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Polarographic behavior of cobalt(II)–2,4-dihydroxydeoxybenzoin complexes in 65% ethanol-water media

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Polarographic behavior of cobalt(II)–2,4-dihydroxydeoxybenzoin (2,4-DHDB) complexes have been investigated using Crow's mean diffusion coefficient method. Stability constant values have been determined. Co^{II} forms 1 : 1, 1 : 2 and 1 : 3 complexes with 2,4-DHDB. Thermodynamic parameters have also been evaluated.

Potentiometric[1] behavior of Co^{II}-hydroxydeoxybenzoins shows that complexation occur with metal-ligand ratio of 1 : 5. Polarographic[2] behavior shows some unusual behavior with *o*-hydroxydeoxybenzoin upto metal-ligand ratio of 1 : 500. In the present communication polarographic studies of complex of Co^{II} with 2,4-dihydroxydeoxybenzoin (2,4-DHDB) have been described. Stability constants of complexes have been calculated by Crow's method[3] using diffusion current values instead of half-wave potential values. Thermodynamic parameters have also been evaluated at fractional ionic activity ($LiClO_4$, 0.1 mol dm^{-3}).

Results and Discussion

Polarographic behavior of Co^{II} ion and its complexes with 2,4-DHDB at pH 7.1 using $LiClO_4$ (0.1 mol dm^{-3}) in 65% ethanol-water media show well-defined single wave. The linear i_d vs $\sqrt{h}$ plot at 298 K proves diffusion-controlled nature. Slope value shows two-electron irreversible electrode process. The Δi_d vs. log [L] plot (pseudo-formation curve) on integration provides log F'_0 function. The latter was plotted against log [L] to calculate k as 22.2. Then utilizing k value function F_0 were calculated (Table 1). From Leden[4] plots the formation constants were obtained. The log K values for the Co^{II} complexes were 2.90, 1.83 and 1.56 at 298 K. Similarly, log K values for the complexes were calculated at 303 and 308 K (Table 1) and found to be 2.80, 1.74, 1.49 and 2.70, 1.66, 1.45. For 1 : 1 complexes, the thermodynamic parameters calculated are shown in Table 2.

Conclusion : On examining the complexation of Co^{II}

Table 1. Complexation of Co^{II} ions with 2,4-dihydroxydeoxybenzoin in 65% ethanol-water media at different temperatures

pH = 7.1, $[LiClO_4]$ = 0.1 mol dm^{-3}

[L] mol dm^{-3}	log [L]	$E_{1/2}$ V	Slope mV	i_d μA	Δi_d μA	log F'_0	log F_0	F_0	F_1	F_2	F_3
	Temp. = 298K										
0.000	-	1.315	65	0.344	–	–	–	1.00	–	–	–
0.005	–2.3	1.305	55	0.284	0.06	0.035	0.7770	5.98	998	39200	–
0.010	–2.0	1.305	65	0.274	0.07	0.0547	1.2143	16.38	1538	73800	1980000
0.020	–1.7	1.290	65	0.254	0.09	0.0780	1.7316	53.90	2645	92250	1912500
0.030	–1.5	1.280	60	0.244	0.10	0.0967	2.1467	140.10	4633	127766	2458867
0.040	–1.4	1.265	50	0.224	0.12	0.1076	2.3887	244.70	6092	132300	1957500
0.050	–1.3	0.126	50	0.204	0.14	0.1202	2.6680	466.00	9300	170000	2320000
	Temp. = 303 K										
0.000	–	1.315	60	0.376	–	–	–	1.0000	–	–	–
0.005	–2.3	1.310	60	0.318	0.058	0.0326	0.6748	4.7000	744	28800	–
0.010	–2.0	1.305	60	0.308	0.068	0.0515	1.0660	11.6413	1060	46000	1100000
0.020	–1.7	1.280	70	0.288	0.088	0.0751	1.5546	36.8391	1740	57000	1100000
0.030	–1.5	1.280	50	0.278	0.098	0.0945	1.9562	90.4000	2980	79333	1477766
0.040	–1.4	1.265	50	0.258	0.118	0.1057	2.1880	154.1700	3829	80725	1143125
0.050	–1.3	1.265	50	0.242	0.134	0.1182	2.4467	279.7040	5574	99480	1289600

Table-1 (contd.)

	Temp. = 308 K										
0 000	–	1.315	65	0 400	–	–	–	1.0000	–	–	–
0.005	–2.3	1.310	55	0 345	0 055	0.02996	0 5962	3.9464	589	17800	–
0.010	–2 0	1.300	65	0.335	0.065	0 04784	0.9520	8.9536	795	29500	650000
0 020	–1.7	1.285	60	0.315	0.085	0.06232	1 2400	17.3780	819	15950	
0 030	–1.5	1.280	50	0.305	0.095	0.08936	1.7783	60.6205	1987	49570	885666
0.040	–1.4	1.280	50	0.285	0.115	0.10020	1 9939	98.6052	2440	48500	637500
0.050	–1.3	1 280	50	0.272	0 128	0 12000	2.3880	244.3431	4867	87340	1286800

Table 2. Stability constants and thermodynamic parameters for Co^{II}–2,4-dihydroxydeoxybenzoin in 65% ethanol-water media($LiClO_4$, 0.1 mol dm^{-3}) at different temperatures

Temp. K	β_j	log K_j	$-\Delta G^{\neq}$ kJ mol^{-1}	$-\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ JK^{-1} mol^{-1}
298	β_1=800	log K_1=2.90	16.547	38 29	–72 9821
	β_2=54000	log K_2=1.83	10.271		
	β_3=1950000	log K_3=1.56	8.900		
303	β_1=600	log K_1=2.80	16 245		
	β_2=35000	log K_2=1.74	10.095		
	β_3=1100000	log K_3=1.49	8.640		
308	β_1=500	log K_1=2.70	15.920		
	β_2=23000	log K_2=1.66	9.790		
	β_3=640000	log K_3=1 45	8.550		

with 2,4-dihdroxydeoxybenzion in 65% ethanol-water media at ionic strength of 0.1 mol dm^{-3} ($LiClO_4$) by polarographic method upto quite high metal-ligand ratio (1 : 500), it was found that Co^{II} ion yields 1 : 1, 1 : 2 and 1 : 3 complexes with 2,4-DHDB. The stability constant values decreases with increasing temperature, indicating that higher temperatures are not favorable for complexation, which is in agreement with the conclusion of Pitzer[5]. The entropy change of the complexes having negative values signifies greater degree of order in their structures.

Experimental

Percloric acid, lithium hydroxide and cobalt sulfate were of A.R. grade. Lithium perchlorate was prepared by neutralizing perchloric acid with lithium hydroxide and then crystallizing the salt from distilled water. The ligand was prepared using standard method[6].

Stock solution (1.0 mmol dm^{-3}) of 2,4-DHDB was prepared in purified ethanol. Test solution for polarographic analysis contained 0.1 mmol dm^{-3} metal ion, 0.1 mol dm^{-3} of $LiClO_4$, different amounts of the ligand and 65% ethanol. A H-type Kaloušek cell with a decinormal calomel electrode ($NaClO_4$, 0.1 mol dm^{-3}) in second limb was used. Polarograms were recorded using a Radiometer Polarograph Polariter PO_4g. Dropping mercury electrode was made by a Sargent Capillary with characteristic, m = 1.688 mg s^{-1} and t = 4.3 s at h = 70 cm. An Elico LI-120 pH meter was used. Solutions were thermostated at the required temperature. Before recording the polarograms nitrogen gas was passed through the solutions.

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