[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Polarographic Study of *o*-Phthalic Acid and Phthalates

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In connection with some preliminary studies of the reduction of certain unsaturated organic compounds at the dropping mercury electrode, it was observed that a potassium acid phthalate buffer solution gave a characteristic wave that was very noticeably altered with change in the *p*H of the solution or in the presence of multivalent cations such as barium, calcium, cadmium, aluminum or lanthanum. In unbuffered or poorly buffered solutions over a certain *p*H range the presence of multivalent cations may cause the appearance of three waves prior to reduction of the metallic ion, while in well-buffered solutions in the same *p*H range only two of the waves appear in the presence of these ions. In more strongly acidified solutions, of *p*H 1 to 2, a single wave due to the phthalate appears slightly prior to the hydrogen wave. The height of the wave is substantially that which might be accounted for by reduction of undissociated molecules of phthalic acid (or its anhydride), as inferred by comparison with cadmium and maleic acid waves taken at the same molar concentration as the phthalic acid and in the same polarogram. The diffusion coefficient for biphthalate ion calculated from the waves of phthalic acid agrees well with that calculated from conductance data.

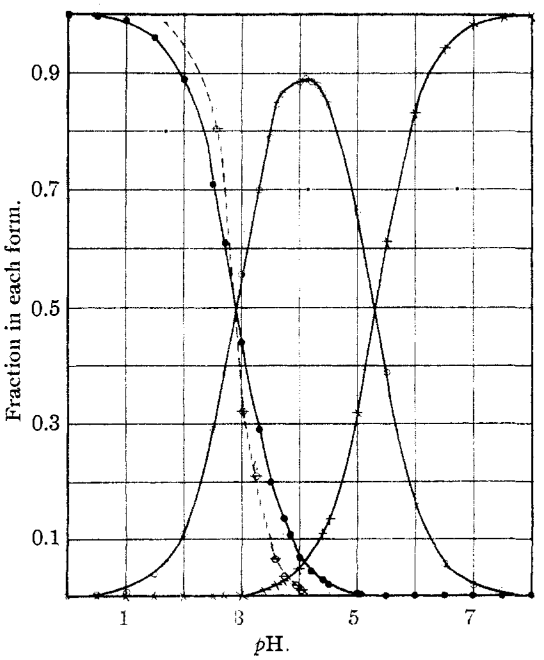

Fig. 1.—Fractions of one part of total phthalate in the various forms as a function of *p*H: solid circles, fraction present as undissociated molecules; open circles, fraction present as biphthalate ion; X-X-X, fraction present as phthalate ions, $C_8H_4O_4^=$; dotted line, polarographic values for fraction present as undissociated molecules.

At acidities higher than *p*H 1 the phthalic acid wave merges with the hydrogen wave. In the *p*H region in which two waves appear (from about *p*H 2.6 to 4.1) in the presence of barium ions, or other multivalent cations, the two wave-heights are not in the same ratio as the concentrations of undissociated molecules and biphthalate ions as calculated from the ionization constants.

The Calculated Ratios of the Forms of *o*-Phthalic Acid as a Function of *p*H.—The data in the literature regarding the first ionization constant of *o*-phthalic acid at 25° are quite concordant and range from 1.05×10^{-3} at ionic strength 0.03[1] to 1.3×10^{-3}.[2] The values for the second ionization constant are more divergent and are given as 3.1,[3] 5.2[4] and 5.4[5] at 25[6] and 4.6[7] and 5.8[8] $\times 10^{-6}$ at 20°. Values as high as 8×10^{-6} are to be found in certain reference books. For purposes of calculation the values $K_1 = 10^{-2.9}$ and $K_2 = 10^{-5.3}$ at 25° have been used to find the fraction of total phthalate in each of the forms: undissociated molecules, biphthalate ion and doubly charged anions.[8] The calculated values are summarized in Fig. 1.

A few of the critical numerical values are given in Table I. From Fig. 1 it can be seen that there should be a sharp transition from the behavior characteristic of the undissociated acid to that of the biphthalate ion in the range from *p*H 1.5 to 4. The transition between the two types of

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[1] W. R. Maxwell and J. R. Partington, *Trans. Faraday Soc.*, **33**, 670 (1937).

[2] R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 44 (1928). Other values are about 1.26×10^{-3} (G. F. White and H. C. Jones, THIS JOURNAL, **32**, 197 (1910)).

[3] E. E. Chandler, *ibid.*, **30**, 694 (1908); A. K. Datta and N. Dhar, *J. Chem. Soc.* (London), **107**, 824 (1915).

[4] W. R. Maxwell and J. R. Partington, *Trans. Faraday Soc.*, **33**, 670 (1937).

