

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Effect of Ethanol in the Electro-reduction of *p*-Nitroaniline at the Dropping Mercury ElectrodeBY O. D. SHREVE<sup>1</sup> AND E. C. MARKHAM

For solubility reasons, many of the organic polarographic reductions reported in the literature have been studied in mixtures of water with ethanol or other water miscible organic solvent. As pointed out by Kolthoff and Lingane,<sup>2</sup> the effect of such solvents on the measured half-wave potentials and diffusion currents is often overlooked, with resulting confusion in the interpretation of organic polarographic data. When reductions at the dropping mercury electrode are carried out in the approved manner, *i. e.*, in well buffered solutions, the over-all effect of added organic solvent on the potential will include: (a) the change resulting from any alteration in the hydrogen ion activity of the aqueous buffers; (b) any change in potential of the quiet mercury anode (or change due to the introduction of a liquid junction if an outside reference anode is used); and (c) any effect on the inherent reduction potential of the reducible compound. The effect on the diffusion currents will reflect the influence of the solvent on one or more of the terms in the Ilkovic equation (diffusion coefficient or capillary characteristics).

Investigations of the effect of organic solvents on metal ion reductions<sup>3</sup> indicate that diffusion currents are depressed but potentials only slightly affected. In the organic field a few experiments on the effect of varying solvent composition<sup>4</sup> have been reported, but these are limited in scope and incidental to the investigator's chief purpose.

The present report describes a complete quantitative study of the effect of ethanol, the most commonly used polarographic solvent, on (a) the *pH* values as calculated from hydrogen electrode potentials, for a series of commonly used buffers covering a wide *pH* range and (b) the usual polarographic values measured in the reduction of *p*-nitroaniline in these buffers. The appreciable solubility of this compound in water makes possible a direct comparison of its polarographic be-

havior in the presence of varying amounts of ethanol with that in water.

## Experimental

Using the polarographic cell-aqueous calomel electrode combination described below, polarographic and glass electrode potential measurements were made on  $5.4 \times 10^{-4}$  *M* *p*-nitroaniline solutions in nine buffer series, each series comprising a commonly used buffer system made up in water and in six ethanol-water mixtures. All solutions contained 0.02% gelatin as maximum suppressor and the total concentrations of buffer constituents in each series were held constant at those calculated to yield an ionic strength of 0.1 in water.<sup>5</sup>

Using the same cell combination, hydrogen and glass electrode potential measurements were made on 5 of the above series (compositions being identical except for the absence of the small amount of *p*-nitroaniline). The glass electrode potentials in these solutions were identical with those in the corresponding solutions containing *p*-nitroaniline and a plot of glass electrode *versus* hydrogen electrode potentials (Fig. 1) yielded a 45° straight line. Hydrogen electrode potentials for the remaining four series were not measured directly, but were derived from glass electrode measurements with the aid of this calibration curve. "Apparent" *pH* values for all solutions polarographed were then calculated from the measured or derived hydrogen electrode potentials.

**Cell Assembly.**—All measurements were made in a polarographic cell-aqueous saturated calomel electrode combination similar to that described by Lingane and Kolthoff<sup>6</sup> except that the cell was all Pyrex glass and was designed to accommodate both hydrogen and glass electrodes as well as a dropping electrode and salt bridge<sup>7</sup> through ground joints. The whole assembly was thermostated at 25°.

**Polarographic Measurements.**—A manually operated polarographic apparatus capable of accurate potential and current measurements was used. The circuit was similar to one which has been described by Lingane and Kolthoff.<sup>8</sup> Potentials were simultaneously applied and measured with a Leeds and Northrup potentiometer. Currents were measured in microamperes with a sensitive, long period Leeds and Northrup D'Arsonval galvanometer in conjunction with a lamp and curved scale. The galvanometer was calibrated in a manner similar to that recommended by Kolthoff and Lingane<sup>8</sup> and was adjusted to a "round number" sensitivity before each run (0.05  $\mu$ a./mm. for most of the work) to facilitate conversion of scale readings to microamperes.

The observed diffusion current in each solution was corrected for residual current by the direct method<sup>8</sup> to obtain the true diffusion current, ( $i_d$ ), and the potential corresponding to  $i_d/2$  was taken as the half-wave applied potential. The half-wave applied potential was then corrected for *iR* drop after measurement of the cell circuit resistance<sup>9</sup> to give the true half-wave potential ( $E_{1/2}$ ).

