

# The Adsorption Behavior of Phenolphthalein at a Mercury Electrode in Water-Ethanol Solutions

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**Summary.** A complete characterization of the adsorption of phenolphthalein at the hanging mercury drop electrode in aqueous buffer solutions containing 10% (v/v) ethanol was obtained employing cyclic voltammetry and double potential step chronocoulometry. At  $pH = 3.4$ , a sharp symmetric cyclic voltammetric wave due to an irreversible weak adsorption of the monoanionic form is obtained at a concentration of  $5.1 \mu\text{mol} \cdot \text{dm}^{-3}$ . Under these conditions, phenolphthalein adsorbs in a compact layer in which the triphenylmethan moiety is arranged perpendicular to the electrode surface. Upon increasing the concentration, the symmetry of the wave decreases; it can now be attributed to a mixed diffusion-adsorption process. In acidic solutions ( $pH < 3.4$ ) the observed electroactivity is ascribed to the adsorption of the neutral lactone form. In solutions of  $pH = 10.58$ , no adsorption was detected.

**Keywords.** Phenolphthalein; Electrochemistry; Adsorption; Cyclic voltammetry; Double potential step chronocoulometry.

## Das Adsorptionsverhalten von Phenolphthalein an einer Quecksilberelektrode in Wasser-Ethanol-Lösungen

**Zusammenfassung.** Eine vollständige Charakterisierung der Adsorption von Phenolphthalein an der hängenden Quecksilbertropfelektrode in wäßrigen Pufferlösungen mit einem Ethanolgehalt von 10% (v/v) wurde mit Hilfe cyclischer Voltammetrie und Doppelschritt-Chronocoulometrie durchgeführt. Bei  $pH = 3.4$  und einer Konzentration von  $5.1 \mu\text{mol} \cdot \text{dm}^{-3}$  zeigt eine scharfe symmetrische voltammetrische Welle die irreversible schwache Adsorption des Monoanions an. Unter diesen Bedingungen wird das Phenolphthalein als kompakte Schicht adsorbiert, in der das Triphenylmethanfragment orthogonal zur Elektrodenoberfläche angeordnet ist. Bei höheren Konzentrationen wird die Welle zunehmend unsymmetrisch und kann dann einem gemischten Diffusions-Adsorptionsvorgang zugeordnet werden. In sauren Lösungen ( $pH < 3.4$ ) wird die beobachtete Elektroaktivität der neutralen Lactonform zugeordnet. In Lösungen mit  $pH = 10.58$  konnte keine Adsorption nachgewiesen werden.

## Introduction

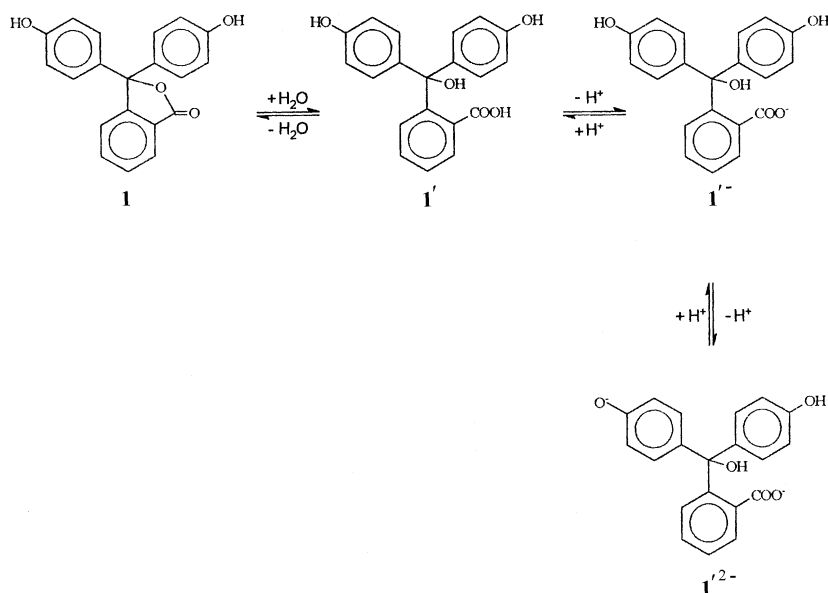
Although there is a variety of applications of phenolphthalein in the preparation of synthetic carbon anodes for lithium secondary batteries [1] and in the synthesis of

