Polarographic & Coulometric Behaviour of Aromatic Nitro Compounds: Part IV—Nitrobenzene in Acetonitrile

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Polarographic study of the reduction of nitrobenzene in aqueous acetonitrile medium shows that the wave heights in this medium are higher than those in aqueous mixtures of ethanol, acetone and dioxane. Further the second reduction step in acid medium is hardly visible. However, coulometric study has shown that the reduction scheme is similar in all the four solvents and uses 4 faradays for the first reduction step and 2 faradays for the second reduction step in acid medium. The product of the first reduction step is found to be β-phenylhydroxylamine. The reduction in pure acetonitrile medium is complicated by a prewave and a current decrease at negative potentials. The negative temperature coefficient of the prewave height indicates some adsorption-like process playing a role in this step. The total wave corresponds to 4 faradays of electricity. Reduction of 1 g mole of nitrobenzene requires 4 g moles of H^+ to be extracted from the solvent. The difficulty involved in mobilizing H^+ of this magnitude from an aprotic solvent system is reflected in the complicated nature of the reduction steps.

POLAROGRAPHY of nitrobenzene in pure acetonitrile using tetraalkyl ammonium perchlorates as base electrolyte has been studied by a number of workers. Runner and Balog[1] obtained two waves and they regard the first wave as a one-electron step. But they did not record the diffusion current constant (d.c.c.) or the half-wave potentials. Geske and Maki[2] have also obtained two waves. The half-wave potential and d.c.c. of the first wave reported by them were −1·15 V and 4·07 respectively. The second wave, appearing around −1·9 V, was distorted and the d.c.c. was nearly double that of the first wave. On the basis of ESR studies, the first wave was shown to represent the formation of $PhNO_2^-$. No conclusion was reached regarding the

reduction product corresponding to the second wave. Reducing at the diffusion current plateau of the first and the second waves and studying the ESR spectra of the products, Fuginaga and coworkers[3] have shown the formation of mono- and di-negative ions. Holleck and Becher[4] have studied the polarography of a number of substituted aromatic nitro-compounds using different supporting electrolytes like LiCl, NaI, $NaClO_4$, CsI and Et_4NI. They observed a well-defined second step with supporting electrolytes of large ionic radius, and waves with minimum or maximum on the second step in solutions containing cations of small ionic radius.

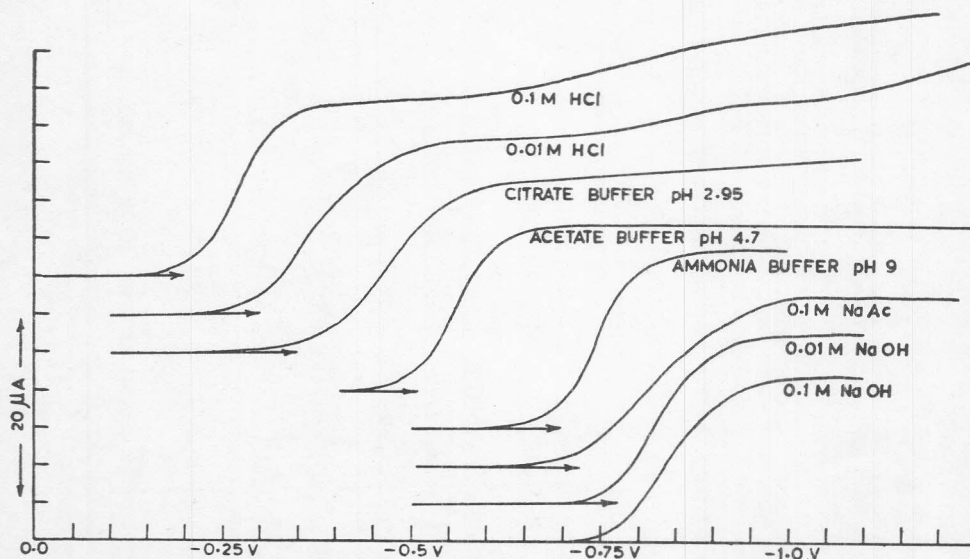In most of the work described above, only one concentration of the depolarizer and one of the

Fig. 1 — Polarograms of nitrobenzene (0·78 m*M*) in different buffers in 50% (v/v) aq. acetonitrile [Zero on the current axis is indicated by an arrow for each polarogram. Supporting electrolyte is a 0·5*M* $NaClO_4$]

supporting electrolytes are used. No detailed investigation is carried out on the nature of the second wave. In the present paper are reported the results of a detailed investigation on the polarographic behaviour of nitrobenzene in anhydrous acetonitrile and aq. acetonitrile.

