946. *A Polarographic Study of Copper Malonate Complexes.*

By E. Gelles and G. H. Nancollas.

Association of the cupric ion with the malonate anion in aqueous solution at 25° has been studied by polarography over a range of concentrations. Association constants for the reactions $Cu^{2+} + CH_2(CO_2^-)_2 \rightleftharpoons CH_2(CO_2)_2Cu$, and $Cu^{2+} + 2CH_2(CO_2^-)_2 \rightleftharpoons Cu[CH_2(CO_2)_2]_2^{2-}$ have been obtained.

In our recent studies of the association of dicarboxylic acid anions with rare-earth ions, successive association constants for the reaction $M^{3+} + A^{2-} \rightleftharpoons MA^+$, and $MA^+ + A^{2-} \rightleftharpoons MA_2^-$, were derived from potentiometric measurements.[1,2] For bivalent cations, the second stage of the association $MA + A^{2-} \rightleftharpoons MA_2^{2-}$ would be expected to be less favoured by the electrostatic energy term. The first association constant for copper malonate has been obtained from both conductometric and potentiometric measurements;[3] it is of the same order of magnitude as that for lutetium malonate.[2] Potentiometric evidence has been obtained for the formation[4] of MA_2^{2-}. Previous workers[3] failed to observe any displacement in the polarographic half-wave potential for cupric ion in copper malonate solutions, probably owing to insufficient resolution of the potential scale.

---

[1] Gelles and Nancollas, *Trans. Faraday Soc.*, 1956, **52**, 98.
[2] Gelles and Nancollas, *ibid.*, p. 680.
[3] Peacock and James, *J.*, 1951, 2233.
[4] Riley, *J.*, 1930, 1642.

The polarographic method, where applicable, is particularly suited to the study of successive equilibria, because it provides the most direct evidence on the number of ligands held by the reducible ion. We have found that in the presence of malonate ion the cupric ion is reversibly reduced, the half-wave potential becoming more negative the higher the malonate concentration. The association is sufficiently strong, and the reactions are sufficiently rapid compared with the rate of diffusion of cupric ions to the electrode surface, to give rise to a single, reversible, two-electron wave, and to shifts in half-wave potentials from which the successive association constants can be deduced.

EXPERIMENTAL

" AnalaR " reagents were used where available. Copper nitrate solutions were analysed iodometrically for copper; sodium malonate solutions were prepared from sodium hydroxide and malonic acid solutions of known concentration. Gelatin solutions were freshly prepared before use from " Polaritan " material. Potassium nitrate was used as supporting electrolyte.

Measurements were made with a Tinsley pen recording polarograph and dropping-mercury electrode. It was found possible to determine potentials to ±1 mv by decreasing the voltage span of the instrument from 3·0 to 0·3 volt. A Tinsley potentiometer reading to 0·1 mv was used to check the applied potential and, in conjunction with a standard resistance, the current at various points along the wave. Current values were taken from the envelope of the tops of the fluctuations of the recorder, operated without damping. For a given copper concentration, $i_d/2$ values were constant to within 0·1 μA. With a cell resistance of 1800 ohms, the effect of iR drop on half-wave potentials was negligible. The capillary was made from marine barometer tubing: the drop time was 3·6 ± 0·1 sec., and the mass rate of flow, 1·41 mg. sec.$^{-1}$, was measured on open circuit in 1·0M-potassium nitrate. The polarographic cell was a 20-ml. " Pyrex " vessel provided with a " Quickfit " neck into which the capillary could be lowered. The vessel was also provided with three side arms : one led to a small cup sealed into the base of the cell to collect the dropping mercury, another was fitted with a small bubbler to prevent back diffusion of oxygen, and the third allowed nitrogen to be passed through the cell, after which it served as a connection to the saturated calomel reference electrode through a saturated potassium chloride agar salt bridge. Nitrogen, freed from oxygen by means of vanadium sulphate solution, was bubbled through the cell for 15 min. before each polarogram was recorded. 0·005% of gelatin was used as a maximum suppressor. All measurements were made at 25° ± 0·1°.