polymers such as phenolphthalein polyether ketone [2], phenolphthalein based polysulfone [3] and phenolphthalein polyether sulfone [4], little has been reported concerning its electrochemistry [5–8]. In aqueous, aqueous-ethanolic, and ethanolic media, phenolphthalein gives a single two-electronic polarographic wave at  $pH < 9$ , whereas two monoelectronic waves are observed at  $pH$  values  $> 9$  [5, 7]. In dimethylformamide, its cyclic voltammograms exhibit an irreversible two-electronic reduction wave at low concentrations [8]. At higher concentrations, adsorption of phenolphthalein occurs and has been measured on the dropping mercury electrode chronocoulometrically in aqueous acid and basic solutions using a step charge potential [6]. It has been concluded that in acid solutions the monomolecular adsorbed film consists of the lactone, whereas in basic solutions the lactone ring is opened.

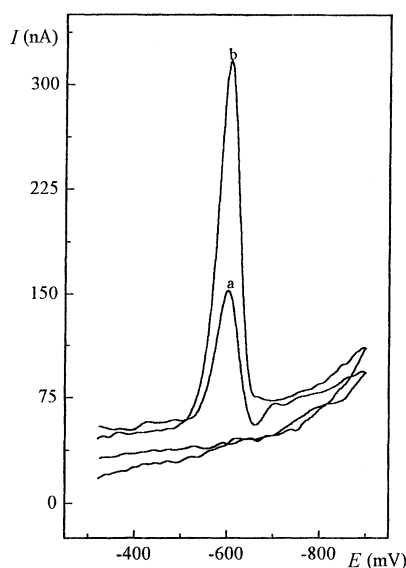
The aim of the present investigation is to establish a complete characterization of the adsorption behavior of phenolphthalein at the hanging mercury drop electrode (HMDE) in aqueous buffer solutions containing 10% (v/v) of ethanol based on an analysis of cyclic voltammetric data [9, 10] and on double potential step chronocoulometry.

## Results and Discussion

In aqueous solutions, **1** can exist in four different forms depending on the  $pH$  value of the solution. Below  $pH$  3 it occurs in two colourless forms, a neutral form with a  $\gamma$ -lactone ring (**1**) and a neutral form in which the  $\gamma$ -lactone ring is opened (**1'**). Between  $pH$  3 and 9, the monoanionic form (**1'<sup>-</sup>**) prevails. At higher  $pH$  values ( $> 9$ ), the dianionic form (**1'<sup>2-</sup>**) predominates (cf. Scheme 1) [7, 13, 14].



Scheme 1



**Fig. 1.** Cyclic voltammograms of **1** at scan rates of  $\nu=200$  mV/s at  $pH=3.4$ ; a:  $2.04$ , b:  $5.1 \mu\text{mol} \cdot \text{dm}^{-3}$

Figure 1 shows the cyclic voltammograms of phenolphthalein at different concentrations at the HMDE. A sharp CV wave is observed. Representative voltammetric data are collected in Table 1. The wave is irreversible, since its anodic counterpart is lacking. The shape of the CV wave suggests that it corresponds to a faradaic surface process especially, at low concentrations ( $2.04 \mu\text{mol} \cdot \text{dm}^{-3}$ ). A doubly logarithmic relationship of peak current and scan rate serves to distinguish diffusion-controlled processes from those involving the adsorption of the electroactive species on the electrode surface [15]. Within the concentration range of  $2.04\text{--}10.20 \mu\text{mol} \cdot \text{dm}^{-3}$  straight lines (correlation coefficients: 0.999) with slopes of 0.88 are obtained. This indicates that the CV wave is due to a mixed diffusion-adsorption process.

**Table 1.** Cyclic voltammetric data for  $10.20 \mu\text{mol} \cdot \text{dm}^{-3}$  **1** in an aqueous ethanolic (10% v/v) buffer solution at  $pH$  3.4

$\nu$ (mV/s)	$-E_p$ (mV)	$i_p$ (nA)	$W_{1/2}$ (mV)	$i_p/C\nu^{1/2}$ $\mu\text{A}/\text{mmol} \cdot \text{dm}^{-3}(\text{V/s})^{1/2}$
100	608	374	53.2	116.0
200	620	722	52.8	158.0
400	634	1288	55.0	200.0
500	638	1534	55.2	213.0
600	641	1738	56.4	220.0
800	648	2309	59.1	253.0
1000	657	2974	62.0	292.0