[5] H. V. Halban and G. Kortüm, *Z. physik. Chem.*, **A170**, 351 (1934).

[6] C. Morton, *J. Chem. Soc.*, 1401 (1928).

[7] M. Mizutani, *Z. physik. Chem.*, **118**, 327 (1926).

[8] The details of the method of calculation are as given by Michaelis in "Hydrogen Ions," translated by W. A. Perlzweig, Williams and Wilkins Co., Baltimore, Md., 1926, p. 55 ff.

TABLE I

FRACTIONS OF TOTAL PHTHALATE IN VARIOUS FORMS

*p*H	Fraction as molecules $C_6H_4(COOH)_2$	Fraction as biphthalate ion, $C_6H_4COOHCOO^-$	Fraction as phthalate ion, $C_6H_4(COO)_2^=$
1	0.987	0.0124	6×10^{-7}
2	.888	.1118	6×10^{-5}
3	.441	.556	0.003
3.6	.164	.820	.016
4.1	.0559	.889	.044
4.5	.021	.845	.134
5.0	.005	.663	.322
6.0	.0001	.166–	.834

behavior as observed polarographically falls into the *p*H range between 2 and about 4.1, as will be clear from the experimental observations which are summarized in the dotted line of Fig. 1. Between *p*H 4.1 and 4.7 waves due to phthalate vanish so that at *p*H 4.7 no distinct wave is observed even if barium chloride is present.

It would be expected that undissociated molecules of phthalic acid could diffuse to the dropping electrode and be reduced readily. The reduction of the anion may occur under certain circumstances in the reduction of dibasic acids, as has been pointed out by Schwaer[9] in the case of mesaconic acid, and by Vopicka[10] for fumaric and maleic acids. As in the case of inorganic anions, the addition of barium, calcium, lanthanum salts, etc., increases the probability that an anion such as the biphthalate ion will come into the reducing zone of the dropping mercury cathode since either ion pairs or ions like $BaHC_8H_4O_4^+$ may form, or dipoles may be induced in the anions so that the positive end of the dipole may be attracted to the cathode and thus facilitate reduction.[11]

Experimental

Apparatus and Materials.—A locally constructed polarograph closely similar to the Nejedly model of the Heyrovsky–Shikata instrument was used—most of the observations were recorded photographically.[12] A Leeds and Northrup Type P galvanometer of rated sensitivity 0.0009 microampere per mm. at 1 meter, 1060 ohms resistance and a 15.5 second period was used in conjunction with a critical damping 10,000 ohm Ayrton shunt made by the Shallcross Manufacturing Co., Philadelphia, Pa. An additional shunt in parallel with the galvanometer was used, on occasion, to make further settings possible. The polarographic drum was run at speeds adapted to the rather long galvanometer period. The galvanometer deflections, in millimeters, plotted against applied voltages gave straight lines for the shunt settings that covered the ranges used.

The majority of the observations in this paper were taken with a single capillary (no. 1). When a second one (no. 2) was used, conditions were adjusted so that it gave waves which were only 1% higher under like conditions than those obtained with the first. A third capillary (no. 3), for which the constant was considerably different, was used for the observations in Figs. 5 and 6.

The capillary constant, P/m, was obtained by weighing the mercury delivered in air at various pressures, as described by O. H. Müller.[13] The significant data are:

Capillary	P/m	P, cm.	Drop time in 0.1 M $BaCl_2$, sec.	$m^{2/3}t^{1/6}$, in mg.$^{2/3}$ sec.$^{-1/2}$
No. 1	12.90	27.7	3.20	2.009
No. 2	14.86	32.1	3.33	2.028
No. 3	22.65	34.1	3.32	1.604

The galvanometer was calibrated by the method described by Kolthoff and Lingane.[14]

The various solutions that were prepared were measured with precise analytical technique, accurate in general to within 2 parts per 1000. Polarographic blank tests were run upon the various supporting solutions, and when necessary, substances were recrystallized. Nitrogen from a cylinder was passed through alkaline pyrogallol, and when necessary through a solution similar to that under examination, and then into the polarographic cell in order to remove air. In general a mercury anode was used, and measurements of its potential relative to a calomel half-cell were made frequently. *p*H measurements were made with a Leeds and Northrup glass electrode *p*H meter of the research type. Resistance measurements were made with a conductivity bridge from the Industrial Instrument Co., with built-in 1000 cycle source and electron-ray tube balancing device. The known resistance of the shunt and galvanometer systems as well as that of the cell was taken into account in calculating the *IR* deduction from the applied voltage for the analysis of waves.

Acetic acid–sodium acetate buffers were used in the range *p*H 3.6–4.7. The first (3.6) is rather poorly buffered, but the concentration of buffer salts was in general 70–100 times that of the reducible substance. Citric acid–sodium phosphate buffers were used below *p*H 3.6.