RESULTS AND DISCUSSION

In solutions containing cupric and potassium nitrate, a reversible two-electron wave was observed at ionic strengths of 0·1 and 1·0 with a half-wave potential $E_{\frac{1}{2}}^{s} = 0{\cdot}017$ v, relative to the saturated calomel electrode.

Half-wave potentials were obtained from the intercept of the plot of $\log_{10} i/(i_d - i)$ against applied voltage, where i is the current corresponding to the particular voltage and i_d is the diffusion current, corrected for residual current. The equation for the wave

$$E = E^{\frac{1}{2}} - (RT/nF) \ln [i/(i_d - i)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

requires for a reversible two-electron reduction that the linear plot shall have a slope of 0·0296 at 25°. Reversibility in a typical experiment is illustrated in Fig. 1; the half-wave potential obtained from the intercept is −0·081 v and the slope is 0·030.

The polarographic behaviour of solutions containing a large excess of malonate ion is summarised in Table 1. C_A represents the total malonic acid concentration, C_M the total metal-ion concentration, and $[A^{2-}]$ the malonate-ion concentration in moles/l.

TABLE 1. *Measurements at high concentrations of malonate ion.*

(Ionic strength = 1)

10^2C_A	10^4C_M	$10^2[Na^+]$	Slope	$E_{\frac{1}{2}}$	$10^3[A^{2-}]$
5·00	3·49	10·00	0·031	−0·126	5·00
2·00	3·49	3·66	0·030	−0·098	1·66
2·00	3·49	3·50	0·029	−0·096	1·50
2·00	3·49	2·80	0·031	−0·083	0·80
1·00	3·49	1·83	0·030	−0·081	0·83

With the malonate ion in large excess, the concentrations of the free malonate ion in solution and on the surface of the mercury drops may be assumed to be equal. The shift in half-wave potential is then given by

$$\Delta E = E_{\frac{1}{2}} - E_{\frac{1}{2}}{}^{s} = -(\boldsymbol{RT}/n\boldsymbol{F})\ln K_2 - (x\boldsymbol{RT}/n\boldsymbol{F})\ln[\mathrm{A}^{2-}] \quad . \quad . \quad . \quad (2)$$

where n is the number of electrons involved in the reduction process, x is the number of malonate ions associated with each cupric ion, and K_2 the association constant for the formation of the complex $\mathrm{MA_2}^{2-}$ from the cupric ion, activity coefficients being neglected.

The linear relation between ΔE and $\log_{10}[\mathrm{A}^{2-}]$ is illustrated in Fig. 2. The slope of the line is 0·058, showing unequivocally that the complex in these solutions is preponderantly $\mathrm{CuA_2}^{2-}$. From the intercept, the association constant at ionic strength $I = 1$ is derived,

$$K_2 = [\mathrm{CuA_2}^{2-}]/([\mathrm{Cu}^{2+}][\mathrm{A}^{2-}]^2) = 2{\cdot}7 \times 10^7 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

At much lower concentrations of malonate ion, eqn. (2) is not applicable since the concentrations of the malonate ion in solution and on the surface of the mercury drop are not equal. The concentrations at the drop surface, $[\mathrm{M}^{2-}{}_0]$ and $[\mathrm{A}^{2-}{}_0]$, and the association constants K_1 and K_2, can be calculated from equations (4)—(6).[5]

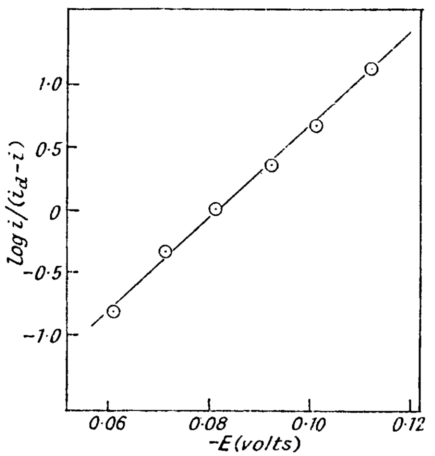

FIG. 1. *Reversibility of reduction for last experiment in Table* 1.

