Hydrodynamic Voltammetry at the Tubular Graphite Electrode. Determination of Diffusion Coefficients of Aromatic Amino and Phenolic Compounds

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Diffusion coefficients of a variety of aromatic amino and phenolic compounds have been determined employing the voltammetric technique involving the use of the tubular graphite electrode. With the exception of a few substances which exhibited maxima in their voltammograms, the diffusion data reported in the paper can be taken as fairly authentic with a maximum variation of ±5%.

Diffusion coefficients of a few organic substances determined voltammetrically using the tubular graphite electrode (*9*) have been reported recently (*10*). The values are found to agree fairly well with the few reported in literature and are seen to fall in the neighborhood of 0.6 × 10^{-5} cm^2 s^{-1}, a value around which diffusion coefficients of most of the substances, both inorganic and organic, are reported to lie (*8*). In view of an uncomfortable dearth of the values of diffusion coefficients of organic substances and the development of a dependable voltammetric technique based on the use of the tubular graphite electrode for the determination of these values (*10*), it has been thought of interest to measure diffusion coefficients of as large a number of organic substances as possible, using the tubular graphite electrode.

Experimental Section

Electrode Assembly. The tubular graphite electrode assembly used in the present investigations is shown, in detail, in Figure 1. It is somewhat different from the assembly fabricated and used earlier by Sharma and Dutt (*9*). The salient feature of the modified assembly is that it considerably reduces the resistance of the cell and also provides for an easy replacement of the electrode as and when required. In ease of fabrication and flexibility of manipulation, the present assembly appears to be a little better than even the tubular carbon electrode assembly reported by Mason and Olson (*7*).

The electrodes proper were made out of spectroscopic grade compressed graphite rods (obtained from M/S Johnson Matthey Chemicals Ltd., England) after wax-impregnation (*3*). Each electrode (with length = 1.20 cm and internal bore of 1 mm diameter) was sealed to the glass tube, as shown with the help of Araldite. (Araldite is the trade name of an epoxy resin—a strong adhesive—formulated by Ciba-Geigy Ltd., Switzerland. It is nonconducting in nature.) Leaving the tubular portion for electrochemical discharge and a small space on the body of the electrode for electrical contact, the rest of the electrode was insulated by a thin coating of Araldite.

Materials. The various amino and phenolic compounds used in the present investigations (and listed in Table I) were of analytical grade or of comparable purity. Since these compounds generally become oxidized on exposure to atmosphere, they were purified before use, invariably, by using standard methods.

Discussion

Current-Voltage Curves. Current-voltage curves for the electrooxidations of the various substances were scanned automatically on Sargent Polarograph Model XXI, under the following conditions: supporting electrolyte, 0.1 M H_2SO_4; concentration of the electroactive material (C), 10^{-4} M; volumetric flow rate of solution (V_f), 10 ml min^{-1}; temperature, 25 ± 1 °C.

In order to check the reproducibility of current-voltage curves, three-four successive waves were taken for each substance on one and the same electrode. In many cases (cf. compounds **1–24** listed in Table I), the successive waves almost exactly superimposed on one another. In many others (cf. compounds **25–59**), the waves were not exactly reproducible. The successive waves exhibited appreciable decrease in the value of limiting current and an increase in the value of the half-wave potential. This was evidently due to the filming of the electrode surface. However, the voltammograms obtained after redrilling the electrode were found to be almost exactly identical with those obtained on fresh electrodes. Since in the tubular electrode the limiting current is independent of the diameter (cf. eq 1 below), the process of redrilling does not introduce any additional calculations or modifications for computing the limiting current (as long as the flow rate remains the same). The limiting currents obtained at one and the same electrode in which no film is formed were reproducible within ±1%. However, the values obtained on different electrodes, either fresh or redrilled, varied within ±3%. This larger variation is due to variation in the surface from one electrode to another. It is very rare that two electrodes prepared even from the same rod may have an identical surface. It was, therefore, considered desirable to scan voltammograms on as many as five different electrodes (either fresh or redrilled), with exactly the same length, for each substance and then take the average value of the current in each case. The variation of the limiting currents in all cases was found to be within ±3%.

The average values of limiting currents obtained for the oxidations of the various substances are given in Table I.