Maxima, encountered in the waves that were formed in the presence of barium and phthalate ions between *p*H 2.6 and 4.1 may be suppressed by the addition of 0.05 ml. of methyl cellulose (0.2% dispersion in water) per 10 ml.

Experiments in Poorly Buffered or Unbuffered Solutions.—A qualitative picture of the effect of salts upon the character of the waves is given in Fig. 2.

In Fig. 2 curve a, only the first wave of the phthalate is shown. Curves a and b of Fig. 3 show that there is a second wave which is of greater

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[9] L. Schwaer, *Coll. Czechoslov. Chem. Commun.*, **7**, 326 (1935).

[10] E. Vopicka, *ibid.*, **8**, 349 (1936).

[11] For detailed discussions of mechanisms of the reduction of anions see Vopicka, *loc. cit.*; also M. Tokuoka, *Coll. Czechoslov. Chem. Commun.*, **4**, 444 (1932).

[12] J. Heyrovsky, "Physikalische Methoden der analytischen Chemie," Vol. II, p. 260 ff., Akadem. Verlagsgt., Leipzig, 1936. For a description of the experimental assembly that was used, see N. H. Furman, C. E. Bricker and E. B. Whitesell (article accepted for publication in *Ind. Eng. Chem., Anal. Ed.*), 1942.

[13] O. H. Müller, *J. Chem. Education*, **18**, 172 (1941).

[14] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 227–229.

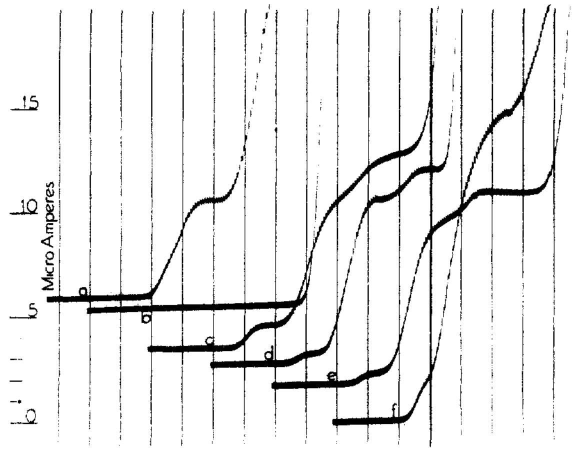

Fig. 2.—Polarograms of phthalate in unbuffered solutions; the ordinates are spaced at intervals of 0.12 volt, the ordinate nearest to the letter for each curve being at 1.32 volt applied: Curve a, potassium acid phthalate, 0.01 *M*; Curve b, barium chloride, 0.1 *M* tested for impurities; Curve c, potassium acid phthalate 0.00333 *M*, potassium chloride 0.0333 *M*, *p*H 4.25, anode 0.0978 v. relative to saturated calomel cell; Curve d, like c except that solution is 0.0333 *M* in barium chloride instead of potassium chloride, *p*H 3.92, mercury anode 0.0928 relative to saturated calomel cell; Curve e, like c but with same molar concentrations of calcium chloride instead of potassium chloride, *p*H 3.81, anode 0.0984 v. relative to saturated calomel electrode; Curve f, as in c except that 0.0333 *M* lanthanum chloride is present instead of potassium chloride, *p*H 3.25, anode 0.0963 v. relative to calomel half cell.

wave height than the first. Upon the addition of potassium chloride, barium chloride, and calcium chloride, respectively (curves c, d, e, Fig. 2), the height of the first wave is less than that calculated from the fact that the concentration of phthalate is one-third as great for cases c, d, and e as for a. This discrepancy is due partially to the fact that the migration current which in all probability contributed to the limiting current in curve a has been nearly eliminated in the remaining curves in Fig. 2. In the case of lanthanum, the *p*H of the solution is materially altered as compared with the other cases. The addition of gelatin tends to coalesce the vague wave at the upper parts of curves c, d, e and to diminish still further the wave at the bottom. This fact and the fact that the presence of air diminished the first wave to about one-fifth and the second to about two-thirds of the height in air-free solution makes it appear that both waves are probably of composite nature, involving reduction of hydrogen ion as well as various forms of the total phthalate. The fact that the addition of salts as supporting electrolytes increases the second wave is our principal reason for identifying this as essentially an anion wave.

For comparison of unbuffered solutions, the wave heights involving different concentrations and different sensitivity settings are summarized in Table II using the common basis of diffusion current per millimole per liter for each wave.

Table II

Diffusion Current, i_d, in Unbuffered Solutions

Expressed in microamperes per millimole per liter for the total phthalate concentration.

