Electrochemical Behaviour of Thymolphthalein

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The polarographic and voltammetric behaviour of thymolphthalein in ethanol-water (1/5 *v/v*) was studied using various electrochemical techniques. The reduction of thymolphthalein on a mercury drop electrode was investigated. The adsorption effect on the electrode surface was observed. The rate constants for the electron transfer steps were determined by and without taking adsorption into occount using the Laviron technique and Nicholson technique respectively. The diffusion coefficients were calculated from the cyclic voltammetric data using the method developed by Garrido. Reversibility for the electrode reaction was investigated and a mechanism for the electrode reaction was proposed.

Key Words: Polarography, voltammetry, thymolphthalein, adsorption, rate constants.

Introduction

There are numerous studies related to the spectroscopic investigation of phenolphthalein and its derivatives[1−3]. Chapin et al.[4], Zanolli et al.,[5] Ellaithy et al.,[6] and Nicholson[7] also investigated the use of phenolphthalein as a laxative and its complications. Wang and Lu determined trace amounts of thallium by complexing them with *o*-cresolphythalein by the use of adsorptive stripping voltammetry[8]. Although studies concerning thymolphthalein are limited there are many electrochemical studies related to phthalein, sulphonephthaleins and *o*-cresolphthalein[9−12].

The electrochemical behaviour of *o*-cresolphthalein was examined by different polarographic and voltammetric techniques and a reaction mechanism was proposed to explain the electrode process[12].

Phenolphthalein and related compounds are known to exist in solution in different hydration and ionic forms in equilibrium. In a previous work, it was found that the lactone form of phthalein was not reducible upon the dropping mercury electrode and the hydrated form was reduced along a single, two-electron reduction wave[13].

The polarographic behaviour of some phthaleins has been investigated at varying pH, solvent and temperature conditions by Ghoneim and Ashy[14]. They examined the reversibility and the mechanism of the

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electrochemical reduction of phthaleins upon a dropping mercury electrode by applying a discontinuously alternating potential.

In this study, the polarographic and voltammetric behaviour of thymolphthalein, a widely used indicator, was investigated in an ethanol-water mixture in Britton-Robinson buffer media at pH 2-12, since the solubility of thymolphthalein in pure water is quite low, by the use of different electroanalytical techniques. The diffusion coefficient and heterogeneous standard rate constant for this compound were determined and reversibility tests were carried out in acidic, basic and neutral media.

Experimental

Apparatus

The polarographic and voltammetric measurements were carried out with a BAS 100B Electrochemical Analyser equipped with a BAS 100B Cell Stand, and a PAR 303A static mercury drop electrode (SMDE). All solutions were deaerated for 10 min with pure nitrogen, deoxygenated with vanadium chloride, concentrated HCl and amalgamated zinc, and blanketed thereafter. The pH values of the solutions were recorded by an ORION 720A pH-meter. The buffer solutions used were Britton-Robinson type with pH values of 2-12. The polarographic and voltammetric experiments were carried out with an SMDE and three-electrode cell equipped with Pt wire auxiliary and Ag/AgCl reference electrodes. Cyclic voltammetric experiments were carried out using a hanging mercury drop electrode (HMDE) having a surface area of 0.0145 cm^2. The pH-meter was calibrated (at pH 4, pH 7 and pH 9) with standard buffer solutions. All the measurements were taken at laboratory temperature (25 ± 1 °C) and no maximum suppressor was used.

Reagents

Thymolphthalein (Merck), acetic acid (BDH, Analar), phosphoric acid (Merck), boric acid (Riedel), ammonium metavanadate (Merck), and sodium hydroxide (Merck) were used without further purification. The water used in the preparation of the solutions was distilled and deionized by an ELGASTAT water purification system.