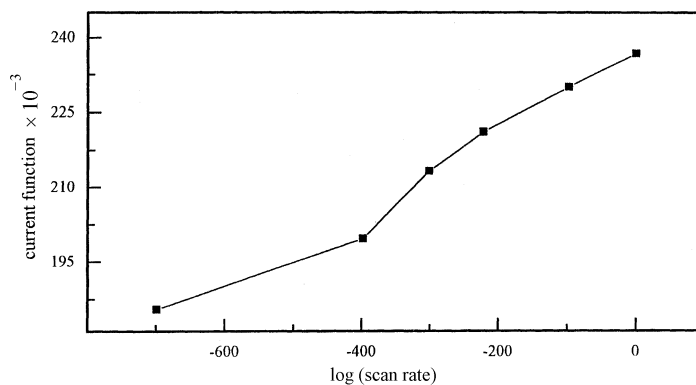
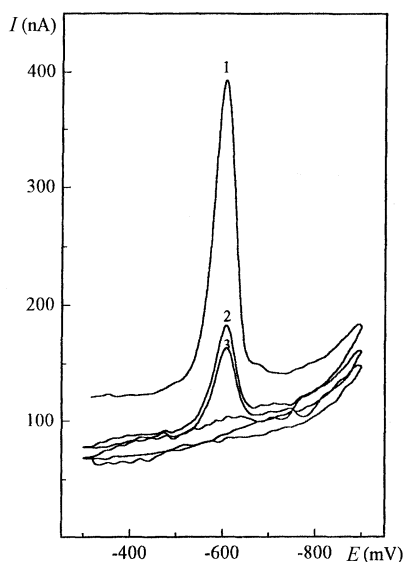


Fig. 2. Relationship between current function and log (scan rate) at  $[1] = 2.04 \mu M$

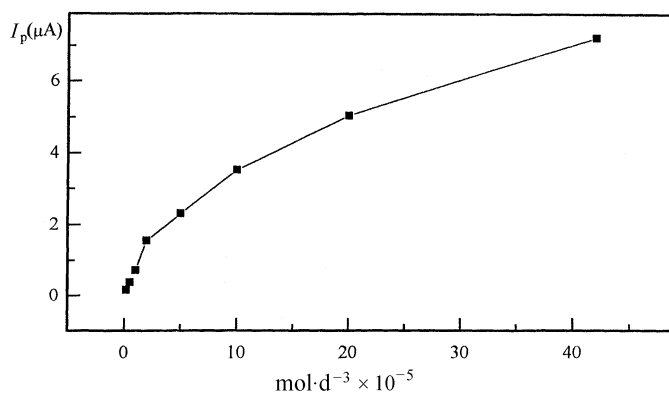
Using diagnostic criteria suggested previously [9, 10], the voltammograms are checked for symmetry around the peak potential. At low concentrations ( $2.04$  to  $5.10 \mu\text{mol} \cdot \text{dm}^{-3}$ ) the voltammograms show a quite symmetric appearance, whereas at higher concentrations ( $51.0 \mu\text{mol} \cdot \text{dm}^{-3}$ ) the symmetry is nearly lost. The highly symmetric appearance at lower concentrations is indicative of adsorption.

Another important criterion is the effect of scan rate ( $\nu$ ) and bulk concentration ( $C^*$ ) on the current function ( $i_p/C^* \nu^{1/2}$ ). Plotting the current functions vs.  $\log \nu$ , at low concentrations of **1** an increase in the scan rate causes an increase in the current function (cf. Fig. 2). This behaviour would be expected for a weak adsorption of the reactant [9]. At a certain scan rate ( $\nu = 200 \text{ mV/s}$ ), the current function deviates from the constant value which would be expected for the uncomplicated diffusion wave caused by adsorption at higher concentrations. The largest deviations are observed at lower concentrations ( $179$ ,  $167$ , and  $158 \mu\text{A}/\text{mmol} \cdot \text{dm}^{-3} \cdot (\text{V/s})^{1/2}$  at  $[1] = 2.04$ ,  $5.10$ , and  $10.20 \mu\text{mol} \cdot \text{dm}^{-3}$ ). This can be interpreted on the basis that the adsorbed molecules of **1** constitute a constant flow of matter and charge, whereas the amount of molecules diffusing to the electrode is time dependent. At sufficiently fast scan rates, the amount of diffusing molecules is small relative to that of the adsorbed ones; at low scan rates, the opposite is true. Thus, an increase in the current function is observed with increasing scan rate.

