

# POLAROGRAPHIC STUDY OF THE COMPOSITION AND STABILITY CONSTANTS OF FORMATE COMPLEXES OF CADMIUM\*

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Polarography of cadmium in complexing and non-complexing media has been studied by a number of workers.<sup>1,2</sup> It was found that cadmium forms complexes with various ligands. Sartori<sup>3</sup> investigated the oxalate and pyrophosphate complexes of cadmium polarographically. Deford and Hume,<sup>4</sup> Turyan<sup>5</sup> and co-workers studied the formation of cadmium thiocyanate complexes by polarographic techniques. The chloro and bromo complexes of cadmium were studied by Eriksson.<sup>6</sup> The nitrite, benzoate, and 1,2-diaminocyclohexanetetraacetate complexes of cadmium have been studied by the authors.<sup>7-9</sup> During polarographic study of cadmium in different supporting electrolytes, it was found that in sodium formate solution the reduction was diffusion controlled and reversible for two-electron reduction. The half-wave potential was found to shift towards more negative values with increasing concentration of sodium formate, which indicated the formation of complexes between  $\text{Cd}^{2+}$  and  $\text{HCOO}^-$ .

## Experimental

All the chemicals used were of reagent grade purity. The solution of  $\text{Cd}^{2+}$  was prepared by dissolving a weighed amount of A.R. cadmium nitrate in conductivity water and standardized as usual. Potassium nitrate was employed to keep constant ionic strength. Triton X<sub>100</sub> (Rohm & Haas) was employed as maximum suppressor. Sodium formate was used as complexing agent.

An L.P. 55 Heyrovsky system polarograph was used manually. The half-wave potentials were checked by a W.G. Pye vernier potentiometer. All the half-wave potentials refer to saturated calomel electrode. The D.M.E. had the following characteristics:  $m$  1.76 mg/sec,  $t$  3.2 sec (0.1M potassium nitrate in open circuit). All the measurements were done at  $30 \pm 0.01^\circ$ .

Solutions containing 1 mM cadmium and 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0M sodium formate were prepared. Ionic strength was kept constant (1.0) by adding the requisite amount of potassium nitrate.

## Results and Discussion

A well-defined single reduction wave appeared in each case. The plots of  $\log(i/i_d - i)$  against  $E_{d.e.}$  for all the solutions were found to be linear, having a slope

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<sup>1</sup> Lingane, J. J., *Ind. Engng Chem., Analyt. Edn.*, 1943, **15**, 583.

<sup>2</sup> Apalenska, M., *Z. Analyt. Chem.*, 1934, **126**, 49.

<sup>3</sup> Sartori, G., *Gazz. Chim. Ital.*, 1934, **64**, 3.

<sup>4</sup> Hume, D. N., Deford, D. D., and Cave, G. C. B., *J. Am. Chem. Soc.*, 1951, **73**, 5323.

<sup>5</sup> Turyan, Y. I., and Seroya, G. F., *Zhur. Neorg. Khim.*, 1957, **2**, 336.

<sup>6</sup> Eriksson, L., *Acta Chem. Scand.*, 1951, **7**, 1176.

<sup>7</sup> Paper at Fifth Seminar on Electrochemistry at C.E.R.I., Karaikudi, Jan. 27, 1965.

<sup>8</sup> Paper at Indian Chemical Society Annual Convention, Allahabad, December 26, 1964.

<sup>9</sup> Paper at Indian Science Congress, 51st and 52nd Session, Calcutta, December 31, 1964.

of  $32 \pm 2$  mV, indicating the reversible reduction of the process. The plot of half-wave potential against  $-\log C_X$  ( $C_X$ , formate ion concentration) was found to be a curve instead of a straight line, showing the formation of two or more complexes in equilibrium. For the determination of composition and stability constants of complexes, Deford and Hume's<sup>10</sup> method as improved by Irving<sup>11</sup> was therefore employed.

TABLE 1  
ANALYSIS OF  $F_j(X)$  FUNCTION

Concentration of $\text{HCOO}^-$ (moles)	$-E_{\frac{1}{2}}$ (V)	$i_d$ ( $\mu\text{A}$ )	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$
0.0	0.5834	5.508	—	—	—	—
0.1	0.5892	5.508	1.56	5.6	—	—
0.2	0.5956	5.265	2.665	8.3	—	—
0.3	0.5995	5.184	3.648	8.8	—	—
0.4	0.6036	4.941	5.363	10.9	—	—
0.5	0.6066	4.536	7.183	12.3	—	—
0.6	0.6083	3.807	9.974	13.3	14.6	20.16
0.7	0.6102	3.726	12.43	16.3	17.0	20.7
0.8	0.6150	3.564	17.42	20.5	20.0	21.8
0.9	0.6175	3.321	22.58	23.9	21.5	21.1
1.0	0.6207	3.321	28.89	27.59	23.39	20.89

The results have been recorded in Table 1. The overall formation constants were obtained by a graphical extrapolation of the  $F_j(X)$  functions to the zero ligand concentration. The overall formation constants for the complex ions,  $\text{Cd}(\text{HCOO})^+$ ,  $\text{Cd}(\text{HCOO})_2$ , and  $\text{Cd}(\text{HCOO})_3^-$  are 4.5, 2.5, and 21.0 respectively. From the above

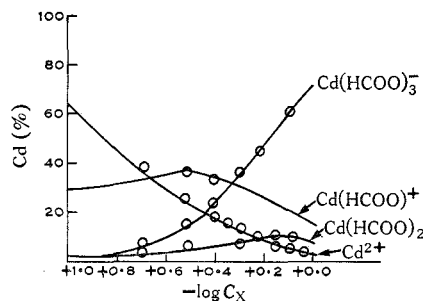


Fig. 1.—Distribution of cadmium ions (%) in various forms as a function of formate ion concentration.

data it is clear that the complex species are very weak, establishing the validity of the above method for the determination of stability constants of very weak complexes. The percentage error is about  $\pm 2.5\%$ .

Figure 1 presents the distribution of cadmium as the cationic or anionic form as a function of the logarithm of the formate concentration.

<sup>10</sup> Deford, D. D., and Hume, D. N., *J. Am. Chem. Soc.*, 1951, **73**, 5321.

<sup>11</sup> Irving, H., "Advances in Polarography." Vol. I. p. 42. (Pergamon Press: London 1960.)