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Mechanism of the Voltammetric Reduction of Phenolphthalein at the Mercury Electrode in *DMF*

Refat Abdel-Hamid

Department of Chemistry, Faculty of Science, Sohag University, Sohag, Egypt

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The electrochemical reduction of phenolphthalein in dimethylformamide solution containing 0.1 mol dm^{-3} tetraethylammonium perchlorate at the hanging dropping mercury electrode showed an irreversible two-electron voltammetric peak. It was found that the CV peak is diffusion-controlled at low concentrations ($\leqslant$ 0.4 mmol dm^{-3}). At higher concentration ($\geqslant$ 0.5 mmol 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.

(Keywords: Dimethylformamide; Electrochemical reduction; Cyclic voltammetry; Convolution and deconvolution voltammetry; ECEC mechanism)

Mechanismus der voltametrischen Reduktion von Phenolphthalein an der Quecksilberelektrode in DMF

Die elektrochemische Reduktion von Phenolphthalein an der tropfenden Quecksilberelektrode in Dimethylformamidlösung mit einem Gehalt von 0.1 mol dm^{-3} an Tetraethylammoniumperchlorat zeigte ein irreversibles voltametrisches Maximum für zwei Elektronen. Es zeigte sich, daß der CV-Peak bei niederen Konzentrationen ($\leqslant$ 0.4 mmol dm^{-3}) diffusionskontrolliert ist. Bei höheren Konzentrationen ($\geqslant$ 0.5 mmol dm^{-3}) entwickelte sich ein nachkommendes Maximum neben dem diffusionskontrollierten, welches dem adsorbierten Depolarisator zugeordnet wurde. Untersuchungen mittels cyclischer Voltametrie zeigten, daß Phenolphthalein einem ECEC-Mechanismus folgt. Konvolutions- und Dekonvolutions-Potential-Sweep-Voltametrie bestätigten diesen Mechanismus.

Introduction

The electrochemistry of phenolphthalein has been investigated in only a few instances especially in non-aqueous media [1, 2], and the reduction mechanism appears to be incompletely understood. *Kolthoff* [1] considered phenolphthalein and its derivatives in solution to exist in different hydrated and ionic forms in equilibrium. It was concluded that the lactone form of phenolphthalein is not reducible at the dropping mercury electrode at least not at potentials more positive than that at which the wave of supporting electrolyte appears. The general mechanism is of the ECEC type, the chemical steps are protonation reactions of the radical formed after the electron-transfer, resulting in the development of the reduction wave.

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

Experimental

The electrochemical measurements were carried out using a conventional three electrode configuration. An E.G. & G. PAR model SMDE 303 mercury-drop system in small hanging-drop mode was used as working electrode. The electrode area was $1.05 \cdot 10^{-2}$ cm^2. The reference electrode was $Ag/AgNO_3$ (0.01 *M*) in 0.1 mol dm^{-3} tetraethylammonium perchlorate, *TEAP*, in N,N-dimethylformamide, *DMF*. A 1 cm^2 platinum sheet auxiliary electrode was used throughout. All experiments were performed at 20 °C in *DMF* containing 0.1 mol dm^{-3} *TEAP* as supporting electrolyte. Solutions were purged with pure nitrogen before experiment and an atmosphere of nitrogen was maintained above the working solution. Internal resistance ohmic drop distortions were minimized by applying positive feedback compensation.

Cyclic voltammetry was performed using an E.G. & G. PAR model 363 scaning potentiostat/galvanostat. The current response and applied potentials were stored on magnetic disk via a fast capture system, based upon twin channel 12-bit analogue-to-digital converter (50 μs conversion time) and a GEMINI GALAXY 2 microcomputer. Data capture was written in Macro 80 Assembler language which allowed a minimum aquisition time of 100 μs per point. In all experiments 500 data points were routinely captured, equally spaced in time and with a time interval appropriate to the time scale of the particular experiment. Background data were also stored and were subtracted from the experimental data set, minimizing effects such as double layer charging currents.

Phenolphthalein (indicator grade, B.D.H.) was used after recrystallization from ethanol. Tetraethylammonium perchlorate (Fluka) was recrystallized from methanol and dried in a vacuum oven at 60 °C. N,N-Dimethylformamide (A.R. grade, B.D.H.) was purified and dried by passing it through neutral active alumina as described elsewhere [3] (a technique pioneered by *Parker* et al. [4]).

Fresh stock solution of tetraethylammonium perchlorate, *TEAP* (0.1 mol dm^{-3}) in N,N-dimethylformamide, *DMF*, was prepared Fresh stock solutions of phenolphthalein ($1.0 \cdot 10^{-2}$ mol dm^{-3}) was prepared from a fresh electrolyte solution (0.1 mol dm^{-3} *TEAP/DMF*) on the same day that measurements were carried out.