Materials and Methods

The details of experimental procedure have already been described[5]. Acetonitrile was purified by the method of Kolthoff and Coetzee[6]. Sodium perchlorate was used as the supporting electrolyte.

Reference electrode used in all cases was SCE with an agar bridge.

The capillaries used have m values of 1·175 and 2·516 mg/sec and t values of 4·0 and 3·8 sec in $1M$ KCl solution. The temperature of investigation was $30° \pm 0·1°$, unless otherwise mentioned.

Results

Behaviour in acetonitrile solutions — Some typical polarograms taken in aq. acetonitrile are given in Fig. 1. In Fig. 2, the plot of half wave potential vs percentage of organic solvent is given. Fig. 2
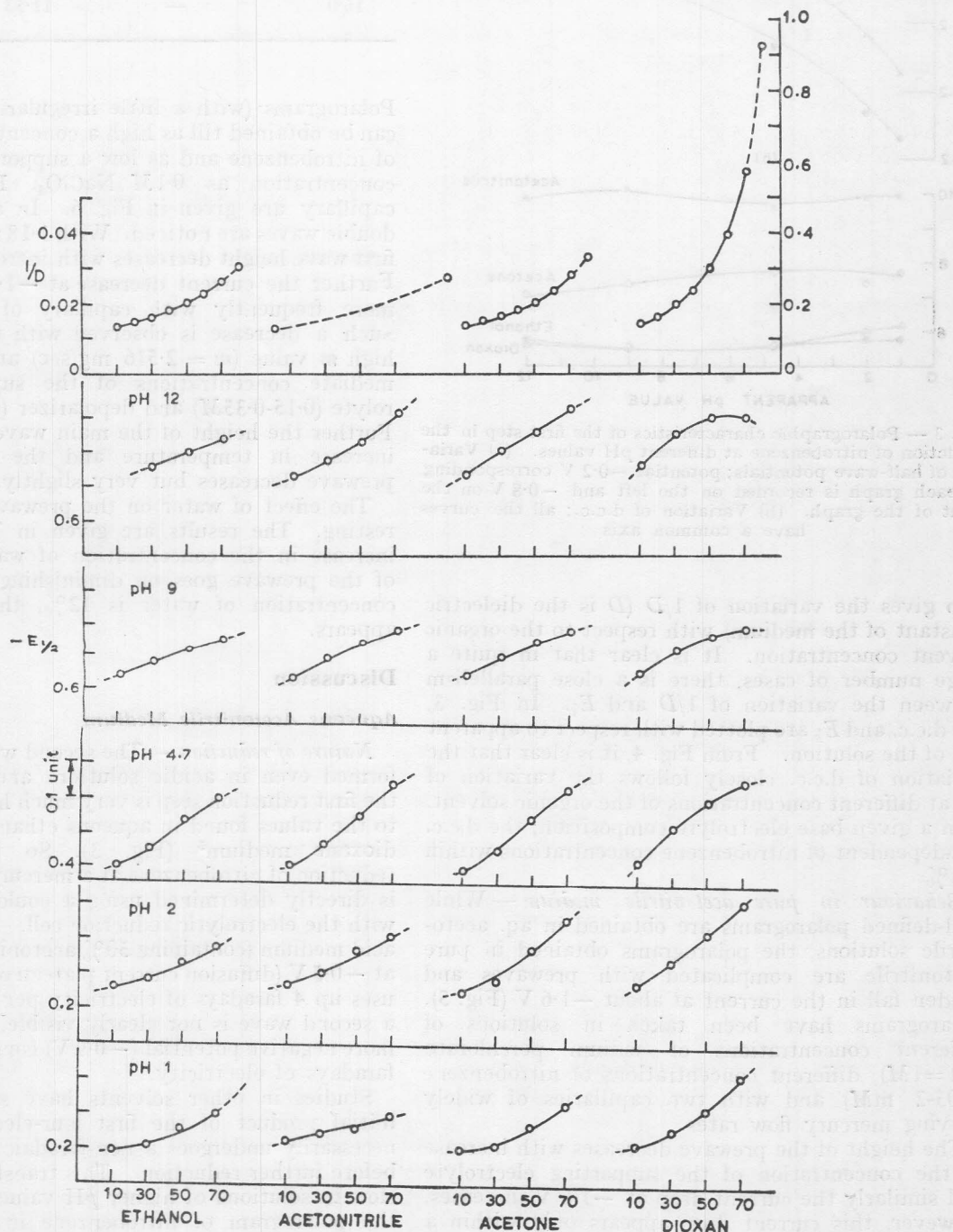