The same dropping capillary sealed directly to a Pyrex glass mercury reservoir was used throughout the study; the pressure on the dropping mercury was maintained constant

(1) Present address: E. I. du Pont de Nemours and Co., Philadelphia Laboratory, Philadelphia, Pennsylvania.

(2) Kolthoff and Lingane, "Polarography," N. Y. Interscience Publishers, New York, N. Y., 1941, p. 344.

(3) Bachman and Astle, THIS JOURNAL, **64**, 1303 (1942); Sartori, *Gazz. chim. ital.*, **71**, 233 (1941); Parracchio and Meloche, THIS JOURNAL, **60**, 1770 (1938); Sartori and Giacometto, *Gazz. chim. ital.*, **70**, 178 (1940); Zanko and Manusova, *J. Gen. Chem. (U. S. S. R.)*, **10**, 1171-76 (1940); Zlotowski and Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 473 (1942); THIS JOURNAL, **64**, 1297 (1942); **66**, 1431 (1944); *J. Phys. Chem.*, **49**, 386 (1945); Gentry, *Nature*, **167**, 479 (1946); Jessop, *ibid.*, 158 (1946); Brasher and Jones, *Trans. Faraday Soc.*, **42**, 775 (1946).

(4) Shikata and Tachi, *Mem. Coll. Agr., Kyoto Imp. Univ.*, **8**, 31 (1930); Tachi, *ibid.*, **40**, 17 (1937); Kolthoff and Lehmiche, THIS JOURNAL, **70**, 1879 (1948); Pasternak and Halban, *Helv. Chim. Acta*, **29**, 190 (1946).

(5) The small contribution of the weakly ionized buffer acids to the ionic strength was ignored in these calculations.

(6) Lingane and Kolthoff, THIS JOURNAL, **61**, 828 (1939).

(7) Irving and Smith, *Ind. Eng. Chem., Anal. Ed.*, **6**, 480 (1934).

(8) Ref. 2, p. 228.

(9) Heyrovsky, *J. Coll. Czechoslov. Chem. Commun.*, **4**, 480 (1932).

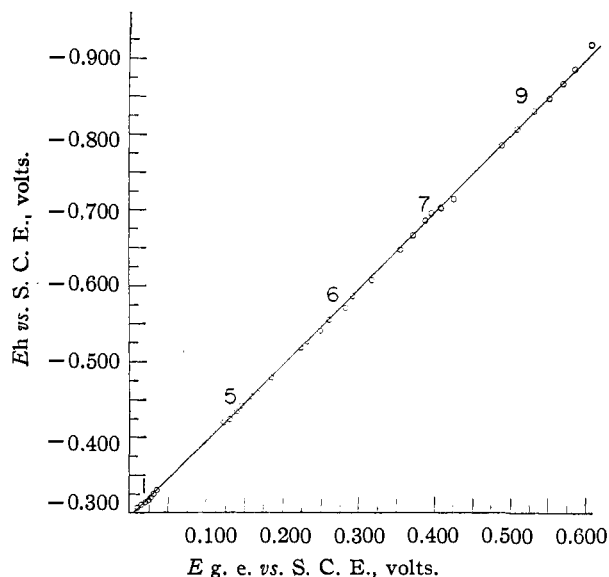


Fig. 1.—Glass electrode *versus* hydrogen electrode potential. Numbers refer to buffers identified in Table II. Points from left to right in each group correspond to increasing ethanol concentrations given in Table II.

at 30.8 cm. of mercury by a pressure regulating device.<sup>6</sup> All solutions were deaerated with purified nitrogen which passed through a portion of the solution under study in a side arm of the cell before entering the cell proper.

**Hydrogen and Glass Electrode Measurements.**—The hydrogen electrode measurements were made with a Leeds and Northrup Type K potentiometer, in the usual way, with a sensitive D'Arsonval galvanometer as null point indicator. The purified hydrogen bubbled through a portion of the solution in the cell side arm before entering the cell proper and measurements were taken until constant within  $\pm 1$  mv. for buffers containing 0–35% ethanol and  $\pm 2$  mv. for those richer in ethanol.

The glass electrode potentials were measured with a Coleman Model 3D pH electrometer, using a Coleman 3001 F electrode.

The cell set-up used in these measurements was exactly the same as that used for the polarographic measurements except, of course, for the replacement of the dropping electrode by a glass or hydrogen electrode.