Results and Discussion

I. Cyclic Voltammetry

The cyclic voltammetry of phenolphthalein was studied on a hanging mercury electrode, HMDE, in 0.1 mol dm^{-3} tetraethylammonium perchlorate/N,N-dimethylformamide, *TEAP/DMF*, solutions. The voltammetric pattern for $3.96 \cdot 10^{-4}$ mol dm^{-3} phenolphthalein 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, v, reactant concentration c and standing period before scanning. By cyclic voltammetry, the peak appears to be electrochemically irreversible, its anodic partner is lacking in all the experimental conditions explored.

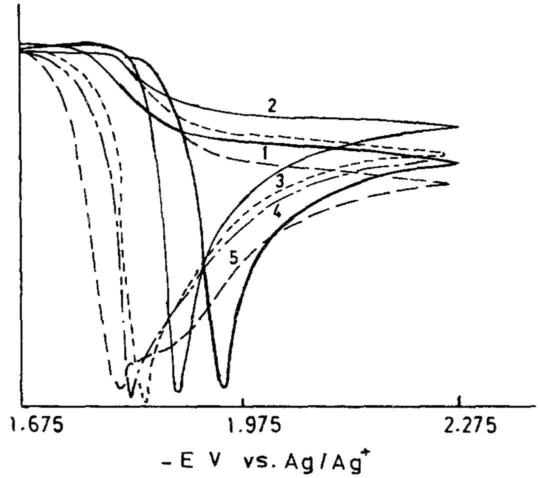


Fig. 1. Cyclic voltammograms of $3.96 \cdot 10^{-4}$ *M* phenolphthalein

At $3.96 \cdot 10^{-4}$ mol dm^{-3} phenolphthalein, the cathodic peak current, i_{pc}, correlates with the square root of the sweep rate, $v^{1/2}$. A plot of i_{pc} versus $v^{1/2}$ yields a linear relationship with a 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 value pertaining to a normal two-electron transfer process [5] over the range of potential sweep rates used. This value is, on the other hand, less than the lower limit for a one-electron transfer, which indicates that the reaction involves the transfer of two electrons. The peak potential, E_p, does shift towards negative potentials on increasing the sweep rate (c.f. Table 1).

Table 1. *Cyclic voltammetric data.* $3.96 \cdot 10^{-4}$ mol dm^{-3} phenolphthalein in 0.1 mol dm^{-3} *TEAP/DMF* solution at 20 °C

Sweep rate mV s^{-1}	$-E_p$ V	i_{pc} μA	$E_{p/2} - E_p$ mV	$i_p/v^{1/2}$ μA V$^{-1/2}$ 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

The variation of the current function, $i_{pc}/v^{1/2}$, with the sweep rate v is an important diagnostic criterion for establishing the type of mechanism by cyclic voltammetry. For an ECE (chemical reaction coupled between two charge-transfer processes) with an irreversible chemical reaction, $i_{pc}/v^{1/2}$ should decrease with an increase of the sweep rate. The current function values for phenolphthalein at different sweep rates are shown in Table 1. It is found that the ratio decreases with the sweep rate indicating that the observed behaviour is consistent with an ECE mechanism.

On increasing the concentration of phenolphthalein from $3.96 \cdot 10^{-4}$ to $1.06 \cdot 10^{-3}$ mol dm^{-3} the peak current, i_{pc}, increases in non-linear manner. It does not correlate with the square root of the sweep rate. Moreover, 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 the sweep rate. These phenomena indicate that phenolphthalein is strongly adsorbed on the mercury electrode [6]. The postpeak results from the greater stability with respect to reduction of adsorbed reactant (Ph III, Scheme 1) compared to solution reactant, Ph I. It seems that an adsorption equilibrium occurs between the adsorbed depolarizer and the dissolved one. The reduction of dissolved phenolphthalein, Ph I, which is responsible for the diffusion-controlled peak at more positive potentials, presumable occurs either through the adsorbed Ph I film or at the free surface.

