POLAROGRAPHIC STUDIES OF PHENOL SULPHOPHTHALEIN

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(*Received* 15 *March* 1971; *revised* 29 *June* 1971)

The polarographic reduction of phenol sulphophthalein in buffered solutions of different *p*H has been investigated in detail. The effect of addition of gelatin, on the reduction for phenol red has also been studied. It has been shown that the first wave can be used for the estimation of phenol red. When the gelatin concentration exceeds about 0·008%, the wave heights have been found to get affected.

Certain phthalein dyes like phenol sulphophthalein[1-3], bromosulphophthalein[4-7] are used in biochemical studies as they form addition products with enzymes, bilirubin etc. The polarographic behaviour of phenolphthalein was studied in detail by Kolthoff & Lehmicke[8]. The object of this investigation is to study the electro-reduction of phenol sulphophthalein (also known as phenol red) in buffered solutions of different *p*H by dc and ac polarographic methods. The influence of gelatin on the reduction of phenol red has also been investigated.

EXPERIMENTAL PROCEDURE

Sodium acetate, *HCl*, *NaOH* used were all of E. Merck (G. R.) quality. KH_2PO_4 of AR quality was used without further purification. Phenol sulphophthalein was recrystallised following the procedure given by Kolthoff & Lehmicke.

A Cambridge Pen Recording Polarograph was used for recording dc polarograms. The half-wave potentials were determined from polarograms obtained with a manual set-up.

The set-up used for obtaining ac polarograms was the same as that used by Doss *et. al.*[9] A Philips 6012 VTVM was used as an amplifier cum rectifier and the rectified output was measured by a calibrated galvanometer (with lamp and scale). Two different capillaries were used in the above studies and their characteristics were as follows :

The capillary used along with Polarograph was the one supplied by Cambridge Co. Ltd. It had the following characteristics :

$t = 4 \cdot 10$ sec. in 0·01% of Phenol red in acetate—*HCl* buffer *p*H 4·45 at —0·36V vs. saturated calomel electrode, (SCE);

$m = 1 \cdot 460$ mg./sec.

Capillaries used for the ac polarographic study and that used in conjunction with manual set-up were supplied by L. K. Blomgren & Co. Ltd., Sweden. These capillaries were cut to the proper length and used. Other characteristics of the DME were as follows :

$t = 5 \cdot 5$ sec. in open circuit in 0·1 M KCl

$m = 1 \cdot 09$ mg./sec. in 0·1 M KCl.

All the measurements were made with respect to saturated calomel electrode. Nitrogen purified by passing through columns containing vanadous chloride was used for deaerating purposes. Gelatin solutions were used for suppressing the maxima.

In the experiments of controlled potential electrolysis, Wenking Potentiostat (model 61 TR) was used for controlling the potential. The cell and reference electrode were of the type described by Lingane[10]. A platinum gauze electrode of 3 cm. dia. and 4 cm height was plated with silver and used as the counter electrode during the electrolysis. To measure the quantity of current passed, the hydrogen-oxygen gas

coulometer of the type described by Lingane[10] was used. Before each experiment, the gauze electrode was plated with silver for about 10 to 15 minutes and then used. Required quantity of potassium chloride was added to the solution which was elecrolysed. Purified nitrogen was bubbled continuously throughout the electrolysis.

RESULTS AND DISCUSSION

The dc polarogram of phenol red in a well-buffered solution shows two waves. The first wave was well defined while the second one was not so and also exhibit a maximum. The maximum, however, could be suppressed by about 0·008% gelatin. The second wave was quite drawn out and appears to be very irreversible. The potential-drop time curves (Fig.1) show that phenol red is strongly adsorbed in the potential range —0·20 to —0·60V and around —0·60 which corresponds to the $E_{\frac{1}{2}}$ of the first wave, the adsorption decreases sharply and a step appears. Perhaps there is a change in the structure of the adsorbed film around —0·60 V and a transition occurs from a condensed film to a gaseous film. The potential-drop time curves obtained with different amounts of gelatin in buffer solution of *p*H 4·45 given show that gelatin is adsorbed in the entire range of potentials and the adsorption reaches a limiting value beyond a concentration of 0·024%. While the effect of gelatin on the first wave is on the wave height, the second wave gets distorted with increasing addition of gelatin.

