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Electroreduction of Phenol Red, Chlorophenol Red and Bromophenol Red in Buffer Solutions at DME

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The polarographic reduction of phenol red, chlorophenol red and bromophenol red has been investigated in buffered aqueous solutions and alcohol-water mixtures over a wide *pH* range (2-12). The results show that the three depolarizers are reduced through two irreversible one-electron waves of equal heights at all *pH* values. The two waves represent the reduction of the triphenylmethane carbon centre. The nature of the waves and the kinetics of the electrode reaction are discussed.

(Keywords: Electrode reaction; Kinetic parameters; Phenol red, bromo-, chloro-; Polarography; Reduction)

Elektroreduktion von Phenolrot, Chlorphenolrot und Bromphenolrot an der Quecksilbertropfelektrode

Die polarographischen Reduktionen wurden in gepufferten wäßrigen Lösungen und in Alkohol—Wasser-Mischungen über einen weiten *pH*-Bereich (2—12) durchgeführt. Es zeigte sich, daß in allen drei Fällen die Reduktion über zwei irreversible Ein-Elektron-Wellen gleicher Höhen bei allen *pH*-Werten vor sich ging. Die Kinetik der Elektrodenreaktion wird diskutiert.

Introduction

Sulphonphthaleins and phenolphthaleins were considered by several authors[1,2] to exhibit different hydration and ionic forms in equilibrium in media of varying *pH*. *Kolthoff*[3] concluded that the triphenyl carbinol forms of phenolphthalein are not reducible at the dropping mercury electrode. The hydrated forms gave a single two-electron wave. The reduction of the red form, however, occurred in two one-electron waves.

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However, no thorough mention of polarographic work on phenol red or its derivatives is available. In the present work, the polarographic reduction of phenol red, chlorophenol red and bromophenol red are studied in aqueous buffer solutions, also in the presence of 4–34% by weight of methanol, ethanol or *n*-propanol. It is also attempted to establish the nature of the electrode reaction.

Experimental

(a) $10^{-2}\,M$ solutions of phenol red, chlorophenol red and bromophenol red were prepared by dissolving the solid (BDH-grade) in the appropriate volume of $0.02\,M$-NaOH solution or alcohol.

(b) As supporting electrolyte, the *Britton-Robinson* buffer series[4,5] was used. The buffer solutions containing purified alcohol (4–34% by weight) were prepared as previously described[5].

(c) The polarograms were recorded on a Radiometer Polariter PO 4 f d.c. polarograph using a SCE as anode and the dropping mercury electrode as cathode ($m = 1.631\,\mathrm{mg\,s^{-1}}$ and $t = 4.4$ s/drop at 52 cm Hg). The electrolysis cell and the working procedure were the same as given before[5]. Solutions in the electrolysis cell were de-oxygenated by means of a stream of pre-purified nitrogen. All the measurements were carried out at 25 ± 1 °C.

Results and Discussion

In pure aqueous solutions of $pH > 3$ and/or in the presence of 4–34% by weight of alcohol, the polarograms of the three depolarizers consisted each of two waves of more or less equal heights (Fig. 1). The second wave did not appear at pH values < 3 which may be due to the early evolution of hydrogen. The $E_{1/2}$ of the first wave for the three depolarizers shifted to more negative values on increasing the pH of the solution up to $pH \simeq 10$, whereas that of the second was more or less pH-independent. Unlike the first wave, the $E_{1/2}$ of the second one became pH-dependent at pH values > 10. The total limiting current, i_l, for the three compounds can be considered as pH-independent. The i_l decreases with increasing alcohol content in the medium. This can be explained by the increased viscosity of the medium and/or the molecular volume of the reducible species[5]. Triton x-100 (3×10^{-4}–3×10^{-5}%) was present in the electrolysis solutions of pH 9.5 for elimination of the polarographic maximum that appeared on the first wave.

The number of electrons involved in the total electrode process was computed from controlled potential coulometric measurements following the procedure outline by *Lingane*[6] and was found to be $\simeq 2$; the total reduction current corresponds therefore to the uptake of two electrons per molecule of the depolarizer. Thus each of the two waves represents a one-electron process.

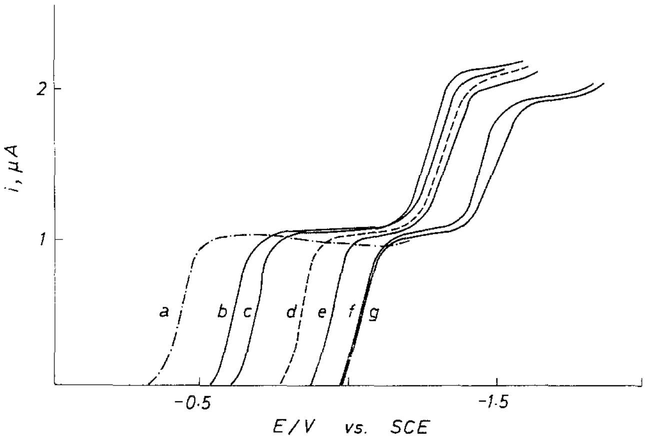


Fig. 1. Polarograms of 5.34×10^{-4} *M*-phenol red in buffer solutions, containing 32% by weight methanol, of different *pH*: *a* 2.72; *b* 5.65; *c* 7.15; *d* 8.88; *e* 9.78; *f* 11.15; *g* 11.52