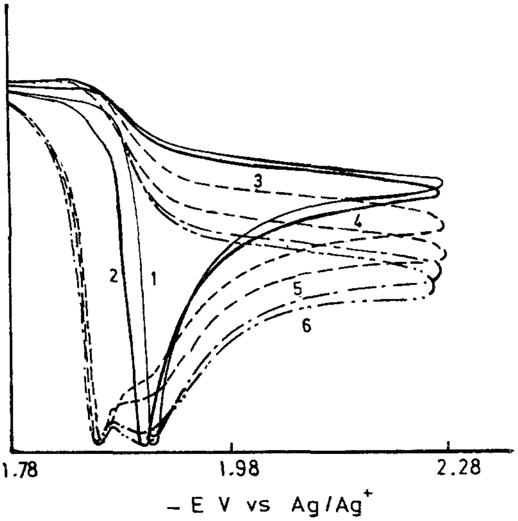


Fig. 2. Cyclic voltammograms of $4.95 \cdot 10^{-4} M$ phenolphthalein in $0.1 M$ *TEAP/DMF* solution at a scan rate of $500\,\mathrm{mV\,s^{-1}}$ at different standing periods: *1* $t = 0.0$; *2* 1.5; *3* 3.0; *4* 4.5; *5* 6.0; *6* 7.5 seconds

On increasing the standing period of the mercury drop, for $4.95 \cdot 10^{-4}\,\mathrm{mol\,dm^{-3}}$ phenolphthalein solution at $v = 500\,\mathrm{mV\,s^{-1}}$, the peak current of the cathodic peak decreases and the peak potential receives an 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 (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. A similar conclusion has been reported for the adsorptive nature of phenolphthalein and its derivatives [7–9].

II. Convolution Potential Sweep Voltammetry

One of the sophisticated techniques which has become popular recently is convolution potential sweep voltammetry [10–14]. Convolution potential sweep voltammetry transforms the broad, asymmetric wave shape of a linear sweep voltammogram into a simple form resembling a dc polarogram. The current data *i* are convoluted making use the following integral:

$$I_1 = I_1(t) = 1/\pi^{1/2} \int_0^t \frac{i(u)}{(t-u)^{1/2}}\,\mathrm{d}u \qquad (1)$$

Blagg et al. [15] developed a general convolution method taking into account the coupled chemical reaction, with an integral of the type:

$$I_2 = I_2(k'_c, t) = 1/\pi^{1/2} \int_0^t \frac{i(u) \cdot \exp[-k'_c(t-u)]}{(t-u)^{1/2}} \, \mathrm{d}u \tag{2}$$

The convoluted current data (I_1 and I_2) are analysed using the following general logarithmic equation:

$$-\frac{(E - E^{\theta})}{RT} nF = \ln\left[\frac{(I_{lim} - I_1)}{I_2 + (D^{1/2}/k_f^{\theta})\, i \exp(1-\alpha)\xi)}\right] \tag{3}$$

where I_1 and I_2 are the convolution currents given by Eqs. (1) and (2), respectively, n is the number of electrons transferred, $I_{lim} = (nFAC^{init}D^{1/2})$ is the limit of I as E approaches infinity, D are the diffusion coefficients of oxidized and reduced species which are assumed to be equal to simplify the equations, A is the electrode area, k_f^{θ} is the forward heterogeneous rate constant, α is the symmetry factor, $\xi = (E - E^{\theta})nF/RT$ and the remaining symbols have their usual electrochemical meaning.

For a reversible electron-transfer reaction the shape of the cyclic convoluted current voltammogram is independent of the way in which the potential is varied. A corollary of this is that, during the first reverse scan of a cyclic voltammetric experiment, the $I_1 - E$ curve is predicted to exactly retrace the curve developed during the forward scan. On convolution of the cyclic voltammetric data i for $3.96 \cdot 10^{-4}\,\mathrm{mol\,dm^{-3}}$ phenolphthalein in $0.1\,\mathrm{mol\,dm^{-3}}$ *TEAP/DMF*, during the reverse half of the sweep the convoluted current I_1 neither reaches the initial (zero) value nor retraces the curve developed during the forward sweep, irrespective of the sweep rate. This behaviour confirms the irreversible nature of the voltammetric wave. Fig. 3 illustrates the cyclic convoluted current voltammograms, I_1 and $I_2 - E$, for phenolphthalein as a representative example.

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 $E_{1/2}$ [16]. 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, i.e. 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 apart peaks (Fig. 4). The peak separation, $E_{pa} - E_{pc}$ (E_{pa} and E_{pc}

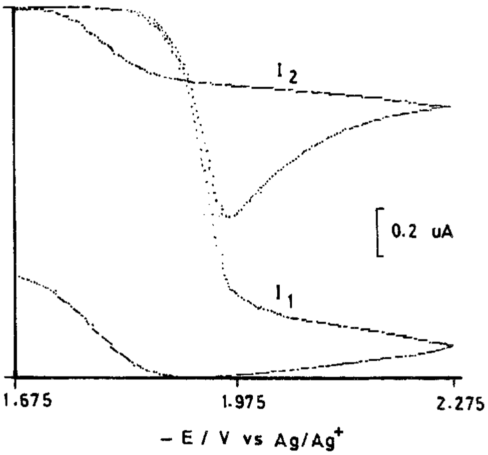


Fig. 3. Cyclic convoluted current (I_1, I_2) voltammograms for $3.96 \cdot 10^{-4}$ mol dm^{-3} phenolphthalein in 0.1 mol dm^{-3} *TEAP/DMF* solution at a sweep rate of 500 mV s^{-1}

