[A CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Polarographic Behavior of Phenolphthalein

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In the course of a polarographic study of the reduction of various acid–base indicators, phenolphthalein was found to exhibit such unusual characteristics that a thorough investigation was made of its polarographic behavior under conditions of varying *p*H, solvent and temperature. A unique current–voltage curve was found in 25% alcohol at a *p*H of about 7, the curve showing a typical diffusion current plateau, the diffusion current then decreasing to a minimum value close to zero at a potential about half a volt more negative than the half-wave potential. The normal diffusion current in 25% ethanol was found to decrease almost to zero when the water in the solvent was being replaced by ethanol. An interpretation of the observed phenomena is given in the discussion section.

In a subsequent paper it will be shown that the polarograph is very suitable, not only to follow the fading of phenolphthalein in alkaline medium, but also to determine the rate of reaction of the colorless carbinol form with hydrogen ions in acid medium, which is not easily followed colorimetrically.

Experimental

Apparatus.—Unless otherwise stated the current–voltage curves were determined using a type VIII Heyrovsky polarograph. Exact data of diffusion currents and sometimes of half wave potentials were obtained with a manual apparatus. The galvanometer had a unit sensitivity of 3.19×10^{-3} microamperes per millimeter.[3] Two capillaries were used with the following characteristics. Capillary 1: droptime, t = 3.55 sec., m = 2.93 mg./sec., $m^{2/3}t^{1/6}$ = 2.52. Capillary 2: t = 2.96, m = 1.427 and $m^{2/3}t^{1/6}$ = 1.52. Unless otherwise noted capillary 2 was used.

The electrolysis cells consisted of 50-ml. Erlenmeyer flasks with side-arms for the admission of nitrogen and for connection with the saturated calomel electrode, which as a rule served as a reference electrode. All the potentials are referred to the saturated calomel electrode (S.C.E.). Several runs were made with a pool of mercury on the bottom of the electrolysis cell as anode. In these instances the anode potential was measured against the S.C.E. All diffusion currents as measured from the polarographic records were corrected for the residual current. In case two diffusion currents were found, their relative values were referred to the same value of $m^{2/3}t^{1/6}$.[4]

The electrolysis experiments were carried out in a thermostat at 25 ± 0.01°.

Materials. Phenolphthalein.—A National Aniline Company product with a melting point of 262–264° (cor.) (Beilstein, XVIII, 143 reports 254° uncor.).

Phenolphthalin.—This substance was prepared by reduction of phenolphthalein with zinc dust in 2 *N* sodium hydroxide according to the directions of Baeyer.[5]

Basic Fuchsine.—A National Aniline product; a 0.1% solution of the dye in water was prepared which served to eliminate maxima.

Nitrogen.—Tank nitrogen, purified by passing through a train consisting of acid chromous chloride solution, sodium hydroxide solution, mercuric chloride solution and water. In all polarographic experiments air was replaced with nitrogen.

Other chemicals were reagent grade. Standard acid and base solutions were prepared and standardized by conventional methods.

Buffer Solutions.—In the range of *p*H between 1 and 10 Clark and Lubs buffer solutions were used. The *p*H was checked with the aid of a glass electrode. The *p*H data refer to water as a solvent and not to solvents containing alcohol. Solutions with a *p*H higher than 10 were prepared using 0.1 *N* sodium carbonate (*p*H 11), 0.01 *N* sodium hydroxide (*p*H 12) and 0.1 *N* sodium hydroxide (*p*H 13).

Medium.—Except where the alcohol content was varied 25% ethanol by volume was present. In other instances the ethanol content is also expressed in per cent. by volume. In general, the concentration of phenolphthalein was 0.001 *M*. In order to work at this concentration it was necessary to have 25% ethanol in the solvent.

The test solutions contained 50% by volume of buffer solution and 0.001% of basic fuchsine. In the absence of the dye pronounced maxima in current–voltage curves were usually found. In addition, the solutions were usually 0.1 *N* in potassium chloride.

Results

Experiments in 25% Ethanol. Effect of *p*H.—Polarograms were run of 0.001 *M* solutions of phenolphthalein in 25% ethanol over the *p*H range between −0.6 and 13. Four different types of curves were obtained as shown in Figs. 1 and 2.