**Materials.**—The *p*-nitroaniline used was an Eastman product purified by recrystallization from water and alcohol, m. p. 146–147°.

Absolute ethanol (U. S. Industrial Chemicals, Inc.) was distilled from alkaline silver oxide and the middle fraction of the distillate redistilled from aluminum amalgam to give the pure dry product used in the experiments.

"Hydron Buffer Salts" (Micro Essential Laboratory, Brooklyn, N. Y.) were used for preparing buffers without further purification. The salts used included potassium chloride, glycine, sodium acetate, monopotassium phosphate and boric acid. The hydrochloric acid, acetic acid and potassium hydroxide stock solutions used in preparing buffers were made from J. T. Baker Analyzed C. P. grade chemicals and were standardized by the usual methods.

The tank nitrogen, used for deaerating, was purified by passing through a train consisting of (a) a Drierite tube; (b) copper gauze, maintained at 500° by an electric furnace; (c) solid potassium hydroxide; (d) phosphorus pentoxide; and (e) a second Drierite tube, before entering the polarographic cell.

The electrolytic hydrogen used for the hydrogen electrode measurements was purified by passing through a train consisting of (a) a soda-lime tube; (b) a bubble counter containing concentrated sulfuric acid; (c) a

Pyrex furnace containing platinized asbestos at 500°; and (d) a Drierite tube before entering the cell.

Baker U. S. P. gelatin was used for suppressing maxima. Fresh solutions were frequently prepared and a trace of thymol added as preservative.

## Results

**Reduction in Aqueous Medium.**—Shikata and Taguchi<sup>10</sup> studied the reduction of the nitroanilines in aqueous buffers at 25°. Since their work was done before the introduction of the half-wave potential concept, however, they reported "tangent" potentials and these were derived from polarograms showing maxima in varying degree. In agreement with the results reported by these investigators, we have observed only one wave in the reduction of *p*-nitroaniline throughout the pH range studied in buffer solutions but two waves in an unbuffered solution consisting of 10<sup>-4</sup> *N* hydrochloric acid in 0.1 *N* potassium chloride.

The effect of varying concentration of the reducible compound on half-wave potential and diffusion current in aqueous acetate buffer (no. 6) is given in Table I. These data indicate that the Ilkovic equation holds reasonably well for the reduction. The half-wave potentials are fairly constant over the range 10<sup>-4</sup> to 10<sup>-3</sup> *M* but decrease below and increase above this concentration range.

TABLE I

EFFECT OF CONCENTRATION OF *p*-NITROANILINE ON HALF-WAVE POTENTIAL AND DIFFUSION CURRENT IN AQUEOUS ACETATE BUFFER OF pH 4.62

Concn., mmol./l.	$E_{1/2}$ , v. vs. S. C. E.	$i_d$ , $\mu$ a	$i_d/C$
0.054	-0.509	1.13	20.9
.100	-.522	2.14	21.4
.140	-.525	2.88	20.6
.279	-.520	5.70	20.4
.400	-.518	8.40	21.0
.541	-.523	11.35	21.0
.729	-.526	15.32	21.0
.940	-.529	19.30	20.5
1.082	-.537	22.45	20.8

**Effect of Ethanol on pH of Buffers and Half-Wave Potentials.**—The pH values for the alcoholic as well as the aqueous buffers were calculated from the hydrogen electrode potentials using the usual equation for the *aqueous* saturated calomel-hydrogen electrode combination,  $pH = (E_h - 0.2438)/0.0591$  as recommended for such cases.<sup>11</sup> It should be emphasized that the observed effect of ethanol on the pH values thus calculated includes the unknown effect on the  $E_0$  value of the hydrogen electrode and the liquid junction potential as well as the effect on the actual hydrogen ion activity of the solutions.

(10) Shikata and Taguchi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **29**, 1 (1934).

(11) Dole, "Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 300.