Substances present $KHC_8H_4O_4$ and:	Wave 1, "Molecule Wave"	Wave 2	Wave 3	Total i_d/millimole/liter	Date
$BaCl_2$	0.136	2.98	0.16	3.28	3/23/41
$BaCl_2$	.11	2.61	.34	3.06	3/21/41
$BaCl_2$	.16	2.56	.43	3.15	3/29/41
$BaCl_2$	.16	2.56	.43	3.15	3/29/41
$BaCl_2$ and air	.03	1.63	.48	2.14	3/29/41
$BaCl_2$ and gelatin	.03	.. 2.98	..	3.01	3/23/41
$CaCl_2$	.14	2.60	.30	3.04	3/29/41
$CaCl_2$	.14	2.44	.19	2.77	7/15/41
KCl	.24	2.20	.68	3.12	3/21/41
KCl	.33	1.87	.53	2.73	7/15/41

The results taken from curves of a single day's work (in general) show excellent reproducibility. There was no provision for thermostating so that results obtained at different times are not closely comparable. The total diffusion current per millimole per liter is less than half of the value that is obtained either by the reduction of phthalic acid at *p*H 1–2, or the total phthalate in well-buffered solutions at *p*H 3.6 or 4.1 with barium present.

The effect of the successive addition of small portions of acid to potassium acid phthalate solution is shown in Fig. 3 which is a tracing of curves taken photographically, but which were poorly spaced for comparative purposes.

In curves a and b the small waves due to phthalate are followed by a portion rising at about a 45° angle that is due to potassium and hydrogen. The addition of acid rapidly increases the first wave to a maximum (the wave is smaller in successive curves due to dilution) after which the second wave increases progressively and merges with the hydrogen wave. We believe that the first wave is substantially due to molecules alone as soon as the *p*H is about 2, and that the second wave is roughly proportional to the sum of the currents due to biphthalate ion and the hydrogen ion, especially if suitable cation concentrations are present.

Experiments in Well-Buffered Solutions.—The general range of phenomena in buffered and unbuffered solutions is shown in Fig. 4.

Solution e is poorly buffered and in addition con-

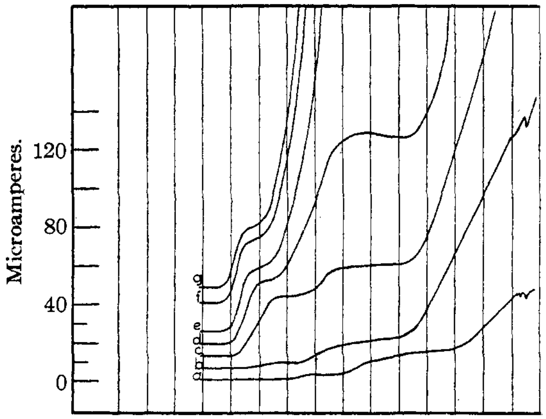

Fig. 3.—The effect of adding acid upon the phthalate wave: Curve a, 0.005 M potassium acid phthalate (4 ml.); Curve b, 0.15 ml. of 0.1 M potassium chloride added to solution from a; Curves c, d, e, f, g, the effect of adding successive 0.15-ml. portions of 0.1 M hydrochloric acid to the solution from b. All curves start at 1.20 volts applied and the spacing between ordinates is 0.15 volt. The displacement of the first wave in this and other figures (2) is caused by the changing concentration of chloride and of hydrogen ions.

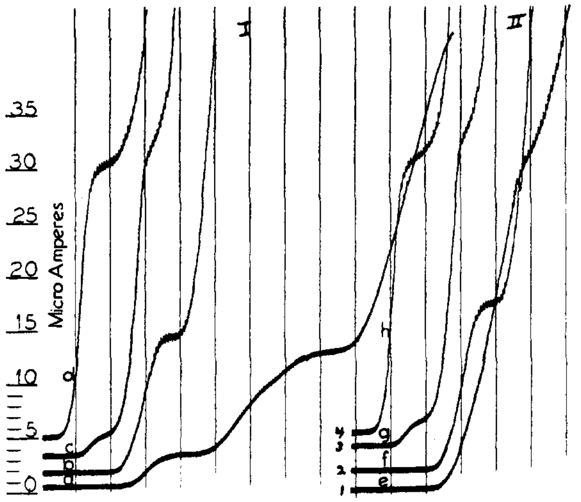

Fig. 4.[a]—The reduction of phthalate under various conditions: Curves a, b, c, d, reduction of 0.00333 M potassium acid phthalate in various media, a in water, b at pH 3.6 with no barium added, c at pH 3.6 and 0.033 M barium chloride and 0.05 ml. of 2% methyl cellulose, d at about pH 2.1 with hydrochloric acid; Curves e, f, g, h, reduction of 0.0033 M phthalic acid, e in water, f in 3.6 buffer, g in 3.6 buffer 0.033 M in barium chloride, h at pH about 2 with hydrochloric acid present. The letters for each curve are nearest to the ordinate for 1.35 volts applied and the spacing between ordinates is 0.15 volt.