Results and Discussion

Voltammetric results

Polarographic and voltammetric studies of thymolphthalein were carried out in ethanol-water (1/5 *v/v*) in Britton-Robinson buffers at pH 2-12. The DPP polarograms and CV voltammograms of thymolphthalein are given in Figures 1 and 2, respectively.
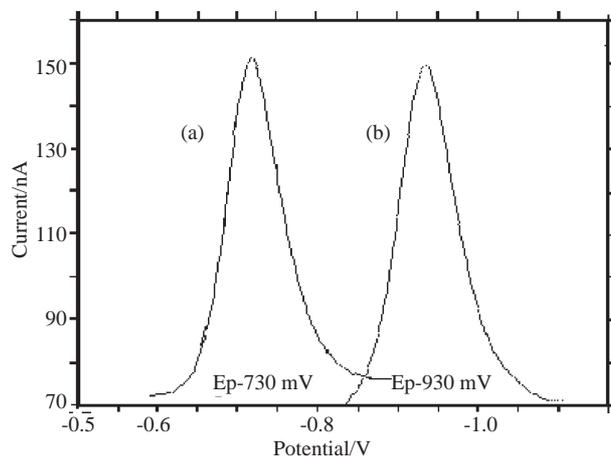
Figure 1. DPP polarograms of 1.67×10^{-5}M thymolphthalein a) pH 5.06, b) pH 9.51 *[The medium: 1:5 v/v (EtOH:BR), Scan rate = 10 mV/s, Drop time = 1 s, Pulse height = 50 mV with SMDE and Ag/AgCl reference electrode].*
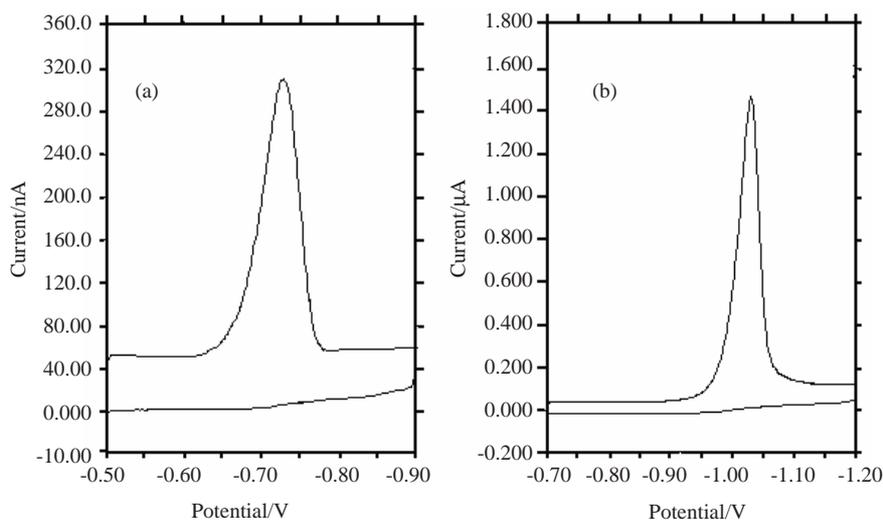

Figure 2. CV voltammograms of 1.67×10^{-5}M thymolphthalein in (a) acidic (pH 4.07) (b) basic (pH 10.40) media *[The medium: 1:5 v/v (EtOH:BR), Scan rate = 100 mV/s, at HMDE and Ag/AgCl reference electrode].*

The reduction peak of thymolphthalein was observed at –728 mV in acidic medium (pH 4) and at –1028 mV in alkali medium (pH 10) (Figure 2).

It can be see from Figure 3 that there is a deviation from linearity for pH > 11. The fact that half-wave peak potentials shift towards negative values with an increase in pH indicates that the electrode reaction involves proton transfer[15].
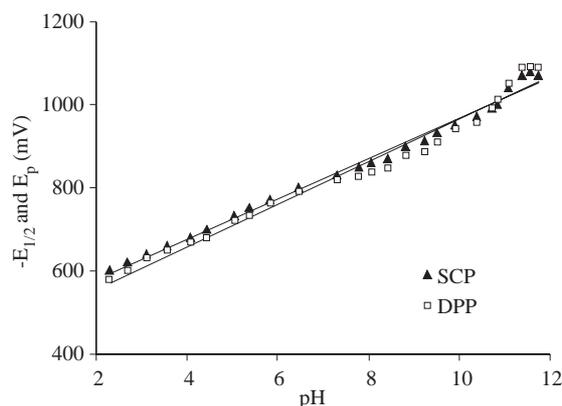
Figure 3. Changes in half-wave potential ($E_{1/2}$) and peak potential (E_p) of 1.67×10^{-5}M thymolphthalein with pH *[The medium: 1:5 v/v (EtOH:BR), Scan rate = 10 mV/s, Drop time = 1 s, Pulse height 50 mV with SMDE and Ag/AgCl reference electrode]*.