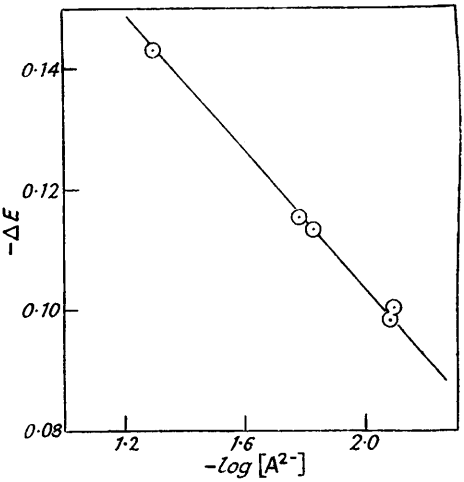

FIG. 2. *Shift in half-wave potential with concentration of malonate ion.*

$$\Delta E = -(\boldsymbol{RT}/n\boldsymbol{F})\ln(C_{\mathrm{M}}/2[\mathrm{M}^{2+}{}_0]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\Delta E = -(\boldsymbol{RT}/n\boldsymbol{F})\ln(1 + K_1[\mathrm{A}^{2-}{}_0] + K_2[\mathrm{A}^{2-}]^2) \quad . \quad . \quad . \quad . \quad (5)$$

$$C_{\mathrm{A}} = [\mathrm{A}^{2-}{}_0] + [\mathrm{M}^{2+}{}_0](K_1[\mathrm{A}^{2-}{}_0] + 2K_2[\mathrm{A}^{2-}{}_0]^2) \quad . \quad . \quad . \quad . \quad (6)$$

The relevant data are summarised in Table 2.

TABLE 2. *Measurements at low concentrations of malonate ion.*

(Ionic strength = 0·1)

10^4C_{A}	10^4C_{M}	$E_{\frac{1}{2}}$	$10^6[\mathrm{M}^{2+}{}_0]$	$10^4[\mathrm{A}^{2-}{}_0]$	$10^{-5}K_1$	$10^{-7}K_2$
10·00	4·40	−0·038	3·03	7·00	0·64	5·4
8·00	4·40	−0·033	4·49	5·22	0·65	5·2
6·00	4·40	−0·027	7·14	3·36	0·68	6·0
5·00	4·40	−0·022	10·57·	2·52	0·64	5·8
4·00	4·40	−0·017	15·6	1·73	0·67	5·0
2·00	4·40	0·001	63·4	0·38	0·63	5·0
				Mean	0·65	5·4

---

[5] Ringbom and Eriksson, *Acta Chem. Scand.*, 1953, **7**, 1105.

[6] Davies, *J.*, 1938, 2093.

An approximate thermodynamic association constant K_1° may be calculated from the above value of K_1 at ionic strength 0·1, by using activity coefficients obtained from the Davies equation:[6]

$$K_1^\circ = \{\text{CuA}\}/(\{\text{Cu}^{2+}\}\{\text{A}^{2-}\}) = 5{\cdot}0 \times 10^5 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The polarographic value is in good agreement with the potentiometric ($6{\cdot}9 \times 10^5$) and conductometric ($5{\cdot}6 \times 10^5$) values.[3] The difference between the values of K_2 at ionic strengths 0·1 and 1·0 is presumably accounted for by the change in value of the activity coefficient. At an ionic strength of approximately 0·3, Riley's potentiometric measurements[4] gave a value for K_2 of 3×10^7.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW, W.2.

[*Received, April 30th.* 1956.]