TECHNICAL REPORT

ELECTROCHEMICAL BEHAVIOUR AND THERMODYNAMIC FUNCTIONS OF Cd AND Zn CAMPHORATE SYSTEMS

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The complexation of dibasic acids with cadmium and zinc has been reported by Gaur and coworkers[1–3] and have shown that it is possible to study the complexes of zinc which is quasireversibly reduced at d. m. e. by knowing the reversible half wave potentials. The tartrate, citrate and acetate complexes of zinc have been studied by Matsuda and coworkers[4,5]. Polarographic studies of zinc in aqueous ethylene glycol and propanol have been reported earlier[6]. This investigation is on the complexes formed by cadmium and zinc with dl-camphoric acid and their thermodynamic properties.

Experimental

Disodium salt of dl-camphoric acid was used as complexing agent. The solution of Cd^{2+} was prepared by dissolving a weighed quantity of A. R. cadmium nitrate in double distilled water.

The polarograms were taken at constant pH-6.5 which was adjusted by adding perchloric acid or NaOH in solutions containing 1 mM Cd^{2+} and varying concentrations of complexing agent at the ionic strength 1.5M kept constant by using requisite amount of $NaClO_4$ 0.005 gelatin was added in Zn-dl camphorate system. The polarograms were recorded after deareation of test solutions by purified nitrogen gas for 20 minutes. The d.m.e. had the following characteristics: m = 2.14 mg/sec and t = 4.5 sec in open circuit.

Results and Discussion

By the addition of dl-camphorate ion, the half-wave potential shifted to more negative value and the diffusion current decreases. The reduction was diffusion-controlled as evident from the straight line plots of i_d vs $h^{\frac{1}{2}}$ The slopes of the plots of log $\frac{i}{(i_d - i)}$ vs E_{dc} were found to be of the order of 31 ± 1 mV for cadmium and 37 mV for zinc. For this purpose $E^r_{1/2}$ value was determined by Gellings[9] method. The plots of $E_{1/2}$ vs—log C_x were found to be smooth curves indicating that more than one complex species formed.

The number of species were determined with the help of DeFord and Humes[7] treatment which involves the determination of F_j (X) functions and their plots against C_x. In case of Cd—dl camphorate system the plots of F_o (X), F_1 (X) and F_2 (X) vs C_x were found to be smooth curves confirming that more than two complex species are formed. The plots of F_3 (X) vs C_x and of F_4 (X) vs C_x were straight lines. Thus four complex species exist in solution having the compositions [Cd(dl-camphorate)], [Cd(dl-camphorate)$_2$]$^{2-}$, [Cd (dl-camphorate)$_3$]$^{4-}$ and [Cd (dl-camphorate)$_4$]$^{6-}$ with the following values of over all formation constants $\beta_1 = 40$, $\beta_2 = 300$, $\beta_3 = 1320$, and $\beta_4 = 8500$ at 30 ± 1°C. The system was studied at 40 ± 1°C also under identical conditions and here also the number of complex species remains the same except that the stabilities of the complex species decrease i.e. $\beta_1 = 40$, $\beta_2 = 250$, $\beta_3 = 1600$ and $\beta_4 = 5500$.

The values of thermodynamic function for the cadmium dl—camphorate system determined for 1 : 4 complex species are summarised below :

TABLE 1. **Thermodynamic Functions of Cadmium-dl Camphorate System**

Complex Species	Thermodynamic functions		
	$\Delta H°$ KCals/mole	$\Delta F°$ KCals/mole	$\Delta S°$ Cals/mole/deg
1 : 4	– 8.256	– 5.4839	– 19.38

Since in the case of Zn-dl camphorate system, the slope of log plots was of the same order, the observed $E_{1/2}$ may be used for calculating[8] the over all formation constants by DeFord and Humes method. Here also the number of complex species remains the same as were in the case of Cd-dl camphorate system with the compositions $[Zn(dl\text{-camphorate})_3]^{4-}$ and $[Zn(dl\text{-camphorate})_4]^{6-}$ having the overall formation constants $\beta_1 = 16$, $\beta_2 = 160$, $\beta_3 = 900$ and $\beta_4 = 912$ at 30°C and $\beta_1 = 15$, $\beta_2 = 150$, $\beta_3 = 690$ and $\beta_4 = 880$ at 40°C respectively.

The complex formation between Zn^{2+} and dl—camphorate ions is also supported by the results of thermodynamic constants for 1 : 4 complex species which are shown below :

TABLE II. Thermodynamic Functions of Zinc-dl Camphorate System

Complex Species	Thermodynamic constants		
	ΔH° KCal/mole	ΔF° KCal/mole	ΔS° Cals/mole /deg
1 : 4	-0.677	-4.131	+3.685

Zn^{2+} and Cd^{2+} thus get reduced with controlled diffusion at DME, and hence may be analysed in presence of dl-camphorate.

REFERENCES

1. J. N. Gaur, and D. S. Jain Nat. Inst. Chemist. Calcutta 39 (1967) 230.
2. M. M. Palrecha, and J. N. Gaur, J. Polawgr. Soc., 14 (1968) 31.
3. K.K. Choudhary, D.S. Jain and J.N. Gaur, J. Electrochem. Soc. India, 4 (1976) 169.
4. H. Matsuda, Z. Electrochem. 65 (1961) 489; 62 (1958) 977.
5. H. Matsuda and Y. Ayabe, Ibid., 63 (1959) 1164.
6. K. Zutshi and J. N. Gaur, Acta Chim. Hung. Tomus. 46, (1965) 91.
7. D. D. DeFord and D. N. Hume, J. Am. Chem. Soc. 73 (1951) 5321.
8. A.A. Vlcek, Progress in Inorganic Chemistry, Interscience Publication 5 (1963) 240.
9. P. J. Gellings, Z. Electrochem. Ber. Bunsenges. Phyasir. Chem., 66 (1962) 477, 481, 799; 67 (1963) 167.