MECHANISM OF THE VOLTAMMETRIC REDUCTION OF PHENOLPHTHALEIN IN DMF

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The electrochemical reduction of phenolphthalein in dimethylformamide solution containing 0.1 mol dm^{-3} tetraethylammonium perchlorate at hanging dropping mercury electrode showed an irreversible two-electron voltammetric peak. It was found that the CV peak is diffusion-controlled at low concentration ($\leq$ 0.4 m mol dm^{-3}). At higher concentration ($\geq$ 0.5 m mol dm^{-3}) a postpeak was developed besides the diffusion-controlled one which was assigned to the adsorbed depolarizer. Cyclic voltammetric studies indicate that phenolphthalein follows an ECEC mechanism. Convolution and deconvolution potential sweep voltammetry confirm that mechanism.

Electrochemistry of phenolphthalein has been investigated in only a few instances especially in non-aqueous media [1], and the reduction mechanism appears to be incompletely understood. Kolthoff [1] considered phenolphthalein to exist in hydrated and ionic forms in equilibrium and concluded that the lactone form of phenolphthalein is not reducible at dme in these supporting electrolytes. The general mechanism proposed is ECEC type, the chemical steps being protonation reactions of the radical formed after the electron-transfer.

The present communication is concerned with the electrochemical reduction of phenolphthalein in N,N-dimethylformamide at hanging mercury electrode. The study is based on the analysis of the results of cyclic voltammetry, convolution and deconvolution potential sweep voltammetry. The electrode mechanism was proposed and discussed.

EXPERIMENTAL

Instrumentation

The details are as given in ref. 2.

Reagents

Phenolphthalein (indicator grade, B.D.H.) was used after recrystallization from ethanol. Tetraethylammonium perchlorate (Fluka) (TEAP) and N,N-Dimethylformamide (A.R.BDH) (DMF) were purified and dried [2,3,4].

Fresh stock solution of TEAP, (0.1 mol dm^{-3}) in DMF, was prepared. Fresh stock solution of phenolphthalein (1.0×10^{-2} mol dm^{-3}) was prepared in a fresh electrolyte solution on the same day that measurements were carried out.

RESULTS AND DISCUSSION

Cyclic Voltammetry

A typical voltammogram of phenolphthalein (3.96×10^{-4} mol dm^{-3}) is illustrated in Fig.1. One well-defined peak is observed in the cathodic scan, its characteristics being markedly dependent upon the experimental parameters such as potential sweep rate, ν, reactant concentration c and standing period before scanning. The cyclic voltammetric peak indicates that the reduction is irreversible, as the corresponding anodic step is not seen in any case.

A plot of i_{pc} versus $\nu^{1/2}$ is linear with correlation coefficient $r = 0.997 \pm 0.002$, indicating that the wave is due to a diffusion controlled process.

The average difference between the cathodic peak potential and half-peak potential ($E_{p/2} - E_p = 34.4 \pm 3.3$ mV), is significantly greater than the theoretical value of a normal two-electron transfer process [5], but, less than that for a one-electron transfer. Thereby indicating on irreversible two-electron transfer step. The peak potential, E_p, does shift towards negative potentials on increasing the sweep rate (Table 1).

The variation of the current function, $i_{pc}/\nu^{1/2}$ with sweep rate ν is an important diagnostic criterion for establishing the type of mechanism by cyclic voltammetry. The current function values for phenolphthalein (Table 1)

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is found to decrease with sweep rate indicating that the observed behaviour is consistent with an ECE mechanism [5,6].

The peak current (i_{pc}) increase with concentration of phenolphthalein (3.96×10^{-4} to 1.06×10^{-3} mol dm^{-3}) is nonlinear. Further the peak potential, E_p, is positively shifted (Fig. 1) and a postpeak is developed following the original peak at lower concentration (diffusion-controlled peak). The current function for the postpeak increases with sweep rate. These phenomena indicate that phenolphthalein is strongly adsorbed on the mercury electrode [6], there being an equilibrium between the adsorbed and solution species. The adsorbed species (Ph III in Scheme 1) being more stable to reduction than the solution species (Ph I), a postpeak is observed. The reduction of Ph I is responsible to the diffusion controlled peak at positive potentials.

On increasing the standing period of the mercury drop, for 4.95×10^{-4} mol dm^{-3} phenolphthalein solution at ν = 500 mVs^{-1}, the peak current of the cathodic peak decreases and peak potential receives anodic shift. At the same time a new peak developes at more negative potentials. The peak current of the new postpeak increases on increasing the standing time (c.f. Fig. 2). These findings provide a further support for the above conclusion that phenolphthalein, Ph III, is strongly adsorbed on the mercury electrode before reduction. Similar conclusion has been reported for the adsorptive nature of phenolphthalein and its derivatives [7-8].

