POLAROGRAPHIC BEHAVIOUR OF Cu(II) AND Ni(II) COMPLEXES WITH 2-HYDROXY-DEOXYBENZOIN IN 65% ETHANOL-WATER MEDIA

V.K. Sharma+ and N.R. Bannerjee*

Department of Chemistry, University of Delhi, Delhi-110007, India

+ Lecturer in D.A.V. College, Kangra (H.P.)

Complexation behaviour of 2-hydroxy-deoxybenzoin (2HDB) with Ni(II) and Cu(II) ions have been investigated by polarographic method. Crow's mean diffusion coefficient method has been applied to determine the stability constant values. Both Ni(II) and Cu(II) form 1:1 and 1:2 complexes with 2-HDB. Thermodynamic parameters for the complexes also had been determined.

Potentiometric studies of complexation of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 2-hydroxy-deoxybenzoin (2-HDB) had been carried out by Sharma and Bannerjee [1] and Priyokumar [2]. They concluded that the ligand forms 1:1 complex with all the ions. On the other hand polarographic studies [3] of Co(II)-2HDB showed some unusual behaviour; Co(II) and Zn(II) form 1:1 and 1:2 complexes with 2-HDB. In the present communication, polarographic results on complexation of 2-hydroxy-deoxybenzoin with Cu(II) and Ni(II) at different temperatures have been described. The stability constants have been determined by Crow's mean diffusion coefficient method [4] and thermodynamic parameters have been calculated.

EXPERIMENTAL

Copper and Nickel sulphates, lithium hydroxide and perchloric acid were of AR grade. Lithium perchlorate was prepared by neutralizing perchloric acid with lithium hydroxide and then crystallizing the salt from distilled water. 2-Hydroxy-deoxybenzoin was prepared in the laboratory [5.6] and crystallized from ethanol (m.p.333°K). Stock solution (1.0 mol m^{-3}) of 2-HDB was prepared in purified [1] ethanol.

Test solutions for polarographic analysis contained 0.1 mol m^{-3} of metal ion, 0.1 mol dm^{-3} of $LiClO_4$, different amounts of the ligand and 65% ethanol.

An H-type Kalousek cell with a decinormal calomel electrode (NaCl, 0.1 mol dm^{-3}) in the second limb and a coiled pt wire counter electrode dipped along with dme in the test solution, was used for the studies and a Radiometer polarograph Polariter PO4g in conjunction with a Metrohm IR compensator CH9100 was used to record the polarograms. A Sargent capillary with characteristics m =1.688 mgs^{-1} and t =4.3s h = 70 cm Hg was used as dme. The pH of solutions were adjusted using an ELICO digital pH-meter LI-120 (India) The solutions were thermostatted at the required temperature and nitrogen gas was passed through the solutions for fifteen minutes before recording the polarograms

RESULTS AND DISCUSSION

Complexes of Cu(II) Ions

A well-defined wave was obtained for Cu(II) ion (0.1 mol m^{-3}) in 0.1 mol dm^{-3} $LiClO_4$ at pH 5.5 (65% ethanol-water). Polarograms were recorded in the presence of varying concentrations of 2-HDB at a constant pH; shifts in the half-wave potential to more negative values from that of aquo-metal ion and decrease in diffusion currents indicated complexation. The wave-slopes(30 mV) suggested reversible nature of the electrode processes. Their diffusion-controlled nature was proved from the square-root dependence of limiting currents on the height of mercury column and their linear dependence upon the concentration of the depolarizer.

$\Delta \bar{i}_d$ vs. log [L] plot (called pseudo-formation curve) after integration provided log F_o' [L] values at each ligand concentration. The log F_o' [L] values were then plotted against log [L]. From the limiting slope (0.1075, 0.13 and 0.13 at 298, 303 and 308 K) and maximum coordination N_{max} determined by spectrophotrometry, the K-value was calculated to be 18.6. 15.38 and 15.38 at the three temperatures. Multiplying K by log F_o' [L] yielded the

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TABLE 1

COMPLEXATION OF Cu(II) WITH 2-HYDROXY-DEOXYBENZOIN IN 55% EHTANOL-WATER MEDIA

pH = 5.5 m = 1.688 mg s^{-1} t = 4.3 s h = 70 cm Hg
Cu(II) = 0.1 mol m^{-3} $LiClO_4$ = 0.1 mol dm^{-3}