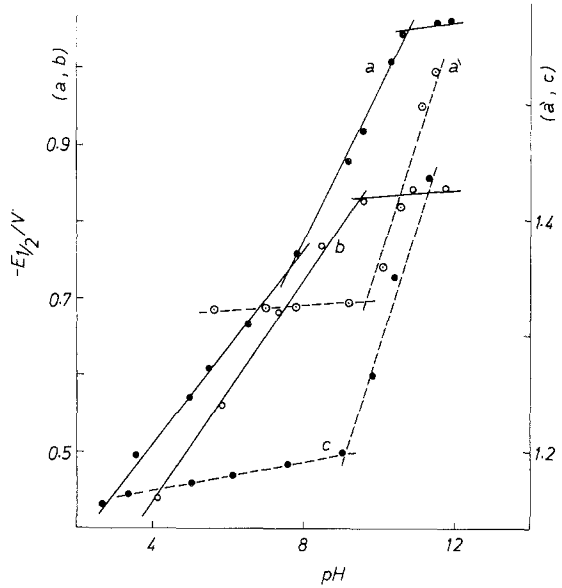


Fig. 2. $E_{1/2}$—*pH* curves: Phenol red (*a* 1st wave; *a'*, 2nd wave) in buffer solutions containing 32% ethanol. Chlorophenol red (*b*, 1st wave) in aqueous buffer solutions. Bromophenol red (*c*, 2nd wave) in aqueous buffer solutions

The diffusion coefficient (D) of the reducible species can be calculated using the *Stokes-Einstein* equation[7] in its simplified form:

$$D = 2.441 \times 10^{-13}/r\ [\mathrm{cm^2\,s^{-1}}] \qquad (1)$$

The values of the radii (r) of the reducible species in aqueous solution are calculated using the following equation[5]:

$$r = K^2/(i_\mathrm{d}\,\eta^{1/2})^2\ [\mathrm{cm}] \qquad (2)$$

where $K = (3.025\,n\,c\,m^{2/3}\,t^{1/6}) \times 10^{-4}$, $i_\mathrm{d}\,\eta^{1/2}$ is the total diffusion current, in μA, corrected for viscosity effect of the medium containing alcohol, n is the total number of electrons and c is the depolarizer concentration in mmol dm^{-3}. The results obtained (Tab. 1) are in accordance with those calculated directly from the *Ilkovic* equation[8].

Table 1. *Values of r and D of the reducible species in aqueous solutions at 25 °C*

Depolarizer	Radius (cm)	$D \times 10^6$ cm^2 s^{-1} *Stokes* Equ.	*Ilkovic* Equ.
Phenol red	7.97×10^{-8}	3.06	3.12
Chlorophenol red	8.88×10^{-8}	2.75	2.80
Bromophenol red	9.95×10^{-8}	2.45	2.50

Nature of the Waves

The exponent x in the relation $i_\mathrm{l} = kh^x$ equals 0.45-0.55 indicating that the electrode processes for the depolarizers under investigation are mainly controlled by diffusion.

Analysis of the waves using the fundamental equation for polarographic waves[9] revealed that the reduction process proceeds irreversibly. Values of the $\alpha\,n_a$ are calculated for different pH values from the slopes of $E/\log(i/i_\mathrm{d}-i)$ plots[9]. The most probable values of the transfer coefficient (α) are obtained for $n_a = 1$ (Tab. 1).

The $E_{1/2}-pH$ curves for the first and second waves of the three depolarizers consist of two segments (Fig. 2). From the slopes of the $E_{1/2}-pH$ and $E_\mathrm{d.e.}$ vs. $\log i/(\mathrm{i_d}-i)$ plots at the different pH values, the number of hydrogen ions ($\mathrm{Z_{H^+}}$) consumed in the rate-determining step was obtained[9]. The obtained results indicate that the value of Z_{H^+} for all the depolarizers under investigation equals $\simeq 1$. Accordingly the rate determining step for the reduction process should involve one proton and one electron.