Fig. 2 — Polarographic characteristics of the first step in the reduction of nitrobenzene at different pH values. [Variation of half-wave potentials; potentials $-0·2$ V corresponding to each graph is represented on the left and $-0·8$ V on the right of the graph. All variation of d.c.c. all the curves have a common axis]

also gives the variation of $1/D$ (D is the dielectric constant of the medium) with respect to the organic solvent concentration. It is clear that in quite a large number of cases, there is a close parallelism between the variation of $1/D$ and $E_{1/2}$. In Fig. 2, the d.c.c. and $E_{1/2}$ are plotted at various pH of the solution. From Fig. 4 it is clear that the variation of d.c.c. clearly follows the variation of $1/D$ at different concentrations of the organic solvent. In a given basic the total composition the d.c.c. is independent of nitrobenzene concentration within $\pm 1\%$.

Behaviour in pure and mixed media — When well-defined polarograms are obtained in aq. acetonitrile solutions, the polarograms obtained in pure acetonitrile are complicated with pressure and sudden fall in the current at about $-1·6$ V (Fig. 1). Polarograms have been taken in solutions of different concentrations of nitrobenzene ($0·1M$), different concentrations of nitrobenzene ($0·1M$–$1·2$ mM) and with three capillaries of widely varying mercury flow rates.

The height of the prewave increase with increase in the concentration of the supporting electrolyte and similarly the prewave increases. However, the current disappears when a

Fig. 2 — Half-wave potentials of the first step in the reduction of nitrobenzene in different aqueous mixtures of solvents, ethanol, acetonitrile, acetone and dioxane at different nominal pH values [The variation of $1/D$ in different aqueous solutions are given at the top of the figure for comparison]
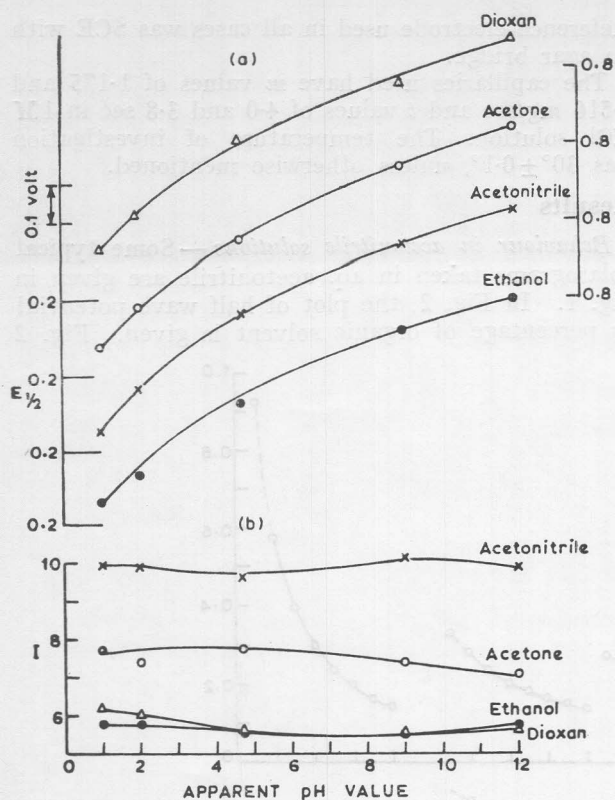
Fig. 3 — Polarographic characteristics of the first step in the reduction of nitrobenzene at different pH values. (a) Variation of half-wave potentials; potential -0.2 V corresponding to each graph is recorded on the left and -0.8 V on the right of the graph. (b) Variation of d.c.c.; all the curves have a common axis