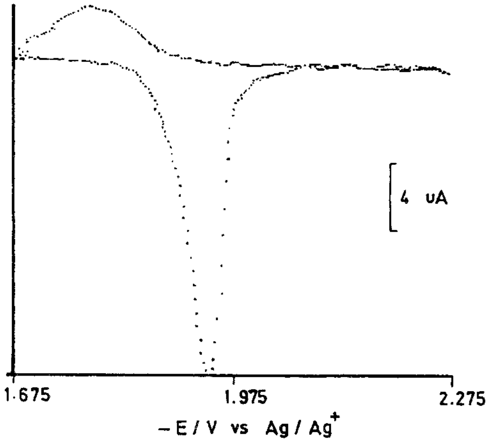


Fig. 4. Cyclic deconvoluted current voltammogram for $3.96 \cdot 10^{-4}$ mol dm^{-3} phenolphthalein in 0.1 mol dm^{-3} *TEAP/DMF* solution at a sweep rate of 500 mV s^{-1}

are the deconvoluted current anodic and cathodic peak potentials e_{pa} and e_{pc}, respectively), ammounts to 166.3 mV at a sweep rate of 500 mV s^{-1}. The ratio of deconvoluted anodic-to-cathodic currents, $\mathrm{d}I_{1pa}/\mathrm{d}I_{1pc}$, 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 $v = 500$ mV s^{-1} which is larger than that expected for reversible two-electron transfer process (44.6 mV at 20 °C). These facts are consistent with an 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 Eq. (3). The data for $3.96 \cdot 10^{-4}$ mol dm^{-3} phenolphthalein fit satisfactorely the following equation:

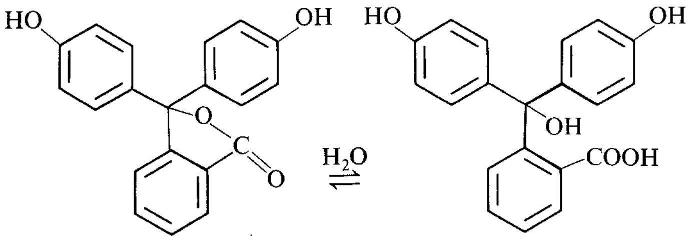
$$-(E - E^{\theta})(nF/RT) = \ln[(I_{lim} - I_1)/i] \qquad (4)$$

On plotting $\ln[(I_{lim} - I_1)/i]$ versus E, straight lines are obtained. The regression slopes of these lines are close to the values expected to an ECE reactions. This is a further verification for an ECE reaction mechanism concluded above.

III. Reduction Mechanism

The electrochemical reduction of phenolphthalein in *DMF* containing 0.1 mol dm^{-3} *TEAP* at the electrode surface can be formulated (on the basis of the above results) by Scheme 1.

According to *Kolthoff* [1], phenolphthalein is represented as an equilibrium between the colourless lactone and colourless hydrated forms. 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 [2] the lactone forms, Ph I, are not reducible at least not at potentials more positive than that at which the wave of the supporting electrolyte appeared and the hydrated forms are reducible at the mercury electrode. It should be mentioned that the voltammetric peak receives no change on the addition of water up to 200 mmol 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 [17], for neutralization of the radical anions after the electron transfer (reactions 7 and 9). Thus, reasonably the lactone forms are the reducible forms of phenolphthalein in $0.1\,\mathrm{mol\,dm^{-3}}$ *TEAP/DMF* medium at HDME.

$$\mathrm{Ph\ I} \rightleftharpoons \mathrm{Ph\ II},\ \mathrm{Ph\ III} = \mathrm{Ph\ I_{(ads)}} \tag{5}$$

$$\mathrm{Ph\ III} + \mathrm{e} \rightleftharpoons \mathrm{Ph\ III}^{\cdot-},\ E_1^0 \tag{6}$$

$$\mathrm{Ph\ III}^{\cdot-} + \mathrm{H}X \rightarrow \mathrm{H\ Ph\ III}^{\cdot} + X^- \tag{7}$$

$$\mathrm{H\ Ph\ III}^{\cdot} + \mathrm{e} \rightleftharpoons \mathrm{H\ Ph\ III}^-,\ E_2^0 \tag{8}$$

$$\mathrm{H\ Ph\ III}^- + \mathrm{H}X \rightarrow \mathrm{H_2\ Ph\ III} + X^- \tag{9}$$

Scheme 1

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

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