Calculation of Diffusion Coefficients. The diffusion coefficients of various organic species were calculated by incorporating the values of various parameters in the theoretical equation

$$I_{\text{diff}} = (5.24 \times 10^5) n C X^{2/3} D^{2/3} V_f^{1/3} \qquad (1)$$

derived (*2, 6*) for the tubular electrode. In this equation, X is the length of the electrode (in cm), V_f is the volumetric flow rate of the solution (in ml s^{-1}), C is the concentration of the electroactive material (in mol ml^{-1}), and the parameters n and D have their usual significance. The above equation is only an extension of the Levich equation (*6*), in which the axial velocity, V_0 (of Levich equation) has been replaced by a more convenient parameter, V_f, i.e., the volumetric flow rate (*2*). The above equation is, evidently, independent of the radius of the tube. As already mentioned, the volumetric flow rate in the present investigations was kept at 10 ml min^{-1}. The value of n involved in the complete anodic oxidation of the amino as well as the phenolic groups has been established (*5*) to be 2. Since the electrode proper was prepared out of wax-impregnated compressed graphite rods, the effective length of the electrode was bound to be slightly smaller than its geometric length. In the case of the electrodes

Table I. Diffusion Coefficients of Various Organic Substances (Concentration (C), 10^{-4} M; Volume Flow Rate (V_f), 10 ml min^{-1}; Effective Electrode Length, 1.082 cm)

No.	Substance	Limiting current (μA) for complete oxidation	Diffusion coefficient (cm^2 s^{-1}) ($D \times 10^5$)	
			Exptl value	Reported value
1	*p*-Toluidine	20.4	0.615	
2	*o*-Ethylaniline	20.4	0.615	
3	*p*-Isopropylaniline	18.8	0.557	
4	2,4-Dimethylaniline	20.6	0.623	
5	2,6-Dimethylaniline	19.8	0.589	
6	2,6-Diethylaniline	21.4	0.661	
7	*p*-Amino-*N*,*N*-dimethylaniline	22.6	0.718	0.76 (*1*)
8	Catechol	21.4	0.661	
9	Hydroquinone	22.8	0.727	0.74 (*1*)
10	*o*-Aminophenol	21.8	0.680	
11	*o*-Anisidine	19.6	0.579	
12	*p*-Anisidine	20.8	0.634	
13	*o*-Phenetidine	20.8	0.634	
14	*p*-Phenetidine	21.4	0.661	
15	*o*-Methoxyphenol	22.8	0.727	
16	*p*-Methoxyphenol	22.6	0.718	0.70 (*1*)
17	*o*-Ethoxyphenol	22.6	0.718	
18	*p*-Ethoxyphenol	21.4	0.661	0.62 (*1*)
19	2,6-Dimethoxyphenol	22.8	0.727	
20	1-Amino-2-naphthol	21.0	0.643	
21	1-Amino-7-naphthol	19.8	0.589	
22	4-Amino-1-naphthol	20.8	0.634	
23	1-Amino-2-naphthol-4-sulfonic acid	19.2	0.562	
24	7-Amino-1-naphthol	20.6	0.623	
25	Aniline	20.6	0.623	
26	Phenol	20.4	0.615	
27	*o*-Toluidine	19.8	0.589	
28	*m*-Toluidine	20.0	0.597	
29	*o*-Cresol	19.6	0.579	
30	*p*-Cresol	20.2	0.606	
31	*m*-Cresol	19.0	0.553	
32	*o*-Ethylphenol	20.0	0.597	
33	*p*-Ethylphenol	20.2	0.606	
34	*o*-*tert*-Butylphenol	18.5	0.531	
35	2,5-Dimethylaniline	20.2	0.606	
36	2,4-Dimethylphenol	19.6	0.579	
37	2,6-Dimethylphenol	21.2	0.651	
38	3,4-Dimethylphenol	19.6	0.570	
39	3,5-Dimethylphenol	19.4	0.571	
40	*m*-Anisidine	20.6	0.623	
41	*m*-Phenetidine	20.2	0.606	
42	*o*-Chloroaniline	22.8	0.727	
43	*o*-Aminobenzoic acid	27.6	0.968	0.84 (*4*)
44	*p*-Aminobenzoic acid	26.8	0.927	0.843 (*4*)
45	*m*-Aminobenzoic acid	23.8	0.775	0.774 (*4*)
46	1-Naphthylamine-5-sulfonic acid	22.2	0.699	
47	1-Naphthylamine-8-sulfonic acid	21.8	0.680	
48	*m*-Ethylphenol	19.6	0.579	
49	*m*-Aminophenol	19.4	0.571	
50	Resorcinol	22.6	0.699	
51	*o*-Nitroaniline	21.8	0.680	
52	*p*-Nitroaniline	21.4	0.661	
53	*m*-Nitroaniline	20.6	0.623	
54	*m*-Chloroaniline	24.6	0.815	
55	2,5-Dichloroaniline	23.4	0.756	
56	*o*-Hydroxybenzoic acid	20.8	0.634	
57	*p*-Hydroxybenzoic acid	19.8	0.589	
58	*o*-Hydroxyacetophenone	19.4	0.571	
59	*m*-Hydroxyacetophenone	19.4	0.571	

used in the present investigations, the effective length determined by following the procedure described earlier (*10*) was found to be about 90% of the geometric length. Thus for an electrode of geometric length 1.20 cm, the effective length was determined to be 1.082 cm.