[a] The faint parts of the lines of the galvanometer trace in Figs. 4 and 8 have been traced over with drawing ink and dots have been put on in ink in Figs. 6 and 7 to enable the eye to follow the faint parts of the lines.

tains no foreign electrolyte to reduce the migration current. The difference in the heights of the waves in curves b and f is accounted for by difference both in pH and in potassium ion content. Curves c and g demonstrate the reproducibility of the two waves in presence of barium ion with good buffering, while d and h show the reliability of the process at a pH close to 2.

The effect of adding small successive portions of dilute barium chloride solution to a well buffered solution of potassium acid phthalate is shown in Fig. 5. The first wave diminishes progressively and the beginning of an inflection for the higher second wave can be observed.

The phthalate concentration is but slightly changed by the dilution, varying from 3.33 to 3.10×10^{-3} M. The addition of much less (about one-seventh) than an equimolar concentration of barium chloride reduces the phthalate first wave to about one-half of its original height. With excess of 5 to 10 fold of barium as observed on other polarograms (*e. g.*, curve c, Fig. 4), the limiting effect is to diminish the first wave to about one-sixth of the original value in the 3.6 buffer with barium absent. The data from Fig. 5 are

Concn. of barium chloride $M \times 10^5$	..	3.33	6.66	9.99	13.2	16.4	32.2	47.6	62.5	3310[a]
Current, microamps.	10.0	8.52	8.10	7.53	7.22	6.80	5.95	4.61	4.37	1.8
Diminution in current, microamps.	..	1.48	1.90	2.47	2.78	3.20	4.05	5.39	5.63	8.2

[a] Value from another polarogram.

In addition to the experiments shown in Fig. 5, similar polarograms were made using potassium chloride, barium acetate, calcium chloride, and lanthanum chloride instead of barium chloride. The *normalities* of the salts added were kept constant in each series of experiments. With potassium chloride, the first wave was not reduced in height and there were no signs of the formation of the second wave. Barium acetate gave identical results with those of barium chloride. Therefore, this effect must be a cation effect. Although calcium chloride gave less diminution of the first wave in every case than barium chloride, and although the appearance of the second wave did not occur until after the third addition of calcium chloride, the effect of the addition of calcium chloride is essentially the same as that for barium chloride. Topp and Davies[15] in their study of the calcium and barium salts of dicarboxylic acids found that the barium salts are all

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(15) N. E. Topp and C. W. Davies, *J. Chem. Soc.*, 87 (1940).

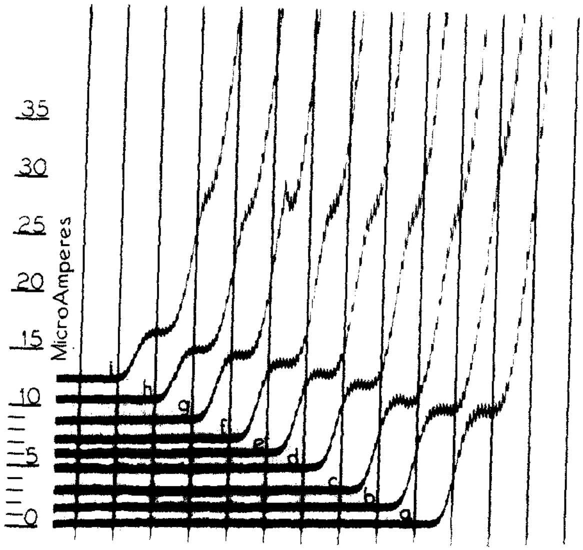

Fig. 5.—The effect of adding small successive amounts of barium chloride: each curve is lettered nearest to the ordinate for that curve corresponding to 1.50 volts applied. The spacing is 0.15 volt between ordinates. This polarogram was made with capillary no. 3: Curve a, for 30.00 ml. of a solution 0.00333 M in potassium acid phthalate and 0.333 M in buffer of pH 3.6; successive additions of 0.100 ml. of 0.01 M barium chloride were made before taking curves b, c, d, e, and f, then 0.500 ml. of the barium chloride solution was added and curve g taken, then 0.500 ml. more of the barium chloride solution and 0.30 ml. of methyl cellulose were added and curve h taken, while 0.500 ml. of barium chloride solution was added between h and i.

stronger electrolytes than the corresponding calcium salts. This probably accounts for the somewhat smaller effect of calcium chloride on the phthalate waves. The first addition of lanthanum chloride (2.19×10^{-5} M with lanthanum chloride) causes the first wave to be decreased nearly 50%. Successive additions of lanthanum chloride continue to decrease the height of this wave slowly.