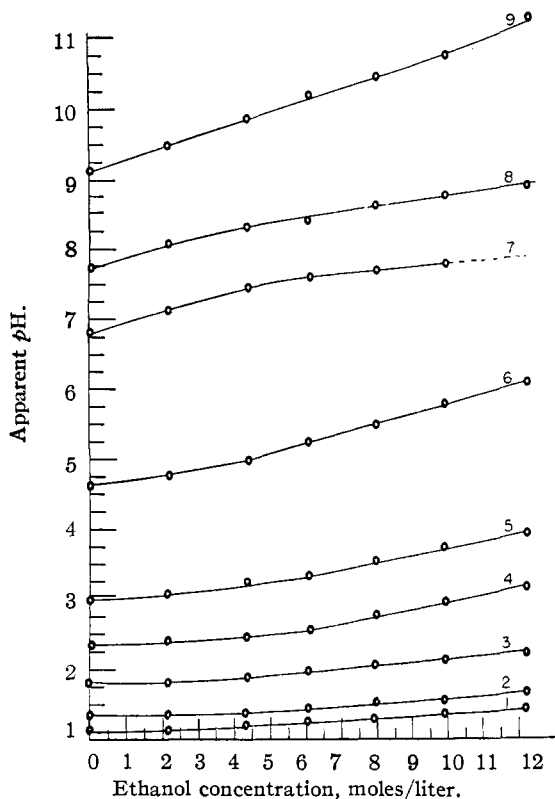


Fig. 2.—Apparent  $pH$  as a function of solvent composition. Curve numbers refer to buffer numbers in Table II.

The  $pH$  values are therefore designated as "apparent"  $pH$  numbers.

The curves of Fig. 2 show the effect of ethanol on the  $pH$  values of the nine buffers studied. It is seen that each of the curves for the acidic buffers undergoes an increase in slope after the addition of a certain amount of ethanol while those for the buffers near the neutral region tend to decrease in slope after the initial additions. The curve for the basic buffer is approximately linear over the entire range. The slopes of the curves beyond their inflection regions increase with increasing original  $pH$  of the buffers through the acid region, decrease in the neutral region and increase again in the case of the basic buffer. It will be noted that the more acidic buffers will tolerate considerable ethanol without serious effect on  $pH$  while the buffers of higher original  $pH$  are affected by relatively low concentrations.

The effect of ethanol on the half-wave potentials in the reduction of *p*-nitroaniline in these buffers is given in Fig. 3. It is seen that the potentials are shifted strongly to more negative values. In the acidic buffers the presence of about 2 to 3 *M* ethanol has little effect but beyond this concentration the curves increase sharply in slope and proceed linearly, the slopes increasing with increasing original  $pH$  of the buffers. In the neutral and basic buffers 2 *M* ethanol has a considerable effect but the slopes

of the main portions of the curves tend to decrease with increasing original buffer  $pH$ .

**Effect of Ethanol on Diffusion Currents.**—The diffusion currents obtained in each buffer in the various solvent media are given in Table II. In all cases the values decrease with increasing ethanol, pass through a flat minimum at 8 to 10 *M* ethanol, and then tend to increase. This behavior is graphically illustrated in Fig. 4 where the diffusion currents in 0.1 *N* hydrochloric acid and in the acetate buffer (no. 6), are plotted as a function of solvent composition. In the case of these two media, it was possible to extend the experiments to higher ethanol content (14.66 *M*) and thus better illustrate the increase in  $i_d$  beyond the minimum.

**Effect of Varying  $pH$  on Half-Wave Potentials, Diffusion Currents and Capillary Characteristics in Each Solvent Medium.**—Plots of half-wave potential *versus* apparent  $pH$  (Table II) in each of the seven solvent media are linear over the entire  $pH$  range studied in water and in 2.17, 4.34 and 6.08 *M* ethanol. In the solvents richer in ethanol the relation is linear up to an apparent  $pH$  of about 8 beyond which point the curves undergo a decrease in slope. Empirical equations for the variation of half-wave potential with  $pH$  in the various solvent media are given in Table III.

In water and 2.17 *M* ethanol the diffusion currents show a slight initial increase with increasing  $pH$  (Table II). In each solvent medium richer in ethanol the diffusion currents are nearly constant over the entire  $pH$  range, no appreciable initial rise occurring.

