values greater than 2.0 have not been obtained. We therefore conclude that not more than two chelates, i.e., 1:1 and 1:2 (M:L) are formed in each system.

The overall free energy, enthalpy and entropy changes at 20°C are reported in Table 2. The results indicate that ΔH and ΔG are negative, which shows that chelate formation takes place spontaneously and with liberation of energy. The entropy is, however, positive for all the chelates showing that the entropy is favourable for the formation of the complexes.

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