Adsorption of **1** at the HMDE is also confirmed by repetitive cyclic voltammograms (cf. Fig. 3). A well defined symmetric cathodic CV wave is observed in the first scan (1) due to the adsorption of the substrate. Later scans (2, 3) show a great decrease in the cathodic peak current, indicating rapid desorption of the reduction products of phenolphthalein from the electrode surface. The almost complete disappearance of the anodic wave is presumably due to complete desorption of the electroactive species upon reduction. Moreover, the reduction peak current increases linearly with the time for which the HMDE was left in contact with the solution of **1** prior to running the CV, and it levels off at an adsorption time of 120 seconds at low concentrations ( $2.04$  to  $10.2 \mu\text{mol} \cdot \text{dm}^{-3}$ ) and at 60 seconds at higher ones ( $20.4 \mu\text{mol} \cdot \text{dm}^{-3}$ ). This process is attributed to the full coverage of the electrode surface with **1**; the rate of coverage increases with increasing bulk concentration.



**Fig. 3.** Repetitive cyclic voltammograms of  $5.10 \mu\text{mol} \cdot \text{dm}^{-3}$  **1** at a scan rate of  $200 \text{ mV/s}$  and a  $pH$  value of  $3.4$



**Fig. 4.** Relationship between peak current and concentration of **1** at  $\nu = 200 \text{ mV/s}$  and  $pH = 3.4$

Upon increasing the concentration of **1**, the peak current increases linearly in the low concentrations range ( $\leq 20.4 \mu\text{mol} \cdot \text{dm}^{-3}$ ). Further increase in concentration causes a marked non-linear influence on the peak current (Fig. 4). This is ascribed to a nearly total coverage of the mercury electrode surface as the concentration is increased. The total current due to the reduction of the adsorbed molecules becomes constant, whereas the total current caused by the diffusing molecules continues to increase with increasing concentration. This results in a decrease of the fraction of the peak current due to adsorption with increasing concentration. Examination of a plot of the current function *vs.*  $\log C^*$  (Fig. 5) reveals that the current function is low value at high concentrations. As the concentration is decreased, the current function increases and finally reaches a limiting value at low concentrations where its behavior becomes independent on

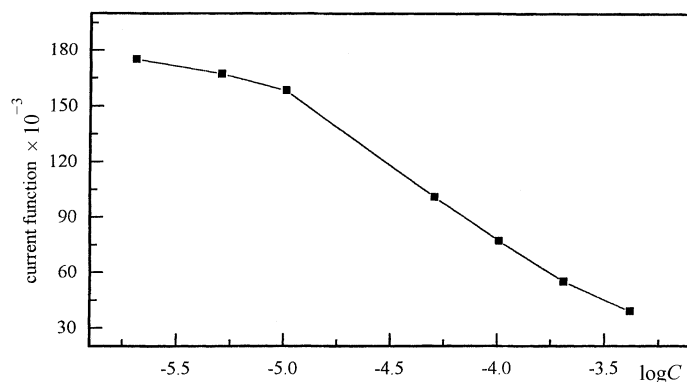


Fig. 5. Relationship between current function and concentration of **1** at  $\nu = 200$  mV/s and  $pH = 3.4$

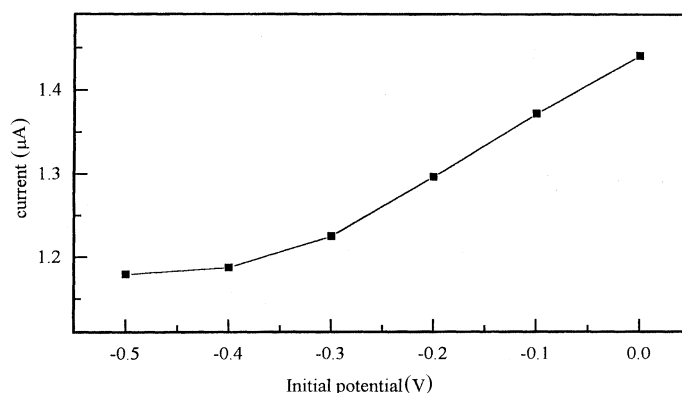


Fig. 6. Relationship between peak current and adsorption potential at  $\nu = 200$  mV/s,  $[1] = 25.5 \mu\text{mol} \cdot \text{dm}^{-3}$ , and  $pH = 3.4$

concentration. The increase in the current function is attributed to a decrease of the current due to diffusing species upon decreasing concentration, whereas the limiting value is due to the constant amount of adsorbate. This behavior supports the above conclusion that the electrochemical response is due to a weak adsorption of **1**.