The ac polarograms of phenol red obtained in two different buffers of *p*H 6·25 and 4·45, with an ac amplitude of 15 mV (r.m.s.) showed that phenol red is strongly adsorbed in the potential range —0·10 to —0·50V vs. SCE and gets desorbed at potentials more negative than —1·0V vs. SCE. Two peaks were observed in the ac polarogram at —0·60V and —1·10V vs. SCE, in a buffer of *p*H 6·25, the height of the first peak being nearly three times that of the second one. The height of both the peaks were found to decrease with addition of gelatin.

The half-wave potential of the waves were found to vary with the *p*H of the buffer solution. The $E_{\frac{1}{2}}$ of the first wave varies with *p*H according to the equation $E_{\frac{1}{2}} = -0{\cdot}05 - 0{\cdot}09$ *p*H. Beyond *p*H 9·0, only one wave was observed. The height of the first wave decreases with increasing *p*H while that of the second wave increases with the total height remaining the same.

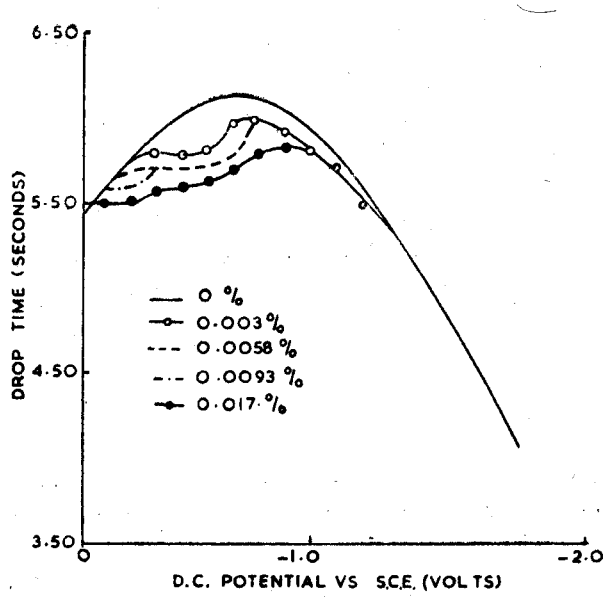

Fig. 1—Potential-drop time curves in the presence of different concentrations of phenol red.

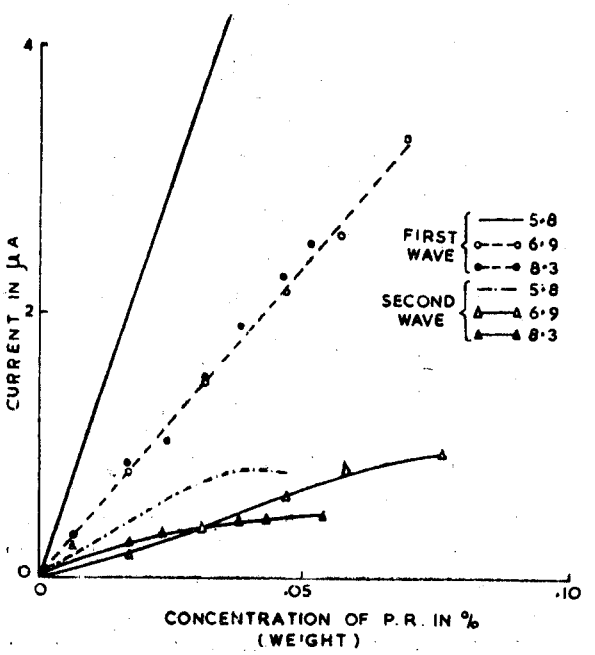

Fig. 2—Variation of i_d with concentration of phenol red of different *p*H in phosphate buffer solution.

Fig. 2 depicts the variation of the diffusion currents of the first and second wave as a function of concentration of phenol sulphophthalein in three supporting electrolyte solutions of different *p*H. It can be seen that in the three solutions, the height of the first wave varies linearly with concentration while that of the second wave varies linearly only upto a certain concentration after which it approaches a limiting value. It can be seen from Fig. 2 that the slope of the i_d vs. concentration curve for the first wave is several times greater than that of the curve for the second wave. Hence the first wave can be used for the estimation of phenol red.

Study of the variation of i_d of the first and second wave as a function of the height of the reservoir showed that for the first wave, the i_d varies linearly with $h^{\frac{1}{2}}$ showing that they are diffusion controlled.

The value of n for the first wave and second wave were obtained by electrolysing solutions of phenol red in a buffer of *p*H 5·80 at controlled potentials of —0·60V and —1·30V vs. SCE respectively corresponding to the first and second wave.

It was found that for both the waves n equals 2. Similarly, the value of n for the single wave obtained at *p*H 10·3 was estimated by carrying out the electrolysis at a potential of —1·48V vs. SCE. In this case also, n was found to be 2.

In solutions of *p*H less than 7·0 the first wave is due to the reduction of the acid form while the second wave appearing at about —1·0V is due to the quinone phenolate form. Due to the negative charge on it the quinone phenolate form is reduced at a more negative potential than —0·60V around which the unionised form gets reduced. In alkaline solutions, the wave is due to the reduction of the quinonoid dissociated form of phenol red.

The ac polarograms were obtained for different concentrations of phenol sulphophthalein in a buffer of *p*H 6·25. The variation of height of the first peak with concentration is given in Fig. 3 and it can be seen that the curve tends to a limiting value beyond a concentration of about 0·03%. The ac polarographic method can be used for the estimation of phenol red when the concentration is less than about 0·03%.

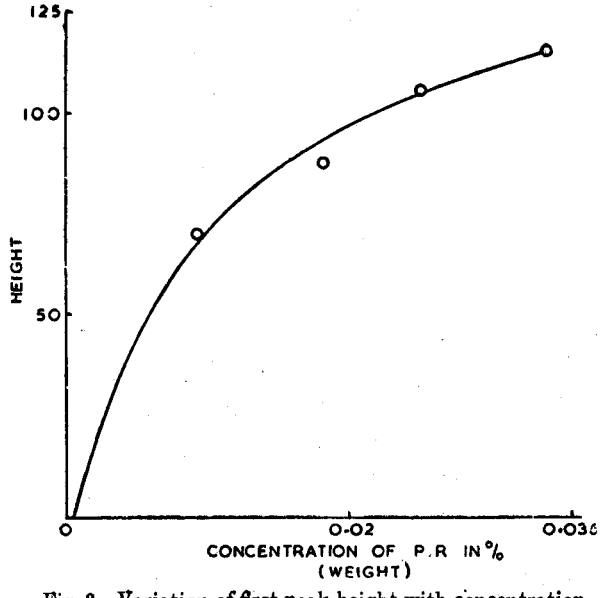

Fig. 3—Variation of first peak height with concentration (*p*H of the buffer 6·25).

CONCLUSION

In buffered solutions of *p*H less than 9·0, the polarogram of phenol red shows two waves. The first wave can be used for the estimation of phenol red. The concentration of gelatin in the solution should not be more than about 0·008% since it lowers the heights of the reduction waves of phenol red at higher concentrations.

ACKNOWLEDGEMENTS

The author thanks Dr. K. S. G. Doss, former Director and Dr. H. V. K. Udupa, Director, Central Electrochemical Research Institute, for the encouragement given.

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