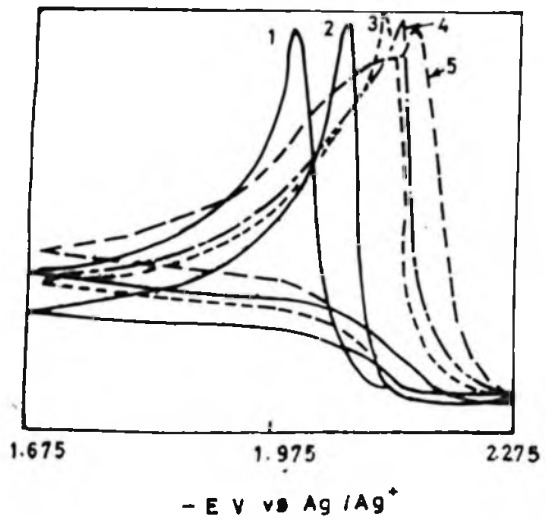


Fig. 1 Cyclic voltammograms of phenolphthalein at different concentrations in 0.1 M TEAP/DMF solution at scan rate of 500 mV/s : 1) 0.396; 2) 0.556; 3) 0.713; 4) 0.856; 5) 1.059 mM.

TABLE 1

CYCLIC VOLTAMMETRIC DATA FOR 3.96×10^{-4} mol dm^{-3} PHENOLPHTHALEIN IN 0.1 mol dm^{-3} TEAP/DMF SOLUTION AT 20°C.

Sweep Rate mV/s	$-E_p$ V	i_{pc} uA	$E_{p/2} - E_p$ mV	$i_p / \nu^{1/2}$ $uAV^{-1/2}s^{1/2}$
50	1.838	1.95	32.0	8.72
100	1.855	2.30	32.1	7.27
200	1.899	3.00	34.4	6.73
500	1.920	3.19	39.2	4.51

Convolution Potential Sweep Voltammetry [2]

Figure 3 illustrates the cyclic convoluted current voltammograms, I_1 vs E & I_2 vs E for phenolphthalein as a representative example. On convolution of the cyclic voltammetric data for 3.96×10^{-4} mol dm^{-3} phenolphthalein in 0.1 mol dm^{-3} TEAP/DMF, the convoluted current I_1 during the reverse half of the sweep neither reaches the initial (zero) value nor retrace the curve developed during the forward

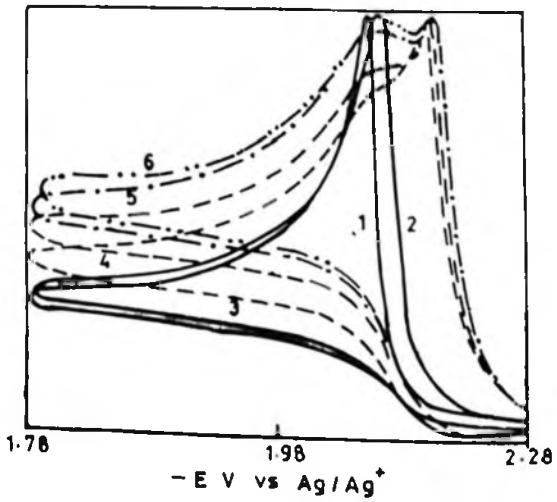


Fig. 2 Cyclic voltammograms of 4.95×10^{-4} M phenolphthalein in 0.1 M TEAP/DMF solution at scan rate of 500 mV/s at different standing period: t = 1) 0.0; 2) 1.5; 3) 3.0; 4) 4.5; 5) 6.0; 6) 7.5 seconds.

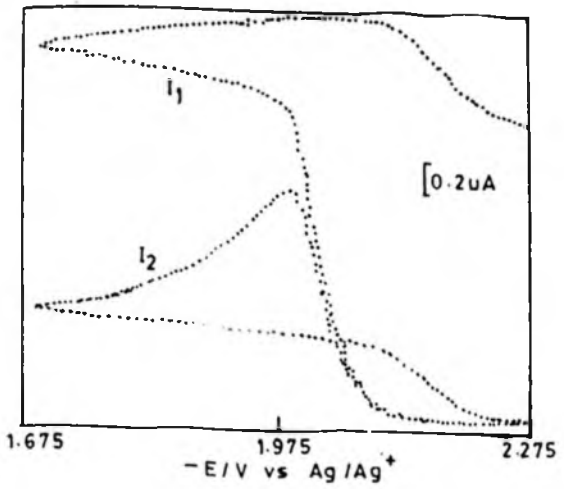


Fig. 3 Cyclic convoluted current (I_1 & I_2) voltammograms for 3.96 x 10^{-4} mol dm^{-3} phenolphthalein in 0.1 mol dm^{-3} TEAP/DMF solution at sweep rate of 500 mV/s

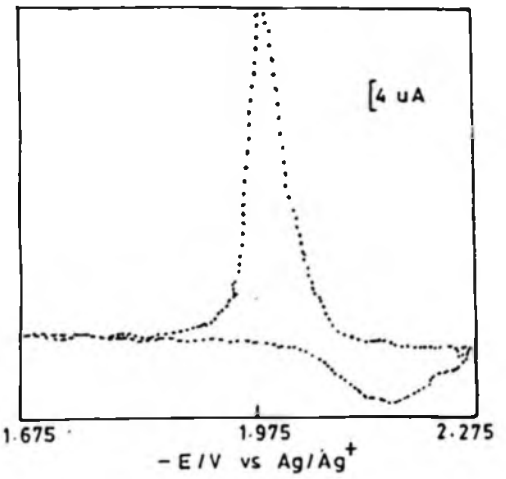


Fig. 4 Cyclic deconvoluted current voltammogram for 3.96 x 10^{-4} mol dm^{-3} phenolphthalein in 0.1 mol dm^{-3} TEAP/DMF solution at sweep rate of 500 mV/s

sweep, irrespective of the sweep rate. This behaviour confirms the irreversible nature of the voltammetric wave.