The potential applied to the HMDE during the adsorption period can either aid or hinder adsorption as a result of coulombic interaction between the charge at the electrode and at the electrolyzed species; thus, one can detect the different forms of phenolphthalein at different conditions. It is found that the peak current depends on the initially applied potential, *i.e.* the adsorption potential. The relation between  $i_p$  and  $E_{\text{ads}}$  at a given scan rate and concentration is shown in Fig. 6. Obviously, the peak current decreases with increasing the adsorption potential to more negative values. This indicates that the adsorbed species are negatively charged. Consequently, at  $pH = 3.4$  the predominant species is the monoanionic colourless form **1'**.

Addition of  $\text{HClO}_4$  to the solutions of **1** results in cyclic voltammograms with a single irreversible CV wave with all characteristics as observed at lower  $pH$  values.

**Table 2.** Cyclic voltammetric data for  $102.0 \mu\text{mol} \cdot \text{dm}^{-3}$  **1** in aqueous ethanolic (10% v/v) buffer solutions at  $\nu = 200 \text{ mV/s}$  at different concentrations of  $\text{HClO}_4$ 

$[\text{HClO}_4]$ (M)	$-E_p$ (mV)	$i_p$ (nA)
0.1	526	494
0.2	505	454
0.3	502	428
0.4	492	457
0.6	482	501

Generally, increasing concentration of  $\text{HClO}_4$  shifts the peak potential to less negative values, whereas the peak current remains more or less constant (Table 2). This is inconsistent with the above conclusion that protons participate in the electrochemical reduction of **1**. On the other hand, there is no effect of the initially applied adsorption potential ( $E_{\text{ads}}$ ) on the peak potential ( $E_p$ ) and the peak current ( $i_p$ ) as well. Therefore, one can deduce that the adsorbed species is neutral. Accordingly, at such conditions the colourless neutral  $\gamma$ -lactone is adsorbed and reduced on the HMDE electrode. It is interesting to mention that *Kolthoff* has proposed that the  $\gamma$ -lactone form is not reducible on the mercury electrode [5].

For an ideal reversible adsorption peak, the peak width at half-height ( $W_{1/2}$ ) is  $90.6/n \text{ mV}$  at 298 K [16, 17]. The observed half width for **1** is  $65.7 \pm 1.6 \text{ mV}$ . This value suggests the transfer of two electrons for the irreversible redox couple of the adsorbate [5–8]. The difference to the expected theoretical value (45.3 mV) is due to an irreversible adsorption of the depolarizer.

A  $0.41 \text{ mmol} \cdot \text{dm}^{-3}$  of **1**, the symmetric cyclic voltammetric wave observed at lower concentrations ( $2.04 \mu\text{mol} \cdot \text{dm}^{-3}$ ) disappears. Therefore, the peak current presumably originates mainly from the diffusion of **1** to the electrode. Upon increasing the scan rate, the peak potential shifts to more negative values, and the peak current increases. It is found that the peak current exhibits a linear dependence on the square root of the scan rate (correlation coefficient: 0.999). Moreover, the doubly logarithmic relationship gives a straight line with a slope of 0.45 and a correlation coefficient of 0.999. The peak potential varies linearly with  $\log \nu$  with a slope of 98 mV per  $\log \nu$  unit and a correlation coefficient of 0.999. These results indicate that the CV wave corresponds to an irreversible diffusion controlled process.

Increasing the  $pH$  value of the solution ( $pH < 9$ ) leads to a single sharp irreversible CV wave corresponding to a two-electron transfer process. The adsorption CV wave at low concentrations is shifted to more negative potentials as the  $pH$  of the solution is increased. This reveals that protons participate in the electrochemical reduction process of the adsorbed species at the mercury electrode. The linear dependence of the peak potential on the  $pH$  value can be represented by Eq. (1).

$$E_p = -0.481 - 0.042pH; \quad r = 0.997 \quad (1)$$

From the slope of Eq. (1) it is evident that two protons are consumed. Moreover, the slope of the adsorption wave is steeper than expected for diffusion control. This reveals that the shift of the peak potential is not only due to the proton dependence of the redox reaction involving the adsorbed species, but also reflects a change in the adsorption strength of the reduced form relative to that of the oxidized form with varying pH. The steeper slope for the adsorbed redox couple indicates that the relative adsorption strength of the reduced form decreases with increasing pH value.

