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Polarographic Behaviour of DL Aspartic Acid at the D.M.E.

By

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With 1 Figure

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DL Aspartic acid is reduced at the d.m.e. in 0.1*M* tetramethylammonium bromide, tetraethylammonium bromide, sodium chloride, potassium chloride, potassium nitrate, sodium perchlorate and lithium sulphate; in aqueous media. The waves are irreversible, diffusion controlled involving one electron transfer process determined by millicoulometry. The values of the kinetic parameters, transfer coefficient (α) and formal rate constant ($k^\circ_{f,h}$) have been calculated by *Koutecky*'s method and are 0.479 and 15.9×10^{-16} respectively.

Amino acids are well known for their important role in human metabolism and physiology and also in protein chemistry. Earlier investigators[1–3] have mostly confined themselves to the study of metal complexes of amino acids and their indirect polarographic determination. In view of their biological and physiological importance it was considered worthwhile to make a detailed electrochemical study of these compounds.

The present communication embodies the results of a detailed polarographic investigation of DL aspartic acid for which no relevant reference is available in the literature.

Experimental

DL aspartic acid (referred herein as *DAA*) was obtained from B.D.H. Poole, England, and all other solutions were AnalaR (B.D.H.) grade. A manual polarograph with scalamp galvanometer and a saturated LiCl electrode (*S. L. E.* as a reference electrode) was used for recording the polarograms. Due to the possible interference of K^+ ions[4], saturated KCl was replaced by saturated LiCl in the S.C.E. The LiCl electrode maintained a stable potential within the given working period. Me_4NBr was used as supporting electrolyte which was found to be polarographically inert in the potential range 0.4 to — 1.8 V vs. *S. L. E.*

The polarograms were run in 0.8 m*M*-*DAA*, 0.1*M*-*Me*$_4$NBr and 0.002% triton X-100 in unbuffered media unless otherwise stated, in an inert atmosphere of nitrogen. The capillary had the following characteristics in 0.8 m*M*-*DAA*, 0.1*M*-*Me*$_4$NBr and 0.002% triton X-100 at 1.55 V with h_{Hg} value of 40 cm:

$$m = 1.50 \text{ mg/sec}; \quad t = 3.83 \text{ seconds.}$$

The value of n, number of electrons involved in the electrode process was determined by millicoulometric method of *Devries* and *Kroon*[5] using a mercury pool cathode. Kinetic parameters, α and $K^{\circ}_{f,h}$ were determined from the polarograms of the solutions containing 0.8 m*M*-*DAA*, 0.1*M*-*Me*$_4$NBr and 0.002% triton X-100. The current was recorded at the end of the drop life instead of average current as the determination of kinetic parameters is based on *Koutecky*'s method.

Results and Discussion

DAA gave a single well defined cathodic wave in the potential range — 1.2 to — 1.70 V vs. *S.L.E.* The conventional log plots were linear but their slopes were not coinciding with the theoretical value for the reversible one electron transfer process as ascertained by millicoulometry[5], indicating the irreversible nature of the electrode reaction. Furthermore, the half wave potentials were slightly dependent on concentration, which confirms the irreversibility of the waves[6].

i_d (diffusion current) changes linearly with the depolarizer and the mean value of I (diffusion current constant) was found to be 6.660. For 0.8 m*M*-*DAA*, $i_d/h_{\mathrm{eff}}^{1/2}$ in the height range 20 to 60 cm of h_{Hg} was calculated to be 1.339 and temperature coefficient of i_d was found to be 0.719% per degree in the range 15—40 °C; which were almost constant within the experimental error, indicating the diffusion controlled nature of the wave (Table 1).

Polarograms of 0.8 m*M*-*DAA* were recorded in presence of 0.1*M* different supporting electrolytes viz. NaCl, KCl, *Et*$_4$NBr, *Me*$_4$NBr, KNO$_3$, NaClO$_4$, and Li$_2$SO$_4$ respectively, and 0.002% triton X-100 in an inert atmosphere of nitrogen, an irreversible cathodic wave was obtained in all cases and their diffusion current constant was found in the following order

$$\mathrm{NaCl} > \mathrm{KCl} > Et_4\mathrm{NBr} > Me_4\mathrm{NBr} > \mathrm{KNO_3} > \mathrm{NaClO_4} > \mathrm{Li_2SO_4}$$

(— $E_{1/2}$ and I are summarised in table 2).