The change in half-wave peak potential with pH for the irreversible reduction of an organic compound on SMDE is given by

$$\frac{\Delta E_{1/2}}{\Delta pH} = \frac{59.15}{\alpha n_a} p \tag{1}$$

where n and α are the number of electrons transferred and the electron transfer coefficient, respectively, and p is the number of protons involved in the electrode reaction[15,16]. The slope of the half-wave potential-pH graph is ($59.15p / \alpha n_a$), and the αn_a value belonging to the reduction of C-O was calculated to be 0.64 (pH 4) and 1.31 (pH 10) [12,14]. The number of protons transferred in the rate-determining step of the C-O group was 0.49 for pH 4 and 0.99 for pH 10. These results showed that there is only one proton transferred in the rate-determined step. The equation relating $E_{1/2}$ to pH for C-O reduction wave at various pH ranges by the SCP technique are as follows (Figure 3):

(pH 2-9)

$$E_{1/2} = -44.53(\pm1.03)pH - 487.63(\pm6.14)(R = 0.99) \tag{2}$$

and in the pH range of 9-12 they were

$$E_{1/2} = -78.78(\pm7.24)pH - 156.81(\pm74.35)(R = 0.98) \tag{3}$$

The half-wave potentials shift towards negative values with increasing pH, but the peak currents remain almost constant at pH < 9.5 (Figure 4). This shows that both protonated and neutral forms of the compound are electroactive[16]. The half-wave potentials are observed to change with the drop time of the SMDE. This indicates that the process is not reversible. For a reversible electrode process, the graph of potential against log (i_d-i)/i is supposed to be linear with a slope of 59/n mV. Our findings show that the slope of this linear graph is more than 59/n mV, which is indicative of irreversibility. This may arise from slow electron transfer, adsorption or chemical complications.
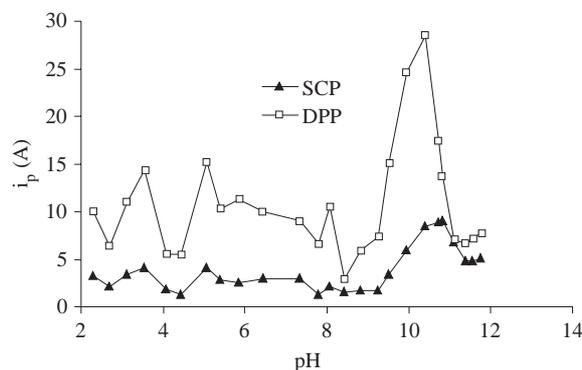
Figure 4. The change peak currents SCP and DPP of 1.67×10^{-5}M thymolphthalein with pH *[The medium: 1:5 v/v (EtOH:BR), Scan rate = 10 mV/s, Drop time = 1 s, Pulse height = 50 mV with SMDE and Ag/AgCl reference electrode].*

Peak potential of thymolphthalein with increasing pH varied between –580 and –900 mV. At higher pH values (pH 10.8) we observed an anodic peak and a cathodic peak with varying scan rates (Figure 5). This shows that the electron transfer is very slow at this pH and the compound displays quasi-reversible behaviour. All these findings confirm the reaction mechanism of the phthalein suggested in previous studies[6,14,17].
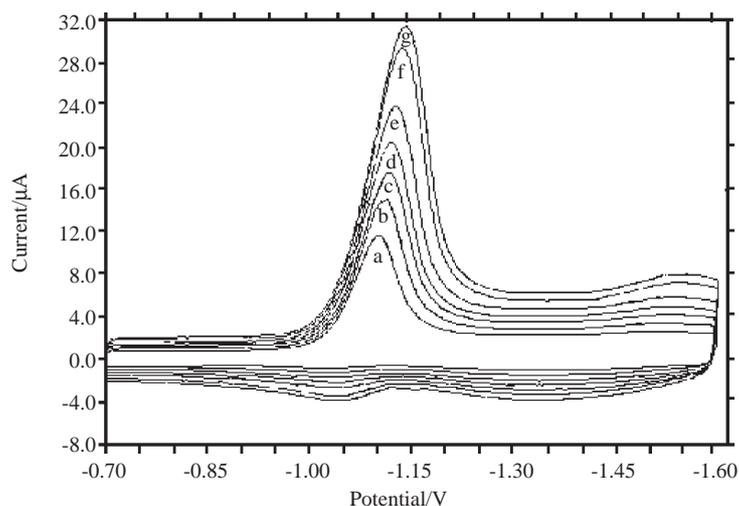