In solutions with a *p*H less than about 3.5 a single wave of the normal type was observed (Fig. 1). In the *p*H range between 4 and 8.5 one step reduction waves were observed, with well defined diffusion currents. The polarogram at a *p*H of 7.4 has quite an abnormal appearance (Fig. 1). The diffusion current remains practically constant in a potential range between about −1 and −1.2 volt, it decreases very slightly between −1.2 and −1.4 volt and then drops suddenly to attain a minimum value at a potential of about −1.6 volt. The minimum value remains constant to a potential of about −1.75 volt, whereupon the wave yielded by the supporting electrolyte appears. At a *p*H of 4.7 the decrease in the diffusion current starts at a potential of about −1.1 volt; however, before a flat minimum as at a *p*H of 7.4 is attained the wave of the supporting electrolyte appears. In still more acid medium (*p*H < 3.5) no decrease of the diffusion current is observed, as the hydrogen wave appears before the decrease of the diffusion current occurs. In the *p*H range corresponding roughly to the color-change inter-

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[2] From a thesis submitted by D. J. Lehmicke to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1946.

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 227.

[4] I. M. Kolthoff and E. F. Orlemann, THIS JOURNAL, **63**, 2085 (1941).

[5] A. Baeyer, *Ann.*, **202**, 80 (1880).

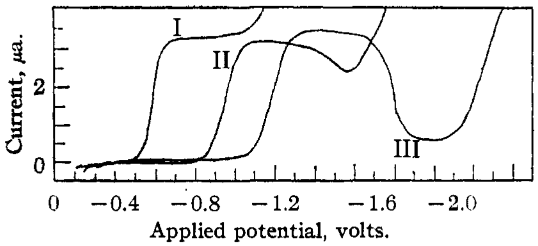

Fig. 1.—Current–voltage curves of millimolar phenolphthalein in 25% ethanol: I, solution is 3.8 *N* in HCl and 0.001% in basic fuchsine; II, biphthalate buffer, *p*H 4.73; III, phosphate buffer, *p*H 7.40. Abscissa scales for curves II and III start 0.1 and 0.2 volts, respectively, to the right of curve I.

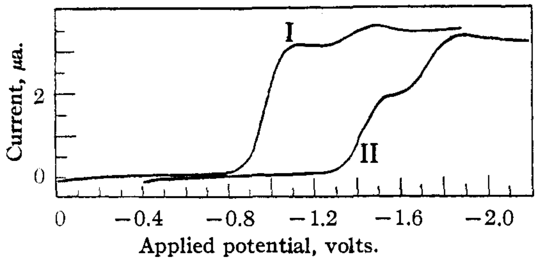

Fig. 2.—Current–voltage curves of millimolar phenolphthalein in 25% ethanol solution: I, in borate buffer, *p*H 9.55; II, in borate buffer, *p*H 10.25. Abscissa scale for curve II starts 0.4 volt to the right of curve I.

val of phenolphthalein two waves are observed. At a *p*H of about 9 the first diffusion current is almost equal to the total diffusion current found at lower *p*H, the second wave comprising only a few per cent. of the total current. In more alkaline medium the second wave increases at the cost of the first one (Fig. 2), the total current remaining the same. At a *p*H of 10.25 (Fig. 2) and at higher *p*H two waves of equal height are found. It is interesting to note that no decrease of the total diffusion current with increasing negative potential is found at a *p*H greater than 9.

The "apparent" diffusion currents (constant value before the dip) found at a *p*H of 7 and in more acid medium, and the total diffusion currents in alkaline medium are all of about the same value, indicating that these currents represent true diffusion currents. The polarograms in strongly alkaline medium must be taken immediately after preparation of the solutions, as the diffusion currents decrease slowly as a result of carbinol formation.

In order to provide further evidence that the apparent diffusion currents at a *p*H of 7 or smaller are true diffusion currents, their variation with concentration was determined. It was found that the diffusion current is proportional to the concentration. A few values of $K = i_d/c$ in a phosphate buffer of *p*H 7 in the presence of 0.1 *N* potassium chloride are: 0.50×10^{-3} *M* phenolphthalein, $K = 3.94$; 0.001 *M*, $K = 3.90$; 0.0015 *M*, $K = 3.90$.

In the phosphate buffer of *p*H 7 the apparent diffusion current is hardly affected by the concentration of electrolyte. However, the decrease in the current and the appearance of the well-defined minimum (Fig. 1) depend on the total electrolyte content of the solution. Experiments were carried out in which the polarograms were determined in a buffer solution of pyridine and pyridinium hydrochloride, the total chloride concentration being 2.4×10^{-4} *M*, the pyridine concentration 2×10^{-3} *M* and the phenolphthalein concentration 1×10^{-3} *M* (*p*H 6.85). The polarogram had a normal appearance, and the diffusion current did not decrease at more negative potentials. It remained constant until the wave of the supporting electrolyte appeared. When the solution was made 2.8×10^{-4} *M* in potassium chloride the dip came into evidence, and it became more pronounced as more potassium chloride was added. The non-appearance of the minimum in the pyridine buffer without salt, therefore, cannot be attributed to an increasing *p*H at the surface of the dropping mercury during the reduction (two hydrogen ions are consumed in the reduction), as the *p*H would change in a similar way in the presence of the potassium chloride. The effect of the potassium chloride must be a typical "electrolyte effect."