A solution of 0.8 m*M*-*DAA*, 0.1*M*-*Me*$_4$NBr and 0.002% triton X-100 was electrolysed in an inert atmosphere of nitrogen for 12 hours at — 1.70 V (corresponding to limiting current). The value of i_d was

Table 1. *Effect of Varying [DAA], Temperature and Hg Pressure*

DAA m*M*/l	$i_{d/c}$	*I*	$D^{1/2}$	h_{Hg} cm	$h^{1/2}_{\mathrm{eff}}$	i_d (μA)	$i_d/h^{1/2}_{\mathrm{eff}}$	Temp., °C	i_d (μA)	i_d (ambient)/ i_d	Temp. coeff., % per °C
0.2	15.0	8.804	2.12×10^{-4}	20	4.27	5.8	1.358	15	6.75	1.000	—
0.3	13.33	7.827	1.66×10^{-4}	25	4.81	6.5	1.349	20	7.00	1.037	0.727
0.4	12.75	7.484	1.52×10^{-4}	30	5.31	7.2	1.355	25	7.30	1.081	0.783
0.5	11.50	6.748	1.23×10^{-4}	35	5.76	7.7	1.337	30	7.50	1.111	0.703
0.6	11.00	6.455	1.13×10^{-4}	40	6.18	8.0	1.294	35	7.75	1.148	0.691
0.7	10.85	6.371	1.10×10^{-4}	45	6.57	8.8	1.339	40	8.05	1.192	0.693
0.8	10.62	6.233	1.05×10^{-4}	50	6.94	9.3	1.340	—	—	—	—
0.9	10.33	6.066	0.99×10^{-4}	55	7.29	—	—	—	—	—	—
1.0	10.55	6.160	1.03×10^{-4}	60	7.63	—	—	—	—	—	—

Table 2. *Effect of Supporting Electrolytes*

Supporting electrolyte	*I*	$-E_{1/2}$	Supporting electrolyte	*I*	$-E_{1/2}$
NaCl	6.896	1.560	KNO_3	5.960	1.591
KCl	6.457	1.590	$NaClO_4$	5.943	1.593
$(C_2H_5)_4NBr$	6.016	1.588	Li_2SO_4	5.649	1.580
$(CH_3)_4NBr$	5.980	1.530			

found to decrease and — $E_{1/2}$ value was found to shift towards more negative potential with the time interval showing the irreversible reduction of the depolarizer.

Before electrolysis		After 12 hours of electrolysis	
i_d	$-E_{1/2}$	i_d	$-E_{1/2}$
8.5 μA	1.55	4.85 μA	1.58

Course of Electrode Process

An aqueous solution of an amino acid has a dielectric constant greater than that of water, probably due to the presence of zwitter ion formation, essential for the reduction of an intermediate in which the carboxyl group is ionized while the amino group is protonated[7]. The protonation essential for the reduction of an intermediate species takes place in an acidic aqueous media and the course of electroreduction of DL aspartic acid proceeds as follows:

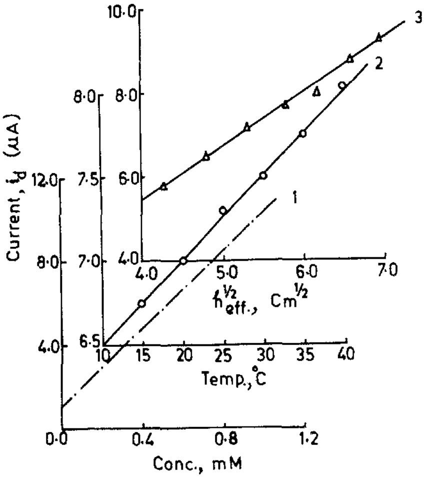

Fig. 1. Curves: 1. Plot of i_d vs. [*DAA*]. 2. Plot of i_d vs. temperature. 3. Plot of i_d vs. $h_{eff.}^{1/2}$

$$R(NH_3^+)COO^- \overset{+H^+}{\rightleftharpoons} R(\overset{+}{N}H_3)COOH \overset{e^-}{\rightleftharpoons} R(\overset{+}{N}H_3)COO^- + \overset{+}{H}$$

where R denotes $—CH_2CH_2COOH$ group.

Kinetic Parameters

The values of kinetic parameters are calculated from *Koutecky*'s[8] treatment as extended by *Meites* and *Israel*[9] which follows for an irreversible wave as:

$$E_{\mathrm{d.e.}} + 0.2412 = \frac{0.05915}{\alpha n} \log \frac{1.349\, K^{\circ}_{f,h}\, t^{1/2}}{D_0{}^{1/2}} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i}$$

which may be written as

$$E_{\mathrm{d.e.}} = E_{1/2} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i}$$

$$\text{with } E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{1.349\, K^{\circ}_{f,h}\, t^{1/2}}{D_0{}^{1/2}}$$

($E_{\mathrm{d.e.}}$ and $E_{1/2}$ are referred to *S.L.E.*).

The value of n was determined by millicoulometry[5] and α was obtained by equating the slope of $E_{\mathrm{d.e.}}$ vs. $\log \frac{i}{i_d - i}$ plot to $\frac{0.0542}{\alpha n}$ and was found to be 0.479. The intercept of the same plot ($E_{1/2}$) was used to calculate $K^{\circ}_{f,h}$ and was found to be 15.9×10^{-16} cm/sec.

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