In every case where the addition of cations causes a reduction in the height of the first phthalate wave, the wave height finally reaches a constant value when enough cation has been added to make its concentration several times that of the phthalate.

In addition, methyl cellulose has been found to reduce the height of the phthalate wave when an excess of bivalent cations is absent. The effect of methyl cellulose on the first wave is not so great as the cation diminution and it does not cause the appearance of a second wave which is characteristic of the cation effect. Because methyl cellulose causes this peculiar effect is further proof that the phthalate wave in the absence of excess barium chloride is a composite wave on which little quantitative interpretation can be placed.

Titration Experiments.—Both conductance and potentiometric titrations of potassium acid phthalate solutions with barium chloride were made to see whether there was any pronounced tendency toward complex ion formation. It was found that the conductance of mixtures of barium chloride and 0.01 M potassium acid phthalate in water was slightly less than the additive conductance found experimentally from similar mixtures of pure water and each salt singly. The effect was a decrease of the order of 4% in conductance in the range up to 1 mole of barium chloride to 2 moles of the phthalate. Beyond this point the difference between additive and directly determined conductances fell off gradually to about 1% when the ratio was 5 moles of barium and 1 mole of phthalate.

The course of pH was followed with a glass electrode during the titration of 0.01 M potassium acid phthalate with 0.1 M barium chloride. There was a gradual decrease of pH amounting to 0.15 unit at a 1:1 molar ratio of the two substances and to a total of 0.33 pH unit at a 1:2 molar ratio. With more concentrated phthalate (0.1 M) the corresponding change was 0.5 unit at 1:1 molar ratio. The dilution effect was measured independently and amounted to 0.05 and 0.06 pH unit for the total dilution. With the more concentrated solution a precipitate of an acid barium phthalate was formed. This substance after being washed sparingly and dried, contained 0.390, 0.391, 0.394% of titratable hydrogen and 29.68 and 29.2% of barium; ratio 1.1 atoms of barium to 2 atoms of hydrogen. Various barium acid phthalates have been reported.[16] The two nearest to the above composition are $BaH_2(C_8H_4O_4)_2 \cdot H_2O$; calcd. Ba, 28.2 %; H, 0.415%; and the double salt $BaC_8H_4O_4 \cdot [10\ BaH_2(C_8H_4O_4)_2]$ containing 30.56% Ba and 0.407% titratable H. The precipitate obtained approximates more closely the composition of the double salt. In polarographic experiments the concentration of the phthalate was so small that the double salt did not form.

The use of a buffer 100 times as concentrated on a molar basis as the most concentrated phthalate solution and a barium concentration at least ten times that of the phthalate was intended to elimi-

(16) F. B. Allan, This Journal, 31, 1061 (1909

nate as far as possible irregular effects due to *p*H changes or variable effects due to the known effect of changing barium ion concentration upon the distribution between waves.

The effect of *p*H upon the reduction of *o*-phthalates with barium present is shown in Fig. 6. A polarogram similar to Fig. 6 was made without barium chloride between *p*H 2.80 and 4.21. When barium chloride is absent, only one wave, which declines in height as the *p*H increases, is obtained. This wave is considerably higher than the first wave obtained with barium chloride for the same *p*H value. Several i_d and *p*H values from the polarogram, which was recorded from solutions containing no barium chloride, are as follows: *p*H 3.46, i_d = 23 microamperes; *p*H 3.75, i_d = 8.6 ma.; *p*H 4.06, i_d = 1.5 ma.; *p*H 4.21, i_d = 0.77 ma. At *p*H 4.7 no well-defined phthalate waves are found but with barium there is a barely perceptible inflection in the rising portion of the curve. In a single experiment at *p*H 8, with and without barium present, the curve with barium present showed a slight truncation of the bend prior to the abrupt rise due to barium reduction. This incipient wave had a mid-point about 0.12 volt prior to the barium mid-point, but it was not conclusively identified as being due to phthalate reduction.

Good proportionality of total wave heights and concentrations is found at either *p*H 3.6 or 4.1 in curves taken under the same conditions, as is shown in the following data taken from a polarogram not reproduced here:

At *p*H 3.6:	Concn. phthalate $M \times 10^3$	3.33	1.665	0.833	Ratios 4:2:1
	Waves, mm.	84	42	22	4:2:1.05−
At *p*H 4.1:	Concn. phthalate $M \times 10^3$	1.98	3.31	Ratio 1.67−	
	Waves, mm.	47.5	79	Ratio 1.66+	

Owing to the complicated nature of the phenomena and the variability with slight changes in condition it is desirable to include a calibration curve on each polarogram. The data of observations taken over a period of two months without temperature correction, and with probable slight unobserved pressure changes and other experimental errors lead to a rather wide variation of i_d per millimole per liter. The presence of cadmium, maleic acid, potassium or other ions as well as barium and the compounds of the buffers changes the total wave heights. It was thought that a correction for probable reduction of hydrogen accompanying the second wave might make the results uniform, but this was found not to be the case for the buffers at 3.6 and 4.1. Typical data are collected in Table III.