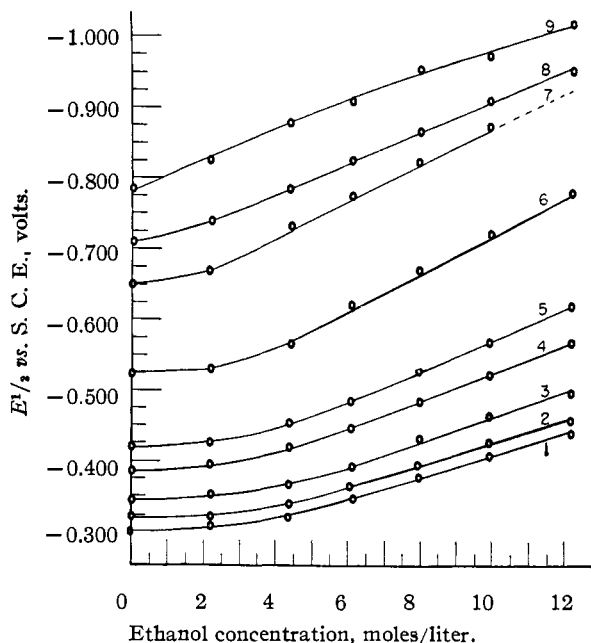


Fig. 3.—Half wave potential as a function of solvent composition:  $5.4 \times 10^{-4}$  *m* *p*-nitroaniline in nine buffers. Curve numbers refer to buffer numbers in Table II.

TABLE II  
 DIFFUSION CURRENTS  $-(5.4 \times 10^{-4} M p\text{-NITROANILINE})$ 

Buffer no. <sup>a</sup>	$\rho\text{H}$ in $\text{H}_2\text{O}$	Ethanol concentration, moles/liter							
		0	2.17	4.34	6.08	7.95	9.92	12.21	14.66
1	1.09	10.7	9.55	8.40	7.65	7.20	7.20	7.35	8.05
2	1.34	11.17	9.60	8.32	7.60	7.35	7.20	7.55	
3	1.79	11.30	10.00	8.50	7.65	7.35	7.40	7.85	
4	2.32	11.50	10.10	8.50	7.60	7.40	7.40	7.60	
5	2.98	11.50	10.10	8.50	7.65	7.25	7.20	7.65	
6	4.62	11.35	9.95	8.45	7.65	7.25	7.30	7.88	8.55
7	6.80	11.30	10.30	8.65	7.73	7.30	7.43	..	
8	7.72	11.40	10.20	8.55	7.70	7.35	7.30	7.85	
9	9.12	11.65	10.25	8.60	7.80	7.40	7.30	8.05	

<sup>a</sup> 1, 0.1 *m* HCl; 2, 0.05 *m* HCl, 0.05 *m* KCl; 3, 0.017 *m* HCl, 0.033 *m* KCl; 4, 0.04 *m* HCl, 0.06 *m* KCl, 0.06 *m* glycine; 5, 0.02 *m* HCl, 0.08 *m* KCl, 0.08 *m* glycine; 6, 0.1 *m* HAc, 0.1 *m* NaAc; 7, 0.025 *m* KOH, 0.05 *m*  $\text{KH}_2\text{PO}_4$ ; 8, 0.032 *m* KOH, 0.036 *m*  $\text{KH}_2\text{PO}_4$ ; 9, 0.03 *m* KOH, 0.07 *m* KCl, 0.06 *m*  $\text{H}_2\text{BO}_3$ .

TABLE III

EQUATIONS FOR THE POLAROGRAPHIC WAVE AND  $\alpha$  VALUES  
 $(5.4 \times 10^{-4} M p\text{-NITROANILINE IN VARIOUS SOLVENT MEDIA})$

Medium	Equation	Valid $\rho\text{H}$ range	$\alpha^a$
Water	$E_{1/2} = -0.244 - 0.061 \rho\text{H}$	1 to 9	0.83
2.17 <i>M</i> Ethanol	$E_{1/2} = -0.244 - 0.062 \rho\text{H}$	1 to 9.5	.81
4.34 <i>M</i> Ethanol	$E_{1/2} = -0.250 - 0.064 \rho\text{H}$	1 to 9.8	.78
6.08 <i>M</i> Ethanol	$E_{1/2} = -0.270 - 0.066 \rho\text{H}$	1 to 9	.75
7.95 <i>M</i> Ethanol	$E_{1/2} = -0.293 - 0.068 \rho\text{H}$	1 to 9	.70
9.92 <i>M</i> Ethanol	$E_{1/2} = -0.308 - 0.072 \rho\text{H}$	1 to 8	.68
12.21 <i>M</i> Ethanol	$E_{1/2} = -0.332 - 0.074 \rho\text{H}$	1 to 8	.63

<sup>a</sup> Average for nine buffers.