S. No.	[L] mol dm^{-3}	log [L]	$-E_{1/2}$ V	Slope mV	$\bar{i}_d$ μA	$\Delta\bar{i}_d$ μA	log F'_o	log F_o	F_o	F_1	F_2
				Temperature 298°K							
1.	0.0000	-	0.015	30	0.344	-	-	-	1.0000	-	-
2.	0.0010	-3.0	0.030	30	0.328	0.016	0.0193	0.3590	2.2856	1285.60	235600
3.	0.0020	-2.7	0.035	30	0.320	0.024	0.0311	0.5785	3.7888	1394.40	172200
4.	0.0030	-2.5	0.035	30	0.316	0.028	0.0422	0.7849	6.0939	1697.97	215990
5.	0.0040	-2.4	0.040	30	0.308	0.036	0.0492	0.9151	8.2243	1806.07	189018
6.	0.0050	-2.3	0.040	30	0.300	0.044	0.0574	1.0676	11.6842	2136.84	217368
7.	0.0075	-2.1	0.040	30	0.280	0.064	0.0788	1.4657	29.2213	3562.84	361600
									β_1= 1050	β_2= 21×10^4	
				Temperature 303°K							
1.	0.0000	-	0.020	30	0.368	-	-	-	1.0000	-	-
2.	0.0010	-3.0	0.035	30	0.356	0.012	0.01288	0.1981	1.5779	578	118000
3.	0.0020	-2.7	0.040	30	0.348	0.020	0.02357	0.3625	2.3041	652	96000
4.	0.0030	-2.5	0.045	30	0.360	0.008	0.03569	0.5489	3.5392	846	128666
5.	0.0040	-2.4	0.050	30	0.320	0.048	0.04389	0.6750	4.7318	933	118258
6.	0.0050	-2.3	0.040	30	0.312	0.056	0.05377	0.8269	6.7140	1143	126600
7.	0.0075	-2.1	0.055	45	0.292	0.076	0.07973	1.2262	16.8300	2111	220133
									β_1= 460	β_2= 11.8×10^4	
				Temperature 308°K							
1.	0.0000	-	0.025	30	0.380	-	-	-	1.0000	-	
2.	0.0010	-3.0	0.050	30	0.364	0.016	0.01320	0.2030	1.5950	595	195000
3.	0.0020	-2.7	0.050	30	0.352	0.028	0.02565	0.3945	2.4800	740	170000
4.	0.0030	-2.5	0.050	30	0.344	0.036	0.03793	0.5834	3.8310	944	181333
5.	0.0040	-2.4	0.055	30	0.340	0.040	0.04545	0.6990	5.0000	1000	150000
6.	0.0050	-2.3	0.055	40	0.320	0.060	0.05613	0.8633	7.2993	1260	171960
7.	0.0075	-2.1	0.070	50	0.304	0.076	0.08373	1.2878	19.3985	2453	273733
									β_1= 400	β_2= 1.7x10	

log F_o[L] values. The intercepts of F_j[L] vs. [L] plots on the F_j[L] axis gave the values of formation constants. Table 1 gives all the data at the three temperatures.

Complexes of Ni(II) Ions

Ni(II) (0.1 mol m^{-3}) and varying concentration of ligand showed a well-defined wave in 0.1 mol dm^{-3} $LiClO_4$ at pH 7.0 in 65% ethanol-water mixture. The half-wave potential shifted to more negative values and the diffusion current decreased. Plots of log $[i/(\bar{i}_d - \bar{i})]$ vs -E were straight lines with the slope indicating irreversibility of the electrode reaction involving two electron transfer.