Figure 5. Changes in peak currents of 1.67×10^{-5} M thymolphthalein with scan rate in CV at pH 10.84 *v=* **a)** 3 V/s, **b)** 4 V/s, **c)** 5 V/s, **d)** 6 V/s, **e)** 7 V/s, **f)** 8 V/s, **g)** 9 V/s *[The medium: 1:5 v/v (EtOH:BR), Drop time = 1 s with HMDE and Ag/AgCl reference electrode].*

Peak potential for the 1.67×10^{-5} M solution of the compound in CV shifts to negative values as the scan rate increases (Figure 5). The difference between the anodic and cathodic peaks is higher than 59/n mV at all scan rates employed. Furthermore, the ratio of i_p^a / i_p^c changed with the scan rate (pH 10.84, $v=$ 3-50 Vs^{-1}). This experimental observation showed that the reduction of the C-O group of thymolphthalein is not reversible[6,14,17]. No anodic peak was observed for the studied substances at pH 2.3-11.1 and scan rate of 10-3000 mVs^{-1} in Britton-Robinson buffer-ethanol (1:5 *v/v*) medium (C = 1×10^{-5} mol. L^{-1}), and this showed that the process is completely irreversible[18]. The fact that the value of the expression i_p^c

/ $v^{1/2}$ (where i_p^c is the height of the cathodic peak and v is the scan rate) is not constant reveals that a complicated electrode process is involved rather than a simple charge transfer process. The i_p^c value may also have been increased as a result of the selective accumulation of thymolphthalein on the surface of the working electrode. These results show that the electron transfer step is slow or that there is a chemical reaction or adsorption incorporated with the electron transfer step. Hence, the effect of pressure at the mercury head on the limiting current showed that the reduction process of the thymolphthalein is mainly diffusion controlled with a small adsorption contribution[6,14,17].

Adsorption effects on the electrode reaction

The peak currents of thymolphthalein are seen to increase up to the concentration, and become constant at higher concentrations. The current increases with the concentration at lower concentration values. It becomes almost constant at higher concentrations, which may be attributed to the complete coverage of the surface by the adsorption critical analyte concentration phenomena.

As thymolphthalein is a macromolecule, the adsorption effect should be taken into account when investigating the reaction. The most useful electroanalytical technique to investigate the adsorption phenomena is cyclic voltammetry, and there are a few ways of determining the adsorption using this technique[19,20].

Figure 6 shows $\log i_p^c - \log v$ graphs of thymolphthalein in acidic, neutral and basic media. In these figures, the slopes are higher than 0.5. The slopes in acidic, neutral and basic media are calculated as 0.68, 0.80 and 0.90 respectively. It is supposed to be 0.5 in a diffusion-controlled reaction. The fact that the slope is higher than 0.5 is indicative of adsorption phenomena[19,21]. In addition, the change of current function (i_p^c / $Cv^{1/2}$) with the scan rate was found to be linear at high scan rates which are also indications of the presence of adsorption[19]. These results show that thymolphthalein is more strongly adsorbed in basic media than in acidic or neutral media and the adsorption affects the electrode reaction. If the adsorption was weak then the difference between the reduction energy of adsorbed "O" and dissolved "O" in solution would not be very significant. Furthermore, if that were the case, there would be no post peak and the cathodic peak would appear higher than that observed in the absence of adsorption[17,19,21].