TABLE 1 — EFFECT OF WATER ON d.c.c. OF POLAROGRAMS OF PhNO$_2$ IN AQ. ACETONITRILE

$\{[\text{PhNO}_2]=1.18 \text{ m}M; \text{NaClO}_4=0.5M\}$

Water % (v/v)	d.c.c. (I) at		
	-0.9V	-1.3V	-1.6V
0	2·37	15·93	4·12
0·4	2·20	15·00	4·39
3·2	1·85	14·10	13·07
6·0	1·10	13·90	13·90
12·0	—	12·83	12·83
16·0	—	11·53	11·53

also gives the variation of $1/D$ (D is the dielectric constant of the medium) with respect to the organic solvent concentration. It is clear that in quite a large number of cases, there is a close parallelism between the variation of $1/D$ and $E_{\frac{1}{2}}$. In Fig. 3, the d.c.c. and $E_{\frac{1}{2}}$ are plotted with respect to apparent pH of the solution. From Fig. 4, it is clear that the variation of d.c.c. closely follows the variation of $1/\eta$ at different concentrations of the organic solvent.

In a given base electrolyte composition, the d.c.c. is independent of nitrobenzene concentrations within $\pm 1\%$.

Behaviour in pure acetonitrile medium — While well-defined polarograms are obtained in aq. acetonitrile solutions, the polarograms obtained in pure acetonitrile are complicated with prewaves and sudden fall in the current at about -1.6 V (Fig. 5). Polarograms have been taken in solutions of different concentrations of sodium perchlorate (0.1=1M), different concentrations of nitrobenzene (0.03-2 mM) and with two capillaries of widely varying mercury flow rates.

The height of the prewave decreases with increase in the concentration of the supporting electrolyte and similarly the current drop at -1.6 V increases. However, this current drop appears only within a limited range of concentration.

It is also observed that polarograms with capillary of low m value are more regular and reasonably good.

Polarograms (with a little irregularity of the drop) can be obtained till as high a concentration as 1 mM of nitrobenzene and as low a supporting electrolyte concentration as 0.1M NaClO$_4$. Data with this capillary are given in Fig. 6. In all these cases, double waves are noticed. With 1.18 mM PhNO$_2$, the first wave height decreases with increase in [NaClO$_4$]. Further the current decrease at -1.6 V is observed more frequently with capillary of low m value. Such a decrease is observed with the capillary of high m value ($m = 2.516$ mg/sec) at certain intermediate concentrations of the supporting electrolyte (0.15-0.35M) and depolarizer (0.5 to 1.2 mM). Further the height of the main wave increases with increase in temperature and the height of the prewave decreases but very slightly.

The effect of water on the prewave is quite interesting. The results are given in Table 1. With increase in the concentration of water, the height of the prewave goes on diminishing and when the concentration of water is 12%, the prewave disappears.

Discussion

Aqueous Acetonitrile Medium

Nature of reduction — The second wave is not well-formed even in acidic solutions and the d.c.c. for the first reduction step is very much higher compared to the values found in aqueous ethanol, acetone and dioxane medium[5] (Fig. 3). So the extent of reduction of nitrobenzene at a mercury pool electrode is directly determined using a coulometer in series with the electrolytic reduction cell. In hydrochloric acid medium (containing 50% acetonitrile), reduction at -0.5 V (diffusion current plateau of the first wave) uses up 4 faradays of electricity per mole. Though a second wave is not clearly visible, reduction at a more negative potential (-0.9 V) consumes two more faradays of electricity.