Variation of $\Delta\bar{i}_d$ vs log [L] plot (called pseudo formation curve) at 298, 303 and 308K after integration provided log F'_o [L] values at each ligand concentration. The log F'_o [L] values are plotted against log [L]. From the

TABLE 2

COMPLEXATION OF Ni(II) WITH 2-HYDROXY-DEOXYBENZOIN IN 65% ETHANOL-WATER MEDIA

pH = 7.0 m_3 = 1.688 mg s^{-1} t = 4.3 s h = 70 cm Hg
Ni = 0.1 mol m^{-3} $LiClO_4$ = 0.1 mol dm^{-3}

S. No.	[L] / mol dm^{-3}	log[L]	$-E_{1/2}$ / V	Slope / mV	$\bar{i}_d$ / μA	$\Delta\bar{i}_d$ / μA	log F'_o	log F_o	F_o	F_1 -4 X10	F_2 -6 X10
		Temperature 303° K									
1.	0.0000	-	1.140	65	0.380	-	-	-	1.0	-	-
2.	0.0010	-3.0	1.145	70	0.320	0.060	0.0490	1.10	12.6	1.16	5.6
3.	0.0020	-2.7	1.160	65	0.312	0.068	0.0680	1.53	34.0	1.65	5.2
4.	0.0030	-2.5	1.170	60	0.304	0.076	0.0820	1.85	70.8	2.327	5.7
5.	0.0040	-2.4	1.190	60	0.296	0.084	0.0900	2.03	107.0	2.65	5.1
6.	0.0050	-2.3	1.205	65	0.264	0.116	0.0999	2.25	178.0	3.54	5.8
7.	0.0075	-2.1	1.215	65	0.234	0.146	0.1260	2.84	692.0	9.21	11
8.	0.0100	-2.0	1.285	50	0.224	0.156	0.1410	3.18	1512.0	15.13	14
									β_1= 6.0x10^3	β_2= 5.6x10^6	
		Temperature 308° K									
1.	0.0000	-	1.130	60	0.408	-	-	-	1.0	-	-
2.	0.0010	-3.0	1.140	60	0.350	0.058	0.0480	1.03	10.7	9200	4.2
3.	0.0020	-2.7	1.155	60	0.343	0.065	0.0660	1.41	25.7	12350	3.67
4.	0.0030	-2.5	1.165	60	0.336	0.072	0.0796	1.70	50.1	16367	3.78
5.	0.0040	-2.4	1.185	55	0.328	0.080	0.0870	1.86	72.4	17850	3.20
6.	0.0050	-2.3	1.200	50	0.298	0.110	0.0970	2.08	120.2	23840	3.77
7.	0.0075	-2.1	1.210	50	0.268	0.140	0.1200	2.57	371.5	49400	5.90
8.	0.0100	-2.0	1.280	50	0.258	0.150	0.1300	2.78	602.6	60610	5.50
									β_1= 5.0x10^3	β_2= 3.8x10^6	

TABLE 3

STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF Cu(II) AND Ni(II)-2 HYDROXY-DEOXY-BENZOIN IN 65% ETHANOL-WATER MEDIA ($LiClO_4$, 0.1 mol dm^{-3})

Temperature / K	log K_j	$-\Delta G$ / KJ mol^{-1}	$-\Delta H$ / KJ mol^{-1}	$-\Delta S$ / JK mol^{-1}	Temperature / K	log K_j	$-\Delta G$ / KJ mol^{-1}	$-\Delta H$ / KJ mol^{-1}	$-\Delta S$ / JK mol^{-1}
Cu(II)					Ni(II)				
298	log K_1 3.02	17.23	80.420	-212.00	303	log K_1 3.78	21.93	34.466	-41.37
	log K_2 2.00	11.41				log K_2 2.97	17.23		
303	log K_1 2.66	15.43			308	log K_1 3.69	21.76		
	log K_2 2.41	13.98				log K_2 2.89	17.04		
308	log K_1 2.60	15.33							
	log K_2 1.63	9.61							

limiting slopes and maximum coordination number N_{max} determined by spectrophotometry, K values were calculated. Multiplying K by log F_o' [L] yielded the log F_o [L] values. The intercepts of F_j [L] vs [L] plots on F_j [L] axis gave the values of formation constants. The value of slope and x are 0.133 and 22.56 at 203 and 0.14 and 21.4 at 308°K. Table 1 contain all the data.

Both the metal ions, Cu(II) and Ni(II) formed 1:1 and 1:2 complexes with 2-HDB. The thermodynamic parameters ΔG, ΔH and ΔS calculated by the usual methods for the 1:1 complexes are given in Table 3. The entropy changes of Ni(II) and Cu(II) complexes were, however, negative signifying greater degree of order in their structures.

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