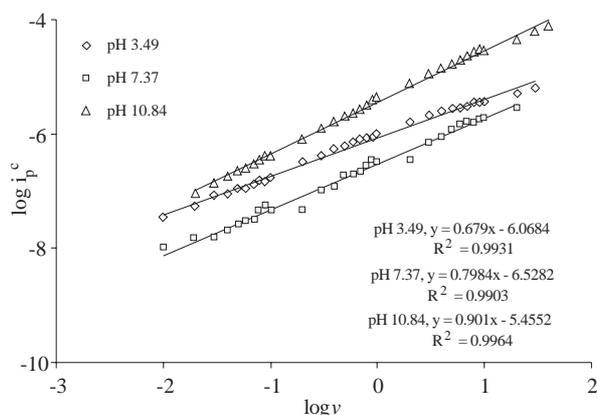**Figure 6.** $\log i_p^c$ - $\log v$ graphs of 1.67×10^{-7} M thymolphthalein in acidic, neutral and basic medium.

It is necessary to employ lower scan rates and higher concentrations to minimize the adsorption upon the electrode surface[19,22].

Determination of diffusion coefficient using cyclic voltammetry

Diffusion coefficients of the compound were determined by the use of the following equation derived by Garrido et al. for cyclic voltammograms complicated by adsorption[23].

$$i_p = 1.06 \times 10^6 n^2 ACvD^{1/2}t_p^{1/2} \tag{4}$$

where a Langmuir type of adsorption was assumed with a non-compact monolayer film of adsorbed molecules upon mercury surface. Here, t_p is the adsorption time from the beginning of the life of the drop until E_p is reached. Other symbols have their usual meanings. Equation (4) enables us to calculate the diffusion coefficient of thymolphthalein at different pH values using cyclic voltammetry at different scan rates.

The diffusion coefficients of this compound at different pH values are given in Table 1. This table shows that diffusion coefficient is approximately equal in acidic and neutral media. This shows that the species which showed the highest adsorption and diffusion was the electroactive form in alkaline media. Diffusion coefficients at pH 3.49, 7.37 and 10.84 were calculated to be 0.1993×10^{-6}, 0.0134×10^{-6}, and 1.1076×10^{-6} cm^{2}s^{-1} respectively.

Table 1. The diffusion coefficient of 1.67×10^{-7} M thymolphthalein using CV techniques and the Garrido method with different pH values, $t_p = 15$ s, *[The medium 1:5 v/v (EtOH:BR), with HMDE and Ag/AgCl reference electrode]*.

v (mV/s)	pH 3.49		pH 7.37		pH 10.84	
	i_p^c (Å)	D_o cm^2/s	i_p^c (Å)	D_o cm^2/s	i_p^c (Å)	D_o cm^2/s
40	8.81×10^{-8}	0.3068×10^{-6}	2.02×10^{-8}	0.0161×10^{-6}	1.77×10^{-7}	1.2380×10^{-6}
50	1.07×10^{-7}	0.2896×10^{-6}	2.61×10^{-8}	0.0172×10^{-6}	2.25×10^{-7}	1.2810×10^{-6}
60	1.10×10^{-7}	0.2126×10^{-6}	2.94×10^{-8}	0.0152×10^{-6}	2.44×10^{-7}	1.0460×10^{-6}
70	1.31×10^{-7}	0.2215×10^{-6}	3.15×10^{-8}	0.0128×10^{-6}	2.93×10^{-7}	1.1080×10^{-6}
80	1.48×10^{-7}	0.2164×10^{-6}	4.39×10^{-8}	0.0190×10^{-6}	3.38×10^{-7}	1.1290×10^{-6}
90	1.44×10^{-7}	0.1619×10^{-6}	5.28×10^{-8}	0.0218×10^{-6}	4.01×10^{-7}	1.2550×10^{-6}
100	1.73×10^{-7}	0.1893×10^{-6}	4.82×10^{-8}	0.0147×10^{-6}	3.98×10^{-7}	1.0020×10^{-6}
200	3.20×10^{-7}	0.1619×10^{-6}	4.79×10^{-8}	0.0036×10^{-6}	7.82×10^{-7}	0.9669×10^{-6}
300	4.15×10^{-7}	0.1210×10^{-6}	1.04×10^{-7}	0.0076×10^{-6}	1.23×10^{-6}	1.0630×10^{-6}
400	5.32×10^{-7}	0.1119×10^{-6}	1.22×10^{-7}	0.0059×10^{-6}	1.58×10^{-6}	0.9867×10^{-6}

pH 3.49, average diffusion coefficient $= 0.1993 \times 10^{-6}$ cm^2/s, standard deviation $= 0.0644 \times 10^{-6}$

pH 7.37, average diffusion coefficient $= 0.0134 \times 10^{-6}$ cm^2/s, standard deviation $= 0.0059 \times 10^{-6}$

pH 10.84, average diffusion coefficient $= 1.1076 \times 10^{-6}$ cm^2/s, standard deviation $= 0.1158 \times 10^{-6}$