Deconvolution (semidifferentiation) of the cyclic convoluted voltammetric data, I_1, for reversible electron-transfer reaction shows a voltammogram with two peaks e_{pc} and e_{pa}. These peaks are located at potentials E_{pc} and E_{pa} each equal to the polarographic half-wave potential $E_{1/2}$ [9]. During a reverse sweep, the predicted shape of the derivative cyclic convoluted current voltammogram is obtained by simply reflecting the forward sweep across the potential axis. The peak width, W_p (the width of the peak at half of its height) has the value of 3.53 RT/nF.

On deconvolution, the cyclic voltammetric data give voltammograms with two peaks apart (Fig. 4). The peak separation, $E_{pa} - E_{pc}$ (E_{pa} and E_{pc} are the deconvoluted current anodic and cathodic peak potentials e_{pa} and e_{pc}, respectively) ammounts to 166.3 mV at sweep rate of 500 mV/s. The ratio of deconvoluted anodic- to cathodic currents, dI_{lpa}/dI_{lpc}, is 0.15 ± 0.02 in the entire sweep rate range. It is found that the peak width, W_p, equals to 53.2 mV at υ = 500 mV/s which is larger than that expected for reversible two-electron transfer process (44.6 mV at 20°C). These facts are consistent with irreversible two-electron process with kinetic contribution and gives a further support to the above conclusion.

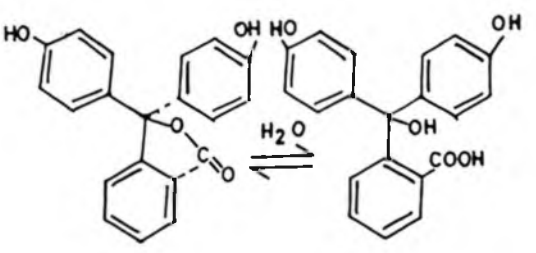
Logarithmic analysis of the convolution potential sweep voltammetric data is tested for different schemes (E_{rev}, E_{irr}, EC, CE, ECE,..) (using the general equation 5 of ref 2).

On plotting the data for 3.96 c 10^{-4} mol dm^{-3} phenolphemalein solution as ln $[(I_{lim} - I_l)/i]$ vs E, straight lines are obtained with regression slopes close to the values expected to an ECE reactions. This is a further verification for an ECE reaction mechanism concluded above.

Reduction Mechanism

The electrochemical reduction of phenolphthalein in DMF can be formulated, on the basis of the above results, by scheme 1.

According to Kolthoff[1], phenolphthalein is represented as an equalibrium between the colourless lactone (Ph I) and colourless hydrated forms (Ph II). Thus, the equilibrium can be formulated as follows



colourless lactone Ph I — colourless hydrate Ph II

It has been concluded that in non-aqueous ethanolic medium, the lactone form, Ph I, is not reducible at least in the potential region accessible in the given supporting electrolyte but hydrated form is reducible at mercury electrode. It is worth mentioning that the voltammetric peak does not change on the addition of water up to 200 m mol dm^{-3} . Taking into account the acid-base properties of phenolphthalein, one can regard phenolphthalein as a proton source, HX, through the "father-son" reaction [10], for neutralization of the radical anions after the electron transfer (reactions 3 and 5). Thus, reasonably the lactone forms are the reducible forms of phenolphthalein in 0.1 mol dm^{-3} TEAP/DMF medium at HDME.

$$\text{Ph I} \rightleftharpoons \text{Ph III (adsorbed Ph I)} \qquad (1)$$

$$\text{Ph III} + e \rightleftharpoons \text{Ph III}^{\cdot}\ ,\ E_1^{\circ} \qquad (2)$$

$$\text{Ph III}^{\cdot -} + \text{HX} \longrightarrow \text{H Ph III}^{\cdot} + X^{-} \qquad (3)$$

$$\text{H Ph III}^{\cdot} + e \rightleftharpoons \text{H Ph III}^{-}\ ,\ E_2^{\circ} \qquad (4)$$

$$\text{H Ph III}^{-} + \text{HX} \longrightarrow \text{H}_2\text{ Ph III} + X^{-} \qquad (5)$$

Scheme 1

The appearance of a single irreversible voltammetric peak reveals that H Ph $III^{\cdot}$ is easier to reduce than the starting reactant Ph III and reduction potential occurs at less negative potentials than the potential of Ph III (i.e. $\Delta E^{\circ} = E_1^{\circ} - E_2^{\circ} > 0$). The irreversibility of that wave is attributed to the chemical instability of H Ph III^{-} which undergoes irreversible chemical reaction giving rise to an ECEC process.

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