The values of diffusion coefficients, calculated as above, are given in Table I. The values reported earlier (*10*) have also been consolidated here for convenience of reference. The values reported in literature (*1*, *4*) are also included in an appropriate column for the sake of comparison.

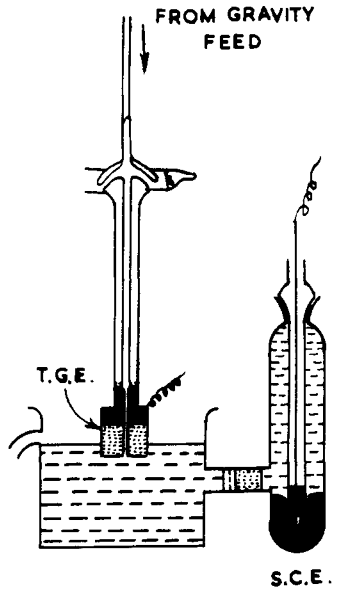

Figure 1. The tubular graphite electrode assembly.

The various values can be divided into three categories as far as their limit of accuracy is concerned.

Category 1. In cases of compounds **1–24,** which do not cause any filming of the electrode (the successive waves almost exactly superimposing on one another), the voltammograms yield ideal values of limiting currents which do not vary by more than ±3% even when different electrodes are used. The values of diffusion coefficients in such cases can be safely taken as sufficiently authentic with a maximum variation of ±5%.

Category 2. In cases of compounds **25–47,** which do cause filming of the electrode surface (the successive waves not superimposing on one another), the voltammograms do not yield ideal values of limiting currents. On account of some surface coverage concurrent with anodic oxidation, the values of the limiting current are likely to be a little smaller than the ideal values. The values of diffusion coefficients for these substances may thus be taken to be slightly on the lower side than the ideal values. The maximum variation of the magnitude of these values, of course, does not exceed ±5%.

Category 3. In cases of compounds **48–59,** which, apart from causing electrode filming, also exhibit distinct maxima, the voltammograms do not yield correct values of limiting currents because of the arbitration involved in computing the limiting current (with reference to the position of the maximum). The variation in the values of diffusion coefficients in such cases is, evidently, greater than ±5%.

It is interesting to note that inspite of the above limitations, the values of diffusion coefficients of the various organic substances are seen to lie fairly close to the generally accepted range of (0.6–0.7) $\times 10^{-5}$ cm^2 s^{-1} (*8*). Not only that, the values also compare favorably with the few reported in literature, keeping in view the wide differences in the nature of the media used by different investigators.

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Densities and Molar Volumes of the Ammonium Nitrate–Water System

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The densities of the ammonium nitrate–water system for water varying between 1.2 and 3.0 mol per mole of the nitrate (R) have been determined. At a given R, density (ρ) is a linear function of temperature. Variation of ρ with R can be expressed by an equation of the type $\rho = a + bR + cR^2$, where a, b, and c are empirical constants. Molar volume of the ammonium nitrate–water system exhibits ideal behavior.

The intermediate range of concentration between anhydrous molten electrolytes and dilute aqueous electrolyte solutions, although important from a theoretical view point (*1–3, 5, 7, 8, 10–12, 14, 15, 17*), has not been extensively studied. Densities of highly concentrated aqueous ammonium nitrate solutions, needed for calculations of structurally important properties, molar volumes, partial molar volumes, and equivalent conductance, etc., are reported in this paper. Data were obtained in the temperature range 295–345 K, limited by solubility and rapid loss of water due to evaporation.

Experimental Section

The densitometer (Figure 1) was essentially of the type used by Husband (*6*) and McAuley (*9*), modified to accommodate a wider range of temperatures. Briefly, it consisted of a calibrated bulb (volume 25–30 cm^3) joined to a graduated capillary on one side (volume 1 cm^3), and a 1-mm bore capillary with three small bulbs (volume *c* 0.5 cm^3 each) connected to a 10-mm tube on the other. The volumes of the main and small bulbs between fiducial points 1 to 5 were determined using triple-distilled water and distilled mercury at seven temperatures in the range 4–50 °C. Using the literature density data (*4*), average volumes at 30 °C between points 1 and 2, 3, 4, 5 were 24.404, 24.089, 23.879, and 23.654 ± 0.005 cm^3, respectively.

Ammonium nitrate, AnalaR (BDH), was vacuum desiccated at 100 °C. The solution for density measurement was prepared