The appearance of the dip at *p*H values between 4 and 8 is a matter of practical consequence, when dealing with a mixture of phenolphthalein and a substance which is reduced at more negative potentials. This is demonstrated in Fig. 3, giving the polarogram of a 0.0015 *M* phenolphthalein and 0.001 *M* cobalt solution in 26% ethanol containing ammonium acetate as a buffer and fuchsine as an eliminator of maxima. First the diffusion current of phenolphthalein is observed; however, just before the diffusion current of cobalt is attained the dip in the phenolphthalein manifests itself and the current decreases to a fairly constant value, this value being equal to the sum of the diffusion current of cobalt and the small minimum current of phenolphthalein.

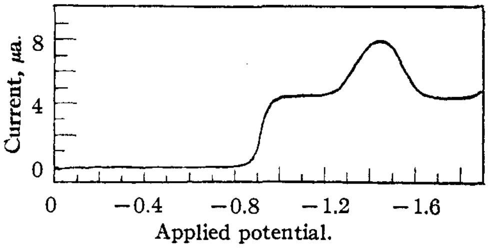

Fig. 3.—Current–voltage curve of millimolar cobalt acetate in the presence of 1.5×10^{-3} molar phenolphthalein in 26% ethanol. Solution is 0.2 *M* in ammonium acetate and contains 0.001% basic fuchsine.

When the solution contains in addition to phenolphthalein a substance which is reduced at more positive values than phenolphthalein the polarogram is simply interpreted, the phenolphthalein wave being superimposed upon the previous wave. This was shown to be true in the electrolysis of a mixture of benzoquinone and phenolphthalein.

Two-step Reduction in Alkaline Medium.—Apparently the red form of phenolphthalein (Fig. 2) gives a two-step reduction, whereas the colorless forms give only a single wave. In Table I are given the values of i_{d_1} (i_1) and i_{d_2} (i_2) at varying *p*H obtained with a 0.001 *M* phenolphthalein solution in 25% ethanol. In all instances the values of i_{d_1} have been corrected to the same value of $m^{2/3}t^{1/6}$ as prevailed at the potential at which i_t was measured ($i_{d_2} = i_t - i_{d_1\text{corr.}}$). The *p*H in the mixture was measured with the glass electrode.

TABLE I

VALUES OF i_{d_1} AND i_{d_2} IN MICROAMPERES OF PHENOLPHTHALEIN IN ALKALINE MEDIUM

i_t = total diffusion current uncorrected for $m^{2/3}t^{1/6}$

*p*H	i_1 (uncor.)	i_t	i_2	$i_2/{}^1/_2 i_t$
9.18	2.99	3.05	0.13	0.08
9.55	2.91	3.15	.33	.21
9.79	2.59	3.14	.61	.39
9.96	2.28	3.11	.90	.58
10.18	2.09	3.22	1.18	.73
10.25	1.70	3.11	1.45	.93
(13.0	1.33	2.51	1.20	.96)
(13.3	1.34	2.61	1.29	.99)

It is seen that the total diffusion current is found reasonably constant, except in the last two solutions which were 0.1 and 0.2 *N* in sodium hydroxide, respectively. In these solutions part of the red form was transformed into the carbinol form which does not give a reduction wave under the above conditions. At a *p*H of 10.3 the two waves become of equal height and remain of equal height with increasing *p*H.

When the ratio of $i_2/{}^1/_2 i_t$ is plotted against *p*H, a curve is obtained which has the appearance of a dissociation curve of an acid. The curve is almost identical with the curve obtained on plotting the fraction of phenolphthalein in the red form against *p*H, as determined by Michaelis and Gyemont.[6] The fact that the two curves practically superimpose indicates that the rate of transformation of the red form into the colorless reducible one is relatively small. If the dissociation equilibrium of the phenolphthalein in buffer solutions with *p*H between 9 and 10.5 were established very rapidly only one wave corresponding to that of the colorless form would have been observed.

Half-wave Potentials.—The half-wave potentials in 25% ethanol at varying *p*H are summarized in Table II.

Reduction of Phenolphthalin.—Solutions of phenolphthalin in 25% ethanol were electrolyzed at the dropping electrode in a *p*H range between 0 and 13. No reduction waves were observed.