Investigation of standard rate constant using CV

Nicholson method

The standard rate constants of the electron transfer reaction of thymolphthalein in basic medium were calculated by the Nicholson method [24].

According to this technique the ψ values were determined from the working graph given by Nicholson

and k_s values were calculated using the following equation:

$$\Psi = \frac{\left(\frac{D_O}{D_R}\right)^{\frac{nFv}{2RT}} k_s}{\sqrt{\pi \frac{nFv}{RT} D_O}} \tag{5}$$

D_O/D_R was taken to be unity. The change in $\Delta E_p \times n$ versus k_s value was found to reach a limiting value at high scan rates (Figure 7). The k_s values reach a limiting value with increased scan rate. The k_s values become almost independent of the scan rate at high scan rates. The average standard rate constant k_s of thymolphthalein was found to be 9.2767×10^{-4} cm/s in basic media (pH 10.84).
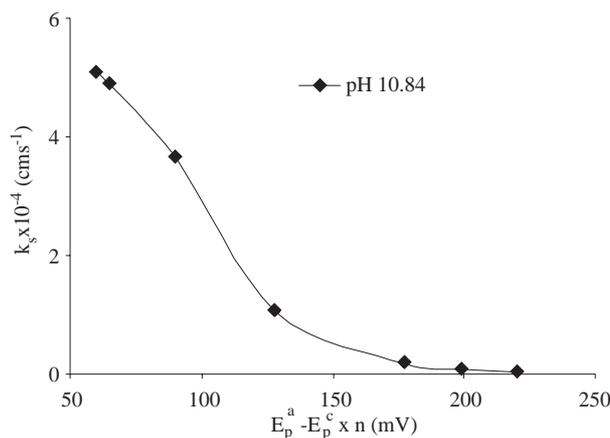

Figure 7. The plot of k_s values of 1.67×10^{-5} M thymolphthalein obtained by Nicholson method against $\Delta E_p \times$ n in basic medium.

Laviron method

Since adsorption phenomena were found to have an effect, the rate constants were determined by the use of the method developed by Laviron, which takes the effect of adsorption into account[25]. The k_s values were calculated using

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log\left(\frac{RT}{nFv}\right) - \alpha(1-\alpha)\frac{nF\Delta E_p}{2.3RT} \tag{6}$$

The α values were determined from the slope of $E_{p,c}$ versus $\log v$ plot for the cases $\Delta E_p > 200/n$ mV (Table 2). The number of electrons (n) transferred was taken to be one for the basic and two for the acidic media. Accordingly, the rate-determining step of the electrode process would involve one proton and two electrons at pH < 8.5 and water addition and one electron at pH $\geq$ 10.5. For intermediate pH values (8.5-10.5) both sequences of events may be contributing in varying proportions[13]. The k_s values determined by these two different methods are shown in Figures 7 and 8. In basic media, the average standard rate constant k_s of thymolphthalein was 9.2767×10^{-4} cm/s, and 6.594×10^{-1} s^{-1} according to the Nicholson and Laviron method respectively. The standard rate constants determined by the Nicholson method were found to be different than those determined by the Laviron method, which indicates the involvement of adsorption.
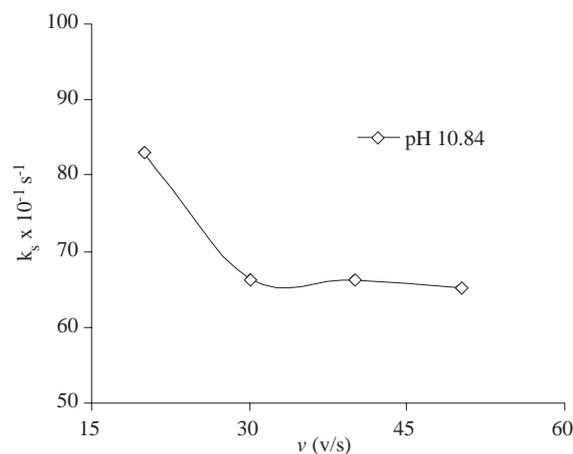
Figure 8. The plot of k_s values of 1.67×10^{-5} M thymolphthalein obtained by Laviron method against scan rate (v).