Studies in other solvents have shown that the initial product of the first four-electron reduction necessarily undergoes a non-faradaic transformation before further reduction. This transformation being slow in solutions of higher pH values (say pH 4.5), the polarogram of nitrobenzene in this buffer in ethanol medium does not show a well-defined second step[5]. The ill-defined second step in acetonitrile solutions of even lower pH (hydrochloric acid
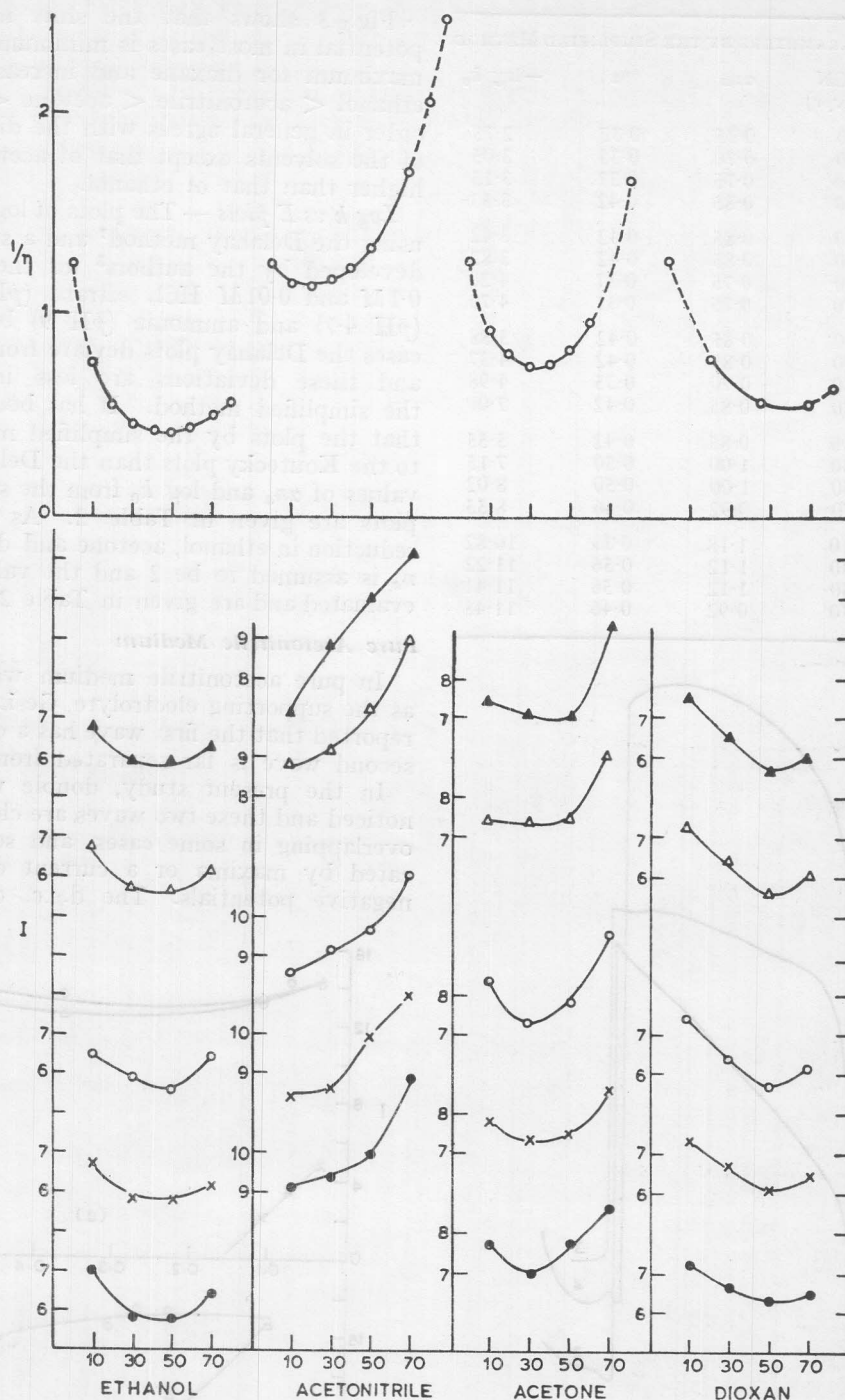
Fig. 4 — Diffusion current constants of the first step in the reduction of nitrobenzene. Different aqueous mixtures of the solvents — ethanol, acetonitrile, aceton and dioxan at different nominal pH values (—, pH 1; ×—×, pH 20; ○—○, pH 4·7; △—△, pH 9; ▲—▲, pH 12. The variation of $1/\eta$ in different aqueous solutions are given at the top of the figure for comparison]

solutions) shows thatt he transformation is much slower in acetonitrile medium.