The  $m^{2/3}t^{1/6}$  value of the capillary is practically independent of solvent composition and  $\rho\text{H}$ . In all solutions, except those comprising the most basic buffer (no. 9), this value is  $1.95 \pm 0.01$   $\text{mg.}^{2/3}\text{sec.}^{-1/2}$ . In buffer 9 a somewhat lower average value of  $1.90 \pm 0.01$  is observed.

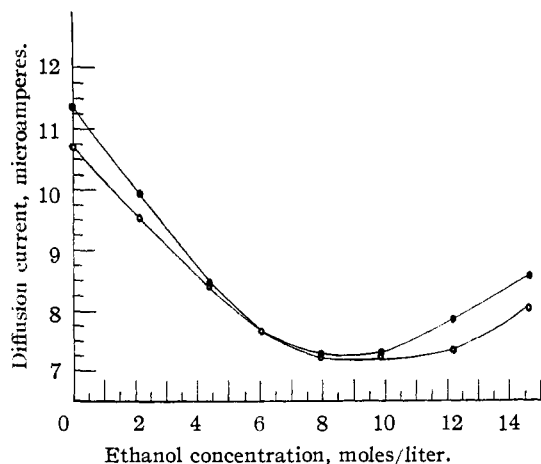


Fig. 4.—Diffusion current as a function of solvent composition:  $5.4 \times 10^{-4} M p\text{-nitroaniline}$ : ●, buffer no. 6 (HAc-NaAc); ○, buffer no. 1 (0.1 *N* HCl).

**Effect of Ethanol on the Potential-Current Relationship at Points on the Polarographic Wave.**—Plots of  $\log i/(i_d - i)$  versus cathode potential at points on the waves yield straight lines for all polarograms in all solvent media

and the potential at which  $\log i/(i_d - i) = 0$  coincides with the measured half-wave potential. The values of  $n$  in the usual expression

$$E = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_d - i}$$

however, as determined from the slopes of the log plots<sup>12</sup> are not integral but are always less than 1. The equation for the waves therefore, takes the form

$$E = E_{1/2} - \frac{0.059}{\alpha} \log \frac{i}{i_d - i}$$

where  $\alpha$  is fractional. The  $\alpha$  values as determined from the slopes of the log plots are practically independent of buffer composition in a given solvent medium but decrease with increasing ethanol concentration as indicated in Table III.

### Discussion

The general equation for the polarographic waves experimentally established in this reduction is of the form which has been found to hold in several irreversible organic reductions.<sup>13</sup> Although numerous theories have been advanced, the mechanism of the electrode reaction in such reductions has not been established. For this reason, and because of the many variables involved, no theoretical interpretation of the effect of ethanol on the half-wave potentials and the slopes of the waves will be attempted.

The variation in the magnitude of the  $\rho\text{H}$  increment produced by the addition of a given quantity of ethanol to each of the nine buffers is attributed mainly to the variable effect of this solvent on the dissociation of the various buffer acids. A similar variation was observed by Smith,<sup>14</sup> who determined  $\rho\text{H}$  values for several buffers in water and in 50% ethanol solutions. Investigations of the effect of ethanol on the dissociation of various acids are reviewed (through 1937) by Kolthoff and Rosenbloom in their monograph "Acid-Base Indicators."<sup>15</sup> There are also

(12) Ref. 2, p. 145.

(13) Ref. 2, p. 195.

(14) R. B. Smith, *J. Am. Pharm. Assoc.*, **17**, 241 (1928).

(15) Kolthoff and Rosenbloom, "Acid-Base Indicators," The Macmillan Co., New York, N. Y.

more recent investigations too numerous to list here. As might be expected the effect is slight in the case of strong acids but the dissociation constants of weak acids may be  $10^4$  to  $10^6$  times smaller in absolute ethanol than in water.<sup>16</sup>

**Diffusion Current Data and Calculation of Diffusion Coefficient.**—The diffusion current behavior illustrated in Fig. 4 may be attributed mainly to the effect of the viscosity of the medium on the diffusion coefficient. No viscosity data for the electrolyte solutions studied are available but if the viscosities of water-ethanol mixtures<sup>17</sup> are plotted against ethanol content, the curve shows a flat maximum over a region coinciding roughly with that of the minimum in the curves of Fig. 4. A similar effect was observed by Pasternack and Halban in the reduction of two ketones<sup>4</sup> and by Zlotowski and Kolthoff in the reduction of barium and strontium.<sup>3</sup>