Table 2. Standard rate constants (k_s) of 1.67×10^{-5} M thymolphthalein by the use of the Laviron method in basic (pH 10.84) medium *[The medium 1:5 v/v (EtOH:BR), with HMDE and Ag/AgCl reference electrode].*

| v (V/s)	$E_{p,c}$ (V)	ΔE_p (V)	$\log k_s$	k_s s^{-1}
20	-1.139	0.128	1.919	8.301
30	-1.139	0.177	1.822	6.644
40	-1.139	0.198	1.830	6.768
50	-1.139	0.220	1.805	6.381

Average standard rate constant (k_s) 6.598 s^{-1}, standard deviation (k_s) 0.197 s^{-1}.

The mechanism of the electrode reaction

When investigating the mechanism of the electrode reaction by CV, the effect of the extent of adsorption was minimized by the use of high concentrations and low scan rates[19,22]. The reduction of the thymolphthalein was found to be irreversible due to the fact that ΔE_p being larger than 59/n (mV) increased with the scan rate, and the shift of cathodic peak potential $E_{p,c}$ towards negative values with the increasing scan rate.

The electrode reaction mechanism of thymolphthalein in acidic and basic media is given as follows according to the scheme proposed by Nicholson[7], Menek[12], and Ghoneim[14].

In an acidic medium, the electrode reaction mechanism can be represented by
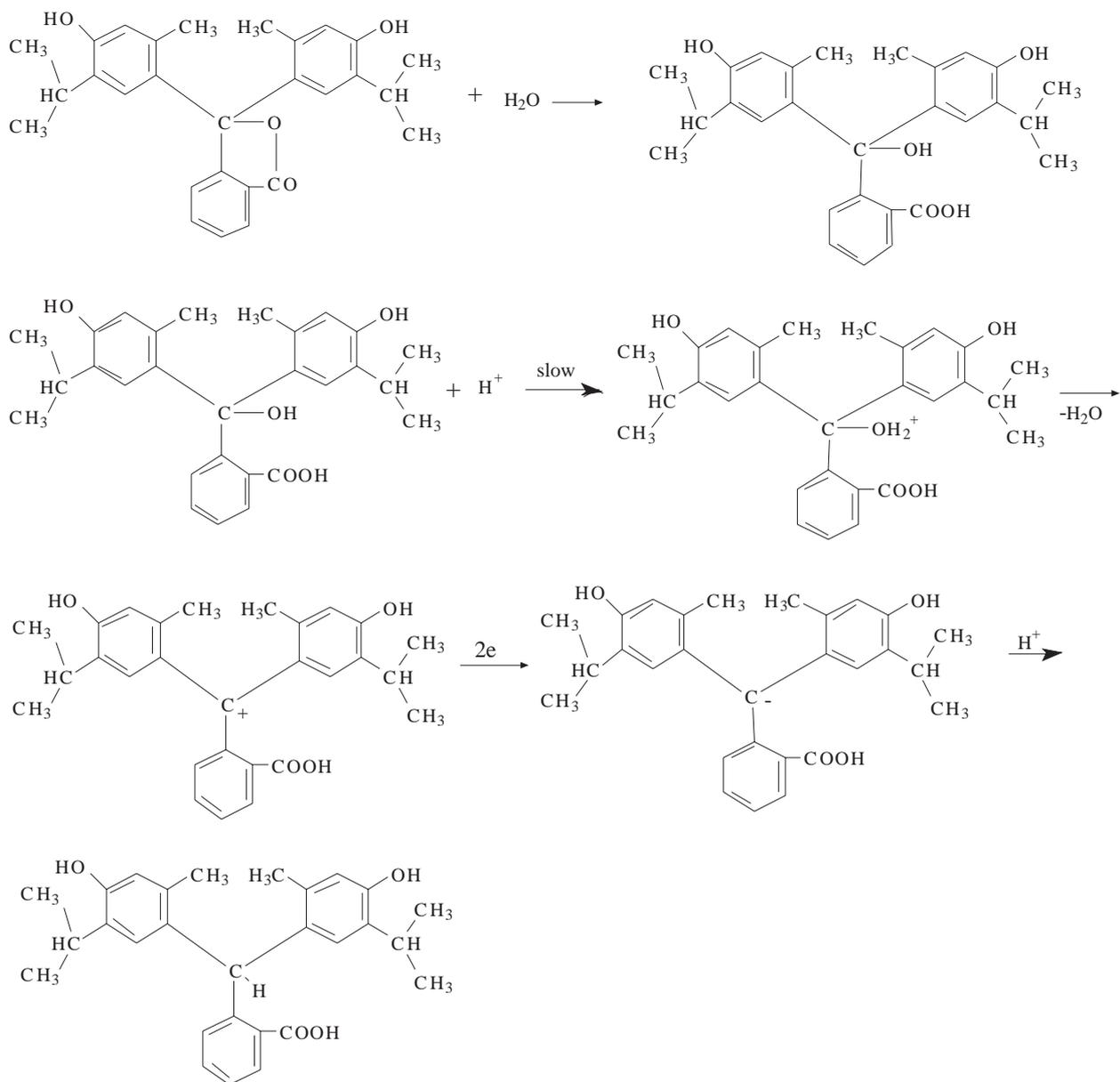
at pH > 10.5, it has been suggested that the electrode reaction involves water as shown below
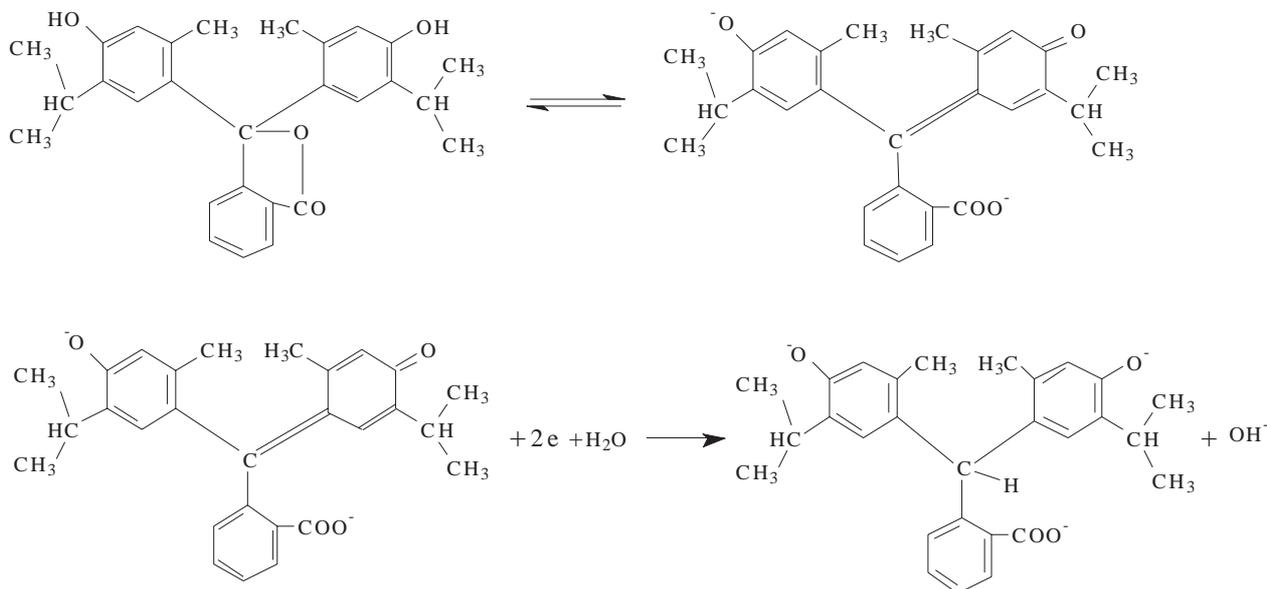
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