In citrate (pH 2·95), acetate (pH 4·7) and ammonia (pH 9) buffers, the reduction step is found to use up four faradays of electricity. The reduced solution (containing 50% acetonitrile) shows an anodic step, the half-wave potential of which is found to be +0·11 V, −0·015 V and −0·21 V respectively in these buffers. In solution of sodium hydroxide,

reduction at mercury pool electrode continues indefinitely indicating that the reduction process in this medium is complicated by side reactions. However, the first wave height in all base solutions are of similar order, indicating that the main reduction even in sodium hydroxide is a four-electron step. The anodic wave observed in the reduced solutions established that the reduction product is β-phenyl-hydroxylamine in these solutions also.

TABLE 2 — KINETIC PARAMETERS BY THE SIMPLIFIED METHOD

Medium/pH	MeCN % (v/v)	αn_a	α	$-\log k_0$
0·1M HCl	10	0·75	0·37	2·75
	30	0·70	0·35	3·05
	50	0·75	0·37	3·15
	70	0·85	0·42	3·53
0·01M HCl	10	0·85	0·42	3·42
	30	0·85	0·42	3·82
	50	0·75	0·37	4·23
	70	0·75	0·37	4·70
Citrate buffer (pH 2·95)	10	0·85	0·42	3·58
	30	0·85	0·42	4·37
	50	0·70	0·35	4·98
	70	0·85	0·42	7·00
Acetate buffer (pH 4·7)	10	0·85	0·42	5·55
	30	1·00	0·50	7·15
	50	1·00	0·50	8·02
	70	0·92	0·46	8·55
Ammonia buffer (pH 9·0)	10	1·18	0·59	10·82
	30	1·12	0·56	11·22
	50	1·12	0·56	11·41
	70	0·92	0·46	11·48
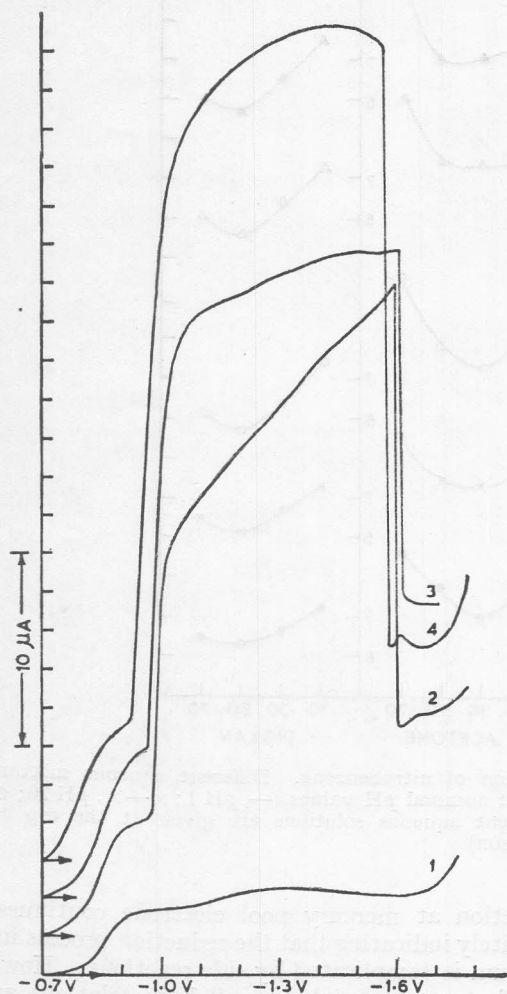
Fig. 3 shows that the shift in the half-wave potential in most cases is minimum for ethanol and maximum for dioxane and increases in the order ethanol < acetonitrile < acetone < dioxane. This order in general agrees with the dielectric constant of the solvents except that of acetonitrile which is higher than that of ethanol.