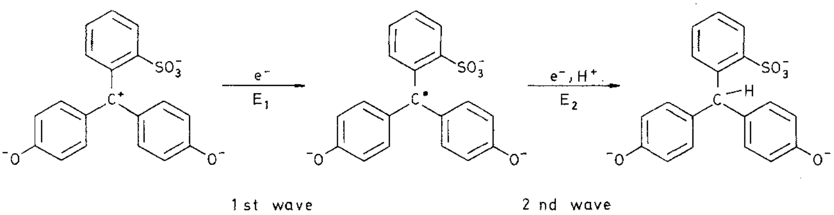
The Electrode Reaction

In the light of the obtained results, the reduction mechanism for the hydrated species can be formulated as follows:

(a) In solutions of $pH < 9$

The first one-electron wave corresponds to the preprotonation leading to the breaking of the C—OH bond at potential E_1, followed by a fast uptake of a second proton through the second one-electron wave at potential E_2. The fast proton interaction is not involved in the rate-determining step. The electrode sequence would be (H^+, e^-, e^-, H_f^+); see Scheme 1.

Scheme 1



In this case E_2 is more negative than E_1, since two one-electron waves are observed; the process does not involve a proton transfer between the uptake of the first and second electron. Hence the $E_{1/2}$ of the first wave is pH-dependent, whereas that of the second is not.

The difference in the behaviour of sulphonphthaleins from that of phenolphthalein[3] in media of $pH < 9$ may be attributed to the change in stability of the reducible species, which is due to the difference in the electron donating character of SO_3^- and COOH substituents. The charge density at the triphenylmethanecarbon centre of sulphonphthaleins increases; hence the acquisition of the second electron is retarded ($E_1 \# E_2$), leading to the separation of the reduction process to two steps.

(b) In solutions of $pH > 10$

In this pH range, the species of the sulphonphthaleins were considered to exist in the form of triphenylmethane carbonium ion[1,10]; the same was observed for fluorescein and its halogene derivatives[11]. The reduction process of the three depolarizers is formulated in Scheme 2.

Scheme 2

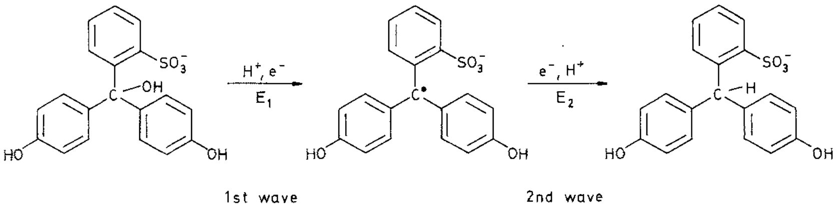


Table 2. *Kinetic parameters of the electrode reaction in solutions of various pH containing 32% ethanol*

pH	slope* (V)	αn_a	$k^0_{f,h}$ cm/s	ΔG^* kcal/mol	1st 2nd wave
Phenol red:					
5.4	0.069	0.86	4.4×10^{-9}	77.7	1
	0.230	0.26	5.0×10^{-8}	71.6	2
7.75	0.074	0.80	9.6×10^{-11}	87.4	1
	0.230	0.26	5.0×10^{-8}	71.6	2
9.15	0.083	0.71	1.8×10^{-11}	91.6	1
	0.230	0.26	5.0×10^{-8}	71.6	2
11.45	0.084	0.70	3.2×10^{-13}	101.7	1
	0.140	0.42	1.4×10^{-12}	98.0	2
Chlorophenol red:					
2.58	0.070	0.84	3.1×10^{-5}	55.5	1
4.9	0.074	0.80	5.9×10^{-7}	65.5	1
6.75	0.065	0.91	2.6×10^{-9}	78.1	1
	0.200	0.30	2.8×10^{-8}	73.1	2
8.48	0.067	0.88	4.5×10^{-11}	91.8	1
	0.220	0.27	2.1×10^{-7}	68.1	2
11.58	0.094	0.63	1.2×10^{-12}	97.6	1
	0.200	0.30	9.1×10^{-10}	81.7	2
Bromophenol red:					
2.35	0.110	0.54	5.4×10^{-5}	54.1	1
5.7	0.093	0.63	1.3×10^{-7}	69.2	1
9.88	0.103	0.57	8.0×10^{-11}	58.7	1
	0.210	0.28	7.1×10^{-9}	76.5	2
11.4	0.100	0.59	2.0×10^{-10}	85.5	1
	0.160	0.38	8.8×10^{-12}	93.3	2

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* $\Delta E_{d.e}/\Delta \log i/i_d - i$.

In solutions of $pH > 10$, the activity of H^+ ion is low and hence the rate of protonation of the carbanion slows down. Thus the $E_{1/2}$ of the second wave appears to be pH-dependent, and the slope of its $E_{1/2}$—pH curve corresponds to one proton contributed in the second reduction step. For intermediate pH values (9–10) both sequences are contributing in varying proportions.

Kinetic Parameters of the Electrode Reaction

The kinetic parameters of the electrode reaction are determined applying the *Koutecky* method[12] and its simplified form given by *Issa* et al.[13]. Representative results are shown in Tab. 2. The rate constant, $k^{0}_{f,h}$, generally decreases with increasing pH of the medium indicating a more difficult electron transfer. The more difficult reduction process is substantiated by the fact that the energy of activation, ΔG^*, increases with increasing pH of the solution and/or the proportion of alcohol; hence the process becomes more irreversible.

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