TABLE II

HALF-WAVE POTENTIALS AS FUNCTION OF *p*H

*p*H	−0.06	0	1	2.5	3.5	4.7	5.8	6.9
$-(\pi^{1/2})_1$	0.49	0.53	0.60	0.67	0.71	0.75	0.80	0.86
$-(\pi^{1/2})_2$								
*p*H	7.4	8.2	9.6	10.06	12	13	13.3	
$-(\pi^{1/2})_1$	0.89	0.93	0.98	1.01	(.84)	(.82)	(.81)	
$-(\pi^{1/2})_2$			1.35	1.33	1.33	1.23	1.24	

Effect of Ethanol Concentration on Current–Voltage Curves in Neutral Medium.—The experiments were carried out with a 0.001 *M* phenolphthalein solution, except in 10% ethanol. The concentration in this medium was 0.0005 *M*, as a 0.001 *M* solution was supersaturated. All solutions contained a phosphate buffer of *p*H 7, and were 0.001% in fuchsine and 0.1 *M* in potassium chloride. Column II of Table III lists the diffusion currents. The value of i_{d_0} in water was found by graphical extrapolation.

Abnormally small values of the diffusion current were found at alcohol concentrations greater than 40%. In order to be quite sure that these small values of the diffusion current were typical for phenolphthalein and not due to a general effect of the solvent, diffusion currents of benzoquinone were determined at the same ethanol concentrations. Column III of Table III lists for phenolphthalein the ratio of the value of i_d in solutions of varying alcohol content to the (extrapolated) value in water (i_{d_0}). Column IV lists the same values for quinone, and Column V the ratio of the values in Columns II and IV.

TABLE III

EFFECT OF ETHANOL CONCENTRATION ON DIFFUSION CURRENT

Ethanol concn., %	$i_{d\,\text{phpht}}$	$(i_d/i_{d_0})_{\text{phpht}}$	$(i_d/i_{d_0})_{\text{quinone}}$	$\frac{\text{Column III}}{\text{Column IV}}$
0	(4.17)	(1.00)	1.00	1.00
10	3.97	0.95	0.90	1.05
20	..	..	.75	..
25	3.29	.79	.69	1.14
30	2.66	.64	.65	0.99
35	1.84	.44	.62	.71
40	0.97	.23	.60	.38
50	0.24	.06	.59	.10
70	0.04	.02	.63	.03

As an illustration Fig. 4 shows the current–voltage curve at an ethanol concentration of 40%.

From the last column in Table III it is seen that up to an alcohol concentration of 30% the diffusion currents of phenolphthalein and quinone are affected in about the same way. At higher alcohol concentrations the diffusion current of phenolphthalein is decreased much more than that of quinone. At an ethanol concentration of 70% the phenolphthalein diffusion current has become vanishingly small.

Assuming that the electroreduction of phenolphthalein involves two electrons it is possible to calculate its diffusion coefficient in water from the

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(6) L. Michaelis and A. Gyemont, *Biochem. Z.*, **109**, 165 (1920).

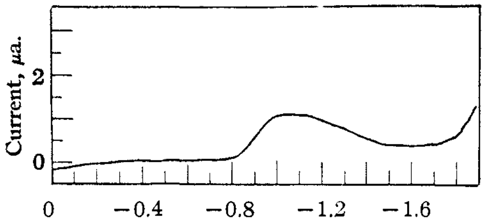


Fig. 4.—Current–voltage curve of millimolar phenolphthalein in 40% ethanol. Solution contains phosphate buffer; *p*H 7.

extrapolated value of the diffusion current with the aid of the Ilkovic equation

$$i_d = 605nD^{1/2}m^{2/3}t^{1/6}$$

The value of $m^{2/3}t^{1/6}$ at −1.0 volt, at which i_d was measured was 1.51 mg.$^{2/3}$ sec.$^{-1/2}$ and i_d in 0.001 *M* solution was 4.17 microamperes. This yields a value of $D = 5.2 \times 10^{-6}$ sq. cm./sec. at 25°. For benzoquinone a diffusion coefficient of $8.6 \pm 0.2 \times 10^{-6}$ was calculated at 25°.[7] The values for phenolphthalein and benzoquinone are of the same order of magnitude, showing conclusively that the reduction of phenolphthalein at the dropping electrode involves two electrons.

Effect of the Temperature on the Current–Voltage Curves in 25% Ethanol in Neutral Medium.—All experiments were carried out with the same solution which was 0.001 *M* in phenolphthalein, 25% in ethanol, 0.1 *M* in potassium chloride, 0.001% in basic fuchsine and which contained 50% of a phosphate buffer of *p*H 7. Experiments at 0° were carried out in an ice-bath, and at temperatures above 25° in a water-bath, the temperature of which was controlled manually. In these experiments the temperature was constant within 2°.

The diffusion current was found to increase with increasing temperature in a predictable fashion, but the current at the minimum of the c.–v. curve showed a relative increase at temperatures above 25°, which was many times greater than that of the diffusion current. This is demonstrated in Table IV in which i_{min} denotes the current at the minimum in the c.–v. curve.