Log k vs E plots — The plots of log k vs E are made using the Delahay method[7] and a simplified method developed by the authors[5] for the polarograms in 0·1M and 0·01M HCl, citrate (pH 2·95), acetate (pH 4·7) and ammonia (pH 9) buffers. In some cases the Delahay plots deviate from linearity badly and these deviations are less in the plots by the simplified method. It has been shown earlier[5] that the plots by the simplified method are closer to the Koutecky plots than the Delahay plots. The values of αn_a and log k_0 from the simplified method plots are given in Table 2. As in the case of reduction in ethanol, acetone and dioxane solutions, n_a is assumed to be 2 and the value of α are also evaluated and are given in Table 2.

Pure Acetonitrile Medium

In pure acetonitrile medium with $(n\text{-Pr})_4\text{N.ClO}_4$ as the supporting electrolyte, Geske and Maki[2] have reported that the first wave has a d.c.c. of 4 and the second wave is far separated from the first wave.

In the present study, double waves have been noticed and these two waves are close to each other, overlapping in some cases, and sometimes complicated by maxima or a current decrease at more negative potentials. The d.c.c. of the individual
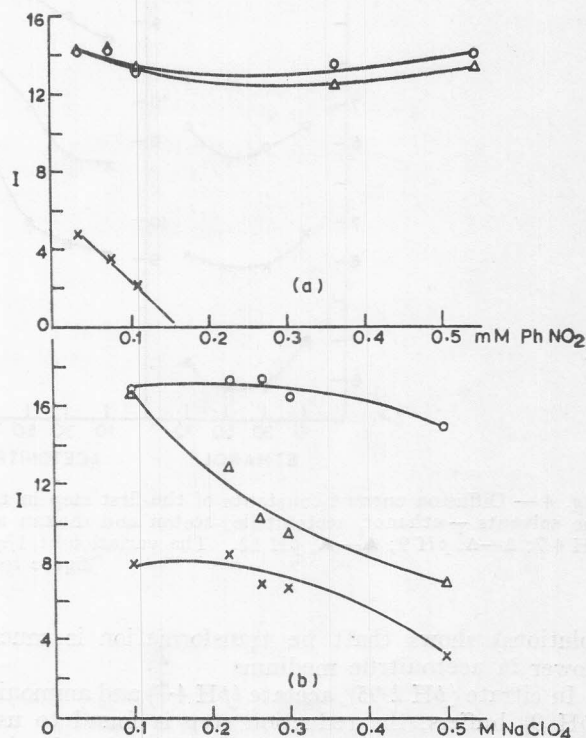

Fig. 5 — Polarograms of nitrobenzene at different concentrations in pure acetonitrile [Zero on the current axis is indicated by an arrow for each polarogram. Supporting electrolyte is 0·5M NaClO₄; curve (1) 0·12 mM PhNO₂; curve (2) 0·59 mM PhNO₂; curve (3) 0·95 mM PhNO₂; and curve (4) 1·18 mM PhNO₂]

Fig. 6 — Diffusion current constants in pure acetonitrile medium. (a) Variation with PhNO₂ concentration; (b) variation with NaClO₄ concentration [×—×, prewave at −0·95 V; ○—○, main wave at −1·3 V; △—△, wave just before final current rise at −1·7 V]

waves of these double waves (denoted here as prewave and the main wave) is strongly dependent on the solution composition and capillary characteristics. But the order of the d.c.c. of the total wave is similar to that in aqueous acetonitrile mixture. So the total wave corresponds to 4 electrons. This needs 4 hydrogen ions also, which must be extracted from the solvent. At higher [depolarizer] or capillary of larger m value, larger amount of H⁺ are to be mobilized and hence the erratic behaviour.

The effect of temperature on the prewave strongly suggests that this polarographic wave has the characteristic similar to the adsorption waves in methylene blue system[8]. It cannot, however, be ruled out that this prewave is due to radical anion. Similar prewave (with a height equal to one-fourth the total height) has been noticed in the reduction of p-chloronitrobenzene by Holleck and Becher[4] and has been attributed by them as due to the reduction to radical anion. In the present system also it is likely that the prewave may be due to the reduction to radical anion although the height is not one-fourth the total height. The lower height noticed in the present system is possibly due to contamination by small amount of water (which would decompose part of the radical anion) since SCE is used as the reference electrode.

In some cases a sudden fall in the diffusion current is noticed at −1·6 V. This sudden fall in current is obviously connected with some process preventing the normal reduction process.

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