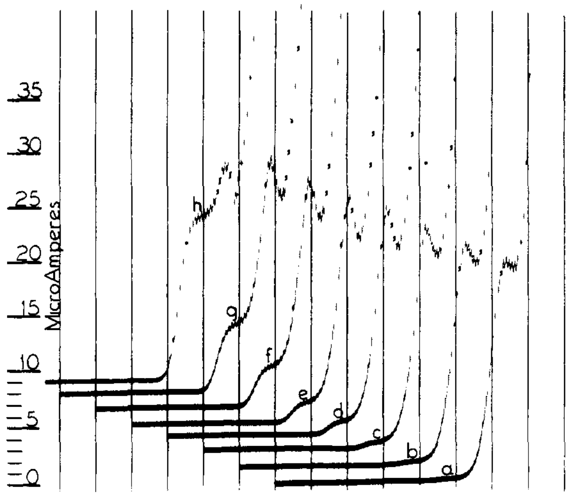

Fig. 6.—The effect of *p*H upon the phthalate reduction; each curve is lettered nearest the ordinate at 1.50 volts applied for that curve, ordinates being 0.15 volt apart; all solutions 0.00333 *M* with potassium acid phthalate and 0.033 *M* with barium chloride in 0.333 *M* buffer: Curve a, at *p*H 2.60; Curve b, *p*H 3.06; Curve c, *p*H 3.25; Curve d, *p*H 3.48; Curve e, *p*H 3.57; Curve f, *p*H 3.75; Curve g, *p*H 3.94; Curve h, *p*H 4.02; polarogram was made with capillary no. 3.

From the conductance data taken from "International Critical Tables" we calculate the diffusion coefficient in cm.^{2}/sec. $\times 10^5$ for biphthalate ion to be 0.80 using the Nernst relation, $D = RT\lambda_0/zF^2$, λ_0 being the limiting conductance of the ion, z its charge and F the faraday. Using this diffusion coefficient in the Ilkovic equation, and assuming that 2 electrons are required for the reduction, the calculated i_d/millimole/liter is 6.92 at 25°. If this is correct, the general tendency toward higher values, especially in complex mixtures, might be due either to changed diffusion coefficient, experimental error, or exaltation of the complex wave either by hydrogen reduction, or when maleic acid is present by reduction of the small fraction present as bimaleate ion along with the biphthalate ion.

The comparative heights for the cadmium, maleic acid and phthalate waves are shown at *p*H 3.6 and 4.1, respectively, in Fig. 7. The cadmium

TABLE III

VALUES OF i_d/MILLIMOLE/LITER FOR REDUCTION OF PHTHALATE UNDER VARIOUS CONDITIONS

Date	Phthalate Concentration $M \times 10^3$	(A) At pH 3.6 i_d first wave	i_d second wave	i_d total	Substance other than phthalate and buffer present in solution
4/22/41	3.33	0.45	5.84	6.29	$BaCl_2$
4/20	3.28	.49	6.43	6.92	$BaCl_2$
4/20	1.64	.49	6.43	6.92	$BaCl_2$
4/20	0.82	.49	6.75	7.24[a]	$BaCl_2$
5/1	3.33	.57	7.46	8.03	$BaCl_2$
5/1	3.33	.58	7.14	7.78	$BaCl_2$
4/24	3.31	.53	6.85	7.24	$BaCl_2$; potassium ion
4/22	3.31	.49	6.49	6.98	$BaCl_2$; potassium ion
5/1	3.306	.53	7.51	8.04	$BaCl_2$; potassium ion
4/22	2.50	.76	6.68	7.44	$BaCl_2$; Cd
4/24	2.50	.48	7.72	8.20	$BaCl_2$; Cd; maleic acid
5/24	2.50	.49	7.41	7.90	$BaCl_2$; maleic acid
5/24	2.00	.65	6.55	7.20	$BaCl_2$; Cd; K; maleic acid
5/26	2.00	.44	7.33	7.77	$BaCl_2$; Cd; K; maleic acid

[a] The smaller the phthalate concentration the greater the experimental error and the more it is multiplied in calculating i_d.