The electroreduction of *p*-nitroaniline at a mercury electrode has been found to involve 6 electrons.<sup>18</sup> Assuming  $n = 6$  in the Ilkovic equation, it is possible to calculate the diffusion coefficient ( $D$ ) for the *p*-nitroaniline molecule from the polarographic data. In the aqueous phosphate buffer of *pH* 6.8 (no. 7, Table II), such a calculation yields a value of  $D = 8.79 \times 10^{-6}$  cm.<sup>2</sup>sec.<sup>-1</sup>. No data permitting a direct calculation of a diffusion coefficient value for this molecule could be found in the literature; an approximate value can be obtained, however, by assuming, as suggested by Kolthoff and Lingane,<sup>19</sup> that the required diffusion coefficient is equal to that of an organic ion of similar size and

(16) Kolthoff and Rosenbloom, ref. 15, p. 97.

(17) "Handbook of Chemistry and Physics," 24th ed., Chem. Rubber Co., Cleveland, O., 1940.

(18) Glasstone and Hickling, "Electrolytic Oxidation and Reduction," D. Van Nostrand Co., New York, N. Y., 1936, p. 204.

(19) Ref. 2, p. 51.

shape for which conductivity data are available and applying the equation

$$D^{\circ} = 2.67 \times 10^{-7} (\lambda^{\circ}/\text{valence})$$

Thus, the diffusion coefficient for the *p*-amino-benzoate ion, for which  $\lambda^{\circ} = 32$  mhos.,<sup>20</sup> is  $8.54 \times 10^{-6}$  cm.<sup>2</sup>sec.<sup>-1</sup>, a value in good agreement with that calculated from the polarographic data above and tending to confirm the assumption that six electrons are indeed involved in the reduction. Using the value  $n = 6$ , together with the  $m^{1/2}i^{1/2}$  values given above, and applying the Ilkovic equation, values for the diffusion coefficient,  $D$ , in all buffer solutions studied can be obtained from the data of Table II.<sup>21</sup>

### Summary

1. "Apparent" *pH* values have been determined for a series of commonly used buffer systems in water and 6 ethanol-water mixtures and the polarographic reduction of *p*-nitroaniline in these buffers has been investigated.

2. The Ilkovic equation has been shown to hold for the reduction and evidence that 6 electrons are involved has been given.

3. Equations relating half-wave potentials to apparent *pH* in each solvent medium have been given.

4. Data showing the effect of ethanol on (a) the equation for the polarographic waves, (b) the magnitude of the half wave potential and (c) the various terms in the Ilkovic equation have been presented and discussed.

5. The polarographic data given affords a means of obtaining diffusion coefficient values for *p*-nitroaniline in the solutions studied.

(20) "International Critical Tables," Vol. VI, p. 278.

(21) Such calculations will of course involve the assumption that ethanol does not affect the validity of the Ilkovic equation or the value of  $n$ .

CHAPEL HILL, N. C.

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## The Ultraviolet Absorption Spectra of Alkoxy- and Hydroxybenzils

BY NELSON J. LEONARD, RICHARD T. RAPALA,<sup>1</sup> HERSHEL L. HERZOG<sup>2</sup> AND ELKAN R. BLOUT

The yellow color of glyoxal and benzil was contrasted by Robinson<sup>3</sup> with the absence of color in ethyl oxalate and crystalline 4,4'-diethoxybenzil. The difference was explained on the basis that ethyl oxalate possesses a neutralized system (an electron-donating group attached to an electron-accepting group) and that the ethoxyl

groups in 4,4'-diethoxybenzil have an influence on the diketone system of benzil through the benzene nuclei similar to that which obtains by direct union in ethyl oxalate. A quantitative comparison of the color of these compounds can be found in the determination of their absorption spectra.

The ultraviolet absorption maximum for ethyl oxalate<sup>4</sup> has been shown to lie at much shorter wave length than the maxima of glyoxal,<sup>5</sup> methyl-

(1) Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

(2) Present address: Department of Chemistry, University of Southern California, Los Angeles, California.

(3) Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London, 1932, p. 30.

(4) Scheibe, *Z. Elektrochem.*, **34**, 497 (1928), reported  $\lambda_{\text{max.}} = 250$  m $\mu$  and  $\log \epsilon = 1.35$  in methanol.

(5) Lüthy, *Z. physik. Chem.*, **107**, 285 (1923), reported  $\lambda_{\text{max.}} = 450$  m $\mu$  and  $\log \epsilon = 0.50$  in ethanol.