Table IV

Effect of Temperature on Current–Voltage Curves of 0.001 *M* Phenolphthalein in 25% Ethanol in Presence of Phosphate Buffer

Temp., °C.	i_d, microamperes	i_{min}, microamperes	i_{min}/i_d
0	2.00	0.14	0.06
25	3.29	0.24	.07
50	4.77	1.15	.24
75	6.41	3.49	.56

Figure 5 illustrates the c.–v. curve at 75°.

A run was also made at 85°, within two degrees of the boiling point of the 25% ethanol solution. At this temperature the diffusion current varied somewhat irregularly (about 7.2 microamperes), but the current–voltage curve did not show a dip. Hence the minimum had practically disappeared.

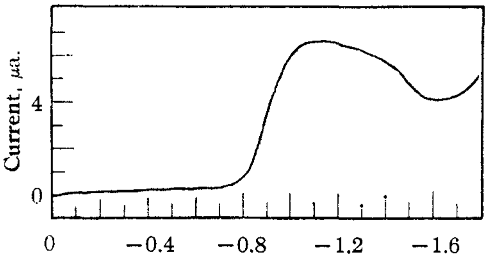
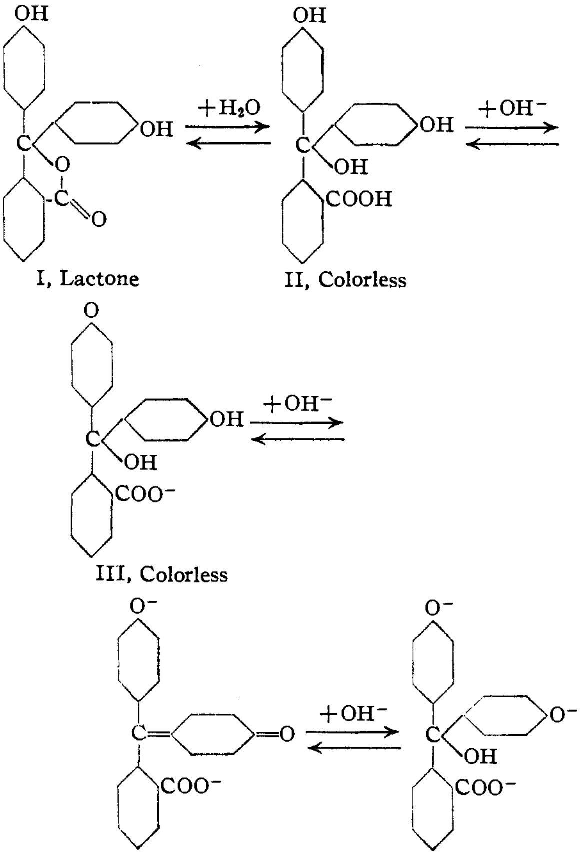


Fig. 5.—Current–voltage curve of millimolar phenolphthalein in 25% ethanol at 75°. Solution contains phosphate buffer; *p*H 7.

Discussion

1. Phenolphthalein in solution can exist in different forms, which are in equilibrium. Representing the various forms by the classical formulas we have



I, Lactone
II, Colorless
III, Colorless
IV, Red
V, Carbinol, colorless

At a *p*H smaller than 8 practically all of the phenolphthalein is present in the lactone form I. It is estimated that the concentration of II is

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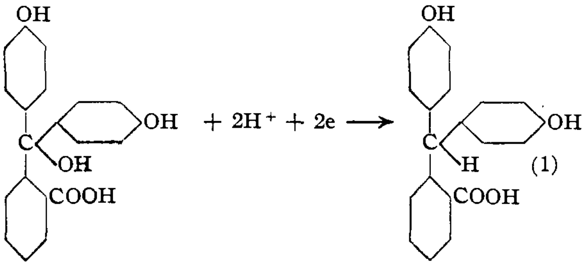
(7) I. M. Kolthoff and E. F. Orlemann, This Journal, **63**, 664 (1941).

less than 0.01% of that of I.[8] For reasons mentioned below it is concluded that form II is reducible at the dropping electrode, but form I is not, at least at potentials more positive than that at which the wave of the supporting electrolyte used appears. Both forms II and III give a single reduction wave. The red form IV gives a two step reduction, both waves being of equal height. The colorless carbinol form V formed in strongly alkaline medium does not give a reduction wave, at least not at potentials more positive than that at which the sodium wave appears. When a strongly alkaline solution of phenolphthalein is permitted to stand the color fades and a corresponding reduction of the diffusion current is observed.