		(B) At pH 4.1 First wave			
4/19	1.995	less than 0.1		6.54	$BaCi_2$
4/19	3.32	less than 0.1		6.48	$BaCl_2$
4/19	3.33	less than 0.1		6.34	$BaCl_2$
5/5	3.08	less than 0.1		7.02	$BaCl_2$; K
4/5	2.50	less than 0.1		8.42	$BaCl_2$; maleic acid
4/5	2.50	less than 0.1		8.15	*No Ba;* K; Al; maleic acid
5/26	2.00	less than 0.1		7.92	$BaCl_2$; Cd; maleic acid

waves are 33 and 33.8 mm. (first wave), the maleic acid waves (second) are 41 and 39 mm. and the phthalate waves (sum for curve a) total 40 and 40 mm. The values of i_d/millimole/liter that we find for cadmium in these complex mixtures on a number of polarograms are 6.06, 6.20, 6.16, 6.26, 6.58, and 6.73 the last two being from curves *a* and *b*, respectively, in Fig. 7. When only potassium chloride is present we find 7.14. The last value, divided by $m^{2/3}t^{1/6}$ for the capillary gives 3.56 as compared with 3.51 found by Kolthoff and Lingane,[16a] and the theoretical value of 3.25.[16b]

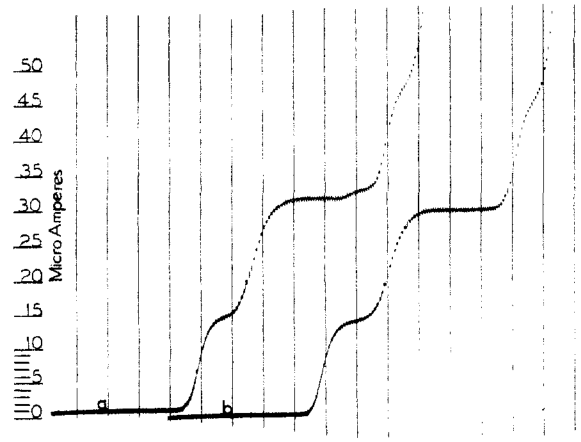

Fig. 7.—Comparative wave heights for cadmium, maleic acid and phthalic acid, the curves being lettered nearest to the 0.30 volt applied ordinate, and ordinates 0.15 volt apart: Curve a, solution 2×10^{-3} M in each of cadmium chloride, potassium acid phthalate, and maleic acid, at pH 3.6 with 0.0333 M barium chloride; Curve b, solution similar to Curve a but at pH 4.1.

The values of i_d for maleic acid on the two curves are (a) 8.15 and (b) 7.75. Other values found were: at pH 3.6, 7.24, and 7.87 and at pH 4.1 : 7.33; 7.07 and 7.07.

An experiment in the reproducibility of the reduction at about pH 1.5 with barium and at 3.6 without barium present is shown in Fig. 8. It will be noticed that at pH 3.6 the height of the wave is less than half of the height for the same concentration of phthalic acid at pH 1.5. This height is greater than corresponds to any probable concentration of the undissociated acid at pH 3.6 (Table I), or to the reduction of the hy-

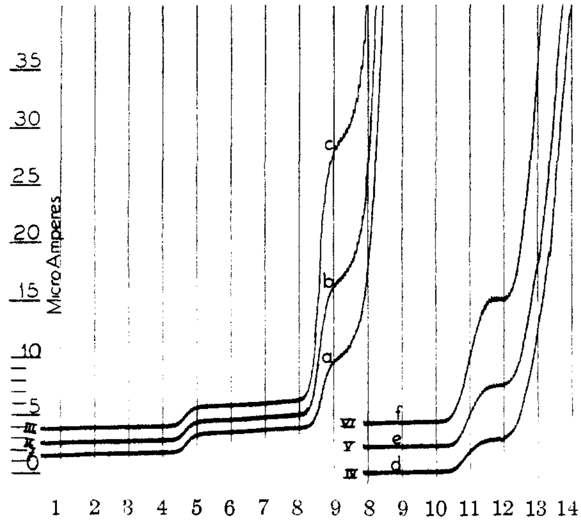

Fig. 8.—Wave heights at various concentrations, the curves being lettered nearest to the ordinate for 1.35 volts applied and the spacing of the ordinates 0.15 volt: Curves a, b, c, are for solutions of pH 1.48, 1.66 and 1.40, respectively, each containing 3 drops (0.15 ml.) of 0.01 M cadmium chloride, 3.22×10^{-2} M barium chloride, and, respectively, 0.805, 1.61 and 3.22×10^{-3} M in phthalic acid. The corresponding wave heights are 21, 42 and 82 mm. Curves for the same three concentrations of the acid in pH 3.6 buffer with no cadmium or barium are shown in curves d, e, and f, with wave heights 9.5