At  $pH > 9$ , two irreversible CV waves are observed, both corresponding to monoelectronic processes. The peak potential of the two waves shift cathodically with the pH. The shift is linear for both processes, and the  $E_p$  vs. pH slopes are 63 and 60 mV/pH unit, respectively. This indicates the consumption of one proton during the reduction process along each wave.

At  $pH = 10.58$ , the cyclic voltammogram of **1** shows two CV waves. As the scan rate increases, the peak current of both CV waves increases, and the doubly logarithmic relation results in straight lines with slopes of 0.47 and 0.45. This reveals that both CV waves have to be attributed to diffusion controlled processes, and no adsorption is detected.

Double potential step chronocoulometry has found considerable use in the investigation of the adsorption of electroactive species [17–21]. In a particular double potential step chronocoulometric experiment, the potential is held at an initial value  $E_i$  where no electrolysis occurs and is rapidly stepped to a value  $E_f$  at which the desired electrode reaction takes place at  $t = 0$ . At  $t = \tau$ , the potential is returned to  $E_i$ . The electrochemical responses are given by Eqs. (3) and (4) for the forward and reverse steps ( $Q$ : amount of charge that has passed at time  $t$  since the application of the potential step;  $C_o$  and  $D_o$ : concentration and diffusion coefficients of the reactants;  $A$ : surface electrode area;  $n$  and  $F$ : usual meanings;  $Q_{dl}$ : charge consumed by the electrode-electrolyte double layer capacitance).

$$Q(t < \tau) = \frac{2nFAD_0^{1/2} C_0}{\pi^{1/2}} t^{1/2} + Q_{dl} \quad (2)$$

$$Q(t > \tau) = \frac{2nFAD_0^{1/2} C_0}{\pi^{1/2}} (t^{1/2} - (t - \tau)^{1/2}) \quad (3)$$

When reactant adsorption occurs, and additional term has to be added to Eq. (2) ( $\Gamma$ : amount of adsorbed reactant).

$$Q(t < \tau) = \frac{2nFAD_0^{1/2} C_0}{\pi^{1/2}} t^{1/2} + Q_{dl} + nFA\Gamma \quad (4)$$

Thus, from Eqs. (3) and (4),  $Q_r(t) = Q(\tau) - Q(t > \tau)$  can be expressed by Eq. (5)

$$Q_r(t) = \frac{2nFAD_0^{1/2} C_0}{\pi^{1/2}} \theta + Q_{dl} \quad (5)$$

where  $\theta = (t^{1/2} + (t - \tau)^{1/2} - t^{1/2})$ .

In solutions of low pH values (3.4), the electrode potential was stepped from an initial value  $E_i = -0.4$  V, where **1** is electrochemically inactive, to a final value  $E_f = -0.7$  V where the electrode reaction proceeds. The potential was held at  $E_f$  for



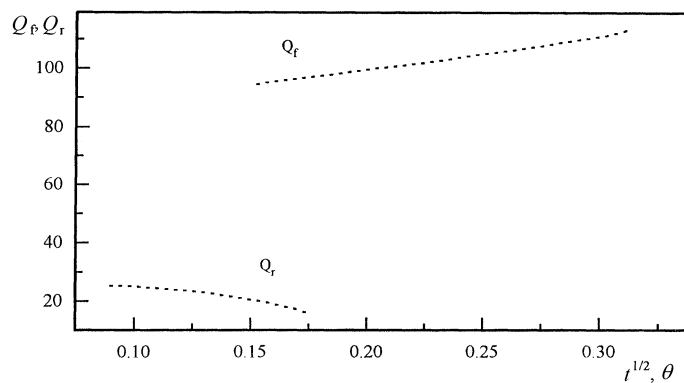


Fig. 7. Anson plots of  $Q_f$  vs.  $t^{1/2}$  and  $Q_r$  vs.  $\theta$  for  $5.10 \mu\text{mol} \cdot \text{dm}^{-3}$  **1** and  $pH = 3.4$

a time  $\tau$  after which it was stepped back to  $E_i$  and maintained there for the same time interval. The charge that passes through the electrode during each of the time intervals is measured. It can be seen that the change of the electrode potential from  $E_i$  to a more negative value  $E_f$  causes reduction of both adsorbed and diffusing phenolphthalein. Upon reversing the potential step, the anodic reaction proceeds, and the charge ratio  $Q(2\tau)_r/Q(\tau)_f$  deviates from the expected theoretical value of 0.586 [19–22]. This can be attributed to an irreversible consumption of the reduced product generated at the forward step. Plots of  $Q(t < \tau)$  of the forward potential step against  $t^{1/2}$  at different duration times give straight lines. According to Eq. (3), the diffusion coefficient of **1** calculated from the slope is  $8.62 \times 10^{-6} \text{ cm}^2/\text{sec}$ . On the other hand, the intercept is larger than that obtained for the quantity of electricity needed to charge the electrode-electrolyte double layer of the supporting electrolyte ( $Q_{dl} = 2.8 \text{ nC}$ ). This indicates the presence of adsorption in addition to the diffusion process.

Plots of  $Q_r$  vs.  $\theta$  according to Eq. (6) afford straight lines for the entire time range. For the different concentrations, the intercepts are always less than that obtained for the  $Q(t < \tau)$  vs.  $t^{1/2}$  plots (Fig. 7). This confirms that only phenolphthalein molecules are adsorbed [18]. Furthermore, the amount of the adsorbate is determined from the difference in the intercepts for the forward and reverse Anson plots (Eqs. (4) and (5)). The charge obtained for a concentration of  $5.10 \mu\text{mol} \cdot \text{dm}^{-3}$  **1** is found to be  $4.75 \text{ nC}/\text{cm}^2$  which is equivalent to a surface excess  $\Gamma_0$  of  $7.2 \times 10^{-10} \text{ mol}/\text{cm}^2$ . On increasing concentration of **1** to  $51.0 \mu\text{mol} \cdot \text{dm}^{-3}$ , the computed surface excess  $\Gamma$  increases to  $39.9 \times 10^{-10} \text{ mol}/\text{cm}^2$ .

Upon further increase of the concentration of **1**, the diffusion fraction of the mixed diffusion-adsorption charge predominates, and the value of  $\Gamma$  cannot be determined accurately. The surface area of the electrode occupied by one molecule,  $\sigma$ , can be estimated from  $\sigma = 1/N_L \Gamma$ , where  $N_L$  is Loschmidt's number and  $\Gamma$  is the surface excess in  $\text{mol}/\text{\AA}^2$ . Examination of Fig. 5 shows that the limiting coverage value is attained at a bulk concentration of  $5.1 \mu\text{mol} \cdot \text{dm}^{-3}$  phenolphthalein. Thus, the surface area occupied by the adsorbed substrate molecules can be calculated from the value of excess surface at  $5.1 \mu\text{mol} \cdot \text{dm}^{-3}$  to be  $23.0 \text{\AA}^2$ . Considering models of **1** [6] it is evident that in acidic solution ( $pH = 3.4$ ) the molecules

of **1** are placed in interlocking Ys, in which each arm of the Y represents an aromatic ring perpendicular to the electrode surface. The value of  $\sigma$  is smaller than the value of  $42.0 \text{ \AA}^2$  reported in Ref [6]. Therefore, under such conditions, **1** develops a more compact adsorbed layer.

## Experimental

### *Reagents and solutions*

Phenolphthalein (**1**) of analytical grade purity was used. Stock solutions (5.0 mM) in triply distilled water containing 10% (v/v) ethanol were prepared, kept in an inert nitrogen atmosphere, and diluted as required. *Britton-Robinson* universal buffer solutions [11] were prepared from analytical grade reagents.

### *Instrumentation*

The cell and the instruments used for cyclic voltammetry (CV) and double potential step chronocoulometry have been described elsewhere [12]. For all experiments, an Ag/Ag<sup>+</sup> electrode was used as the reference electrode. A hanging mercury drop electrode (HMDE) was used throughout. The electrode area was  $3.41 \times 10^{-5} \text{ cm}^2$ . All measurements were obtained at 298 K. Solutions were deaerated by purging with pure nitrogen before measurements, and a blanket of nitrogen was maintained above the working solution.

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