In the region of pH between 0 and about 10 the half wave potential varies according to

$$\pi_{1/2} = -0.54 - 0.046pH$$

The reduction which is irreversible can be represented by the equation

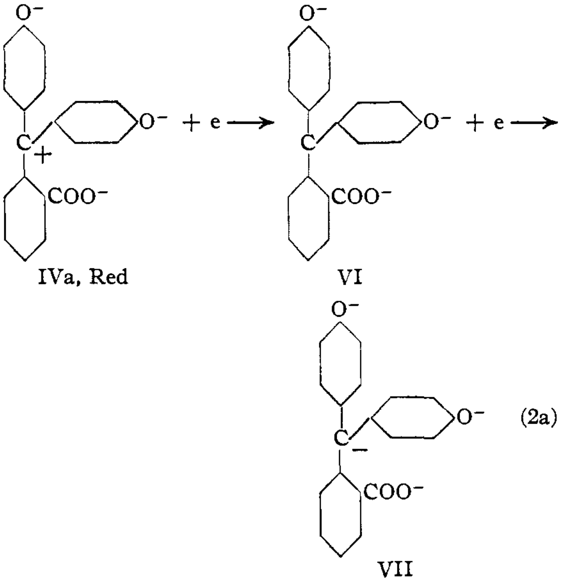


II Phenolphthalin (1)

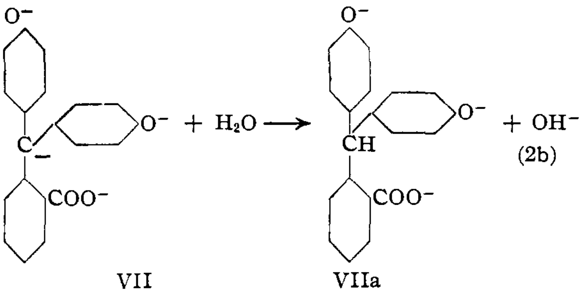
This mechanism is supported by the following facts.

The diffusion current corresponds to a transfer of two electrons as shown in the experimental part. It also has been shown that phenolphthalin does not yield a reduction wave at the dropping electrode.

The reduction of form III can be represented by a similar equation as that of form II. The reduction of the red form IV, however, occurs in two steps. The first wave could correspond to the formation of the trivalent anion of phenolphthalin. As shown in the experimental part, the first wave of the red form is identical with the wave of form III. It does not seem plausible that the quinone form would be reduced at the same potentials as form III. However, it is peculiar that the half wave potential of form III varies with pH, whereas the half wave potentials of both waves of form IV appear to be independent of pH (Table II). Accepting the dipolar structure[9] of forms III and IV the coincidence of the reduction wave of III and of the first wave of IV becomes more reasonable.

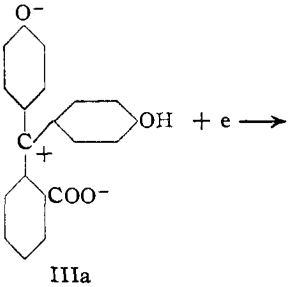


IVa, Red VI VII (2a)

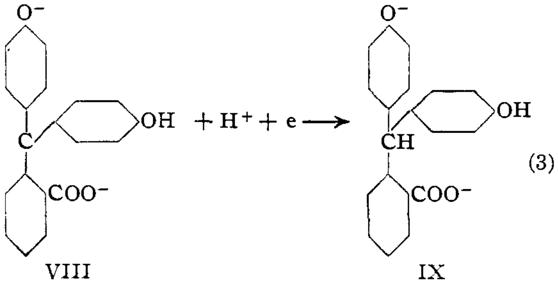


VII VIIa (2b)

Although the final reduction product is VIIa, form VII is formed intermediately at the surface of the electrode. The reduction of the colorless form III is found at higher hydrogen ion concentrations than that of form IV. The reduction of III can be represented by



IIIa



VIII IX (3)

The first steps in the reductions of IVa and IIIa are comparable, but the form corresponding to VII is not formed in the reduction of VIII or if it would be formed it would react instantaneously with hy-

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[8] I. M. Kolthoff and C. Rosenblum, "Acid-Base Indicators," The Macmillan Company, New York, N. Y., 1937, p. 223.

[9] H. Lund, *J. Chem. Soc.*, 1844 (1930).

drogen ions with formation of IX. The potential of reduction of VIII to IX becomes dependent upon the hydrogen ion concentration, and the second wave coincides with the first one.

2. From Table II it is seen that up to 30% ethanol the diffusion currents of phenolphthalein (*p*H 7) and benzoquinone are affected in the same way by the alcohol. This is mainly a viscosity effect. When the ethanol concentration becomes greater than 30% the diffusion current of phenolphthalein decreases much more than that of the quinone and in 70% ethanol the diffusion current of phenolphthalein becomes almost vanishingly small. This can be explained if it is assumed that form II, but not form I, is reducible. In the transformation of I into II the concentration of water becomes rate-determining. The experimental results indicate that at concentrations of less than 25% ethanol the rate of formation of II is so large that it is reformed from I immediately at the surface of the electrode when it is reduced. Therefore, at ethanol concentrations of 25% or less the apparent diffusion current corresponds to the true diffusion current of phenolphthalein. When the alcohol concentration increases the concentration of water decreases and the rate of transformation of I into II decreases. The apparent diffusion current now decreases and becomes partly diffusion and partly rate controlled. At alcohol concentrations greater than 50% the current becomes so small that it is practically entirely rate controlled. Under these circumstances the current should become independent of the height of the mercury in the reservoir.[10]

At the higher alcohol concentrations the polarographic behavior of phenolphthalein becomes comparable to that of some reducing sugars, like glucose and lactose in aqueous medium. As shown by Wiesner[11] the small "apparent" diffusion currents of these sugars are determined entirely by the rate of transformation of the non-reducible form of the sugars into the reducible form.

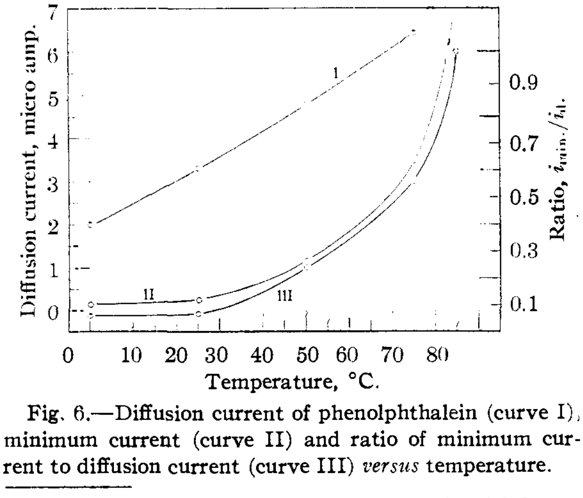

Fig. 6.—Diffusion current of phenolphthalein (curve I), minimum current (curve II) and ratio of minimum current to diffusion current (curve III) *versus* temperature.

3. In 25% ethanol and in the presence of a phosphate buffer (*p*H 7) the diffusion current varies with the temperature in a normal way (see Fig. 6). From the slope of curve I in Fig. 6 it is calculated that the diffusion current increases by about 1.8% per one degree increase of temperature. This value is of the same order of magnitude as that of normal diffusion currents.[12] However, the effect of temperature on the minimum value of the current is quite different. Curve III in Fig. 6 gives the change of the ratio of $i_{\text{min.}}/i_{\text{d}}$ with the temperature. At temperatures between 0 and 30° i_{d} and $i_{\text{min.}}$ vary in about the same way, but at temperatures higher than 30° $i_{\text{min.}}$ increases much more than i_{d}.

First, we tried to explain the occurrence of the unprecedented minimum (see Fig. 1) by assuming that phenolphthalein is reduced only in the adsorbed state and that at potentials corresponding to that of the minimum current the phenolphthalein is desorbed. However, several phenomena are contrary to this interpretation. In general, the adsorption at the surface of the mercury decreases with increasing temperature. If phenolphthalein were reduced only in the adsorbed state the minimum current should decrease rather than increase with increasing temperature. The opposite is found. Another fact of significance is that at a *p*H of 9 a normal polarogram is observed. At this *p*H the second wave is negligibly small, and the (first) diffusion current retains its normal value until the wave of the supporting electrolyte occurs. At a *p*H of 9 little of the non-reducible form I is present, most of the phenolphthalein being in form III, and there is no indication that this form is being reduced in the adsorbed state. If it were reduced in the adsorbed state a desorption would be expected at more negative potentials, before the sodium wave (of the supporting electrolyte) appears. This would be accompanied by a decrease of the diffusion current, which has not been observed.

We attribute the occurrence of the minimum to a decreased rate of transformation of I into II *at the surface* of the electrode. The very large effect of the temperature upon $i_{\text{min.}}$ strongly suggests that we are dealing with a process which is rate controlled. If our interpretation is correct the rate of tranformation of I into II at the interface mercury–water should decrease with increasing potential. This is not strange, if it is realized that the structure of the double layer at the interface mercury–water varies in a complicated manner with the potential, and the type and concentration of electrolyte in the solution. Quite generally, strongly adsorbable organic compounds are being completely desorbed in the presence of electrolyte at negative potentials of the order of −1.5

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(10) Comp. K. Wiesner, *Z. Elektrochem.*, **49**, 164 (1943); R. Brdicka and K. Wiesner, *Coll. Czechoslov. Chem. Commun.*, **12**, 138 (1947).

(11) K. Wiesner, *ibid.*, **12**, 64 (1947).

(12) Comp. I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 37 (1939).

volt. Similarly the orientation of water molecules at and in the interface changes with the potential of the mercury, thus affecting the rate of hydration of I. When the electrolyte content in the solution is small, as was the case in our experiment with a very dilute pyridine–pyridinium hydrochloride buffer, the structure of the double layer, especially at more negative potentials, is quite different from that in 0.1 M potassium chloride solution, which was the normal salt content in our experiments. In the very dilute buffer no dip in the current–voltage curve and no minimum were observed. Although the exact mechanism of the decreasing rate of the reaction I + $H_2O \rightarrow$ II with increasing negative potential needs further study, there is no doubt that the occurrence of the minimum, as in Fig. 1 (curve III), must be attributed to a decreasing rate of the above reaction at the electrode surface with increasing negative potential.

Summary

1. The polarographic behavior of phenolpthalein has been investigated under widely varying conditions. In 25% ethanol phenolphthalein gives a one-step reduction wave in a pH range between 0 and 9. In this range the half-wave potential changes according to $\pi^{1}/_{2}$ ($vs.$ S.C.E.) = 0.54 − 0.046 pH. The red form of phenolphthalein yields two waves of equal height, each wave giving a well-defined diffusion current. The sum of the two diffusion currents is equal to that of the single wave observed at lower pH. The polarographic reduction of phenolphthalein to phenolphthalin is accompanied by a transfer of two electrons.

2. In the presence of a phosphate buffer of a pH of 7 the diffusion current decreases abnormally when the ethanol concentration is increased. In 60% ethanol the "apparent" diffusion current becomes extremely small at 25°. It is concluded that the lactone form of phenolphthalein is not reduced, but its hydrated form is. At alcohol concentrations of 25% or less the rate of hydration at the surface of the electrode is so large that a normal diffusion current is observed. At high alcohol concentrations the "apparent diffusion current" becomes entirely rate- and not diffusion-controlled. Experiments carried out at various temperatures substantiate this interpretation.

3. In 25% ethanol in the presence of a buffer of pH 7 the diffusion current remains constant in a potential range between −1.0 and −1.2 volt; it decreases slightly between −1.2 and −1.4 volt and then drops suddenly to attain a small minimum value at a potential of about −1.6 volt. Experimental evidence has been given substantiating the interpretation that the occurrence of the minimum is to be attributed to a decreased rate of transformation of the lactone form into the reducible hydrated form at the surface of the dropping electrode.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Polarographic Behavior of Nitrosophenylhydroxylamine[1]

BY I. M. KOLTHOFF AND A. LIBERTI[2]

The ammonium salt of nitrosophenylhydroxylamine, called cupferron, is a well-known analytical reagent, which precipitates a great number of metal ions in acid medium. In connection with a study of the use of cupferron as a reagent in amperometric titrations, the polarographic behavior of nitrosophenylhydroxylamine has been investigated over a wide range of pH.

Experimental

Materials Used: Cupferron.—Eastman Kodak Co. and G. F. Smith Chemical Co. products were recrystallized from ethanol. The crystals had the appearance of silver-white leaflets (m. p. 163–164°). The solid product was stored in a dark bottle over solid ammonium carbonate to prevent decomposition. A stock solution (0.02 M) in water was found to be stable for more than two weeks when kept in the dark in a cool place. The solution is not stable in acid medium, as the phenylnitrosohydroxylamine decomposes. The rate of decomposition increases with decreasing pH. When polarograms were determined in acid medium at a pH smaller than 3, a measured volume of an air-free stock solution of cupferron was added to a suitable volume of air-free buffer solution in the cell and the current-voltage curve was determined soon after mixing. In some experiments the lithium salt of nitrosophenylhydroxylamine was used, which was prepared from cupferron and lithium hydroxide.

Buffer Solutions.—In the pH range between 1 and 5.6 Clark and Lubs buffers served to adjust the pH. In the range between pH 3 and 10 the universal buffers of Britton and Robinson[3] were used. The buffer mixtures were prepared by addition of lithium hydroxide to a solution which was 0.04 M in phosphoric, 0.04 M in acetic and 0.04 M in boric acids. In addition, Clark and Lubs buffers, prepared from boric acid and lithium hydroxide and lithium chloride, were used in the pH range between 8 and 10.

Tetramethylammonium Hydroxide Solution.—An Eastman Kodak Co. product of the bromide of this base was purified by repeated recrystallizations from ethanol–water mixtures. A stock solution of the hydroxide was prepared from the purified bromide with silver hydroxide as described by Peracchio and Meloche.[4] Buffer solutions prepared from tetramethylammonium hydroxide and phos-

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[1] From a Master's thesis (1947) of A. Liberti, submitted to the Graduate School of the University of Minnesota.

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[3] H. T. S. Britton and R. A. Robinson, *J. Chem. Soc.*, 1456 (1931).

[4] E. S. Peracchio and V. W. Meloche, THIS JOURNAL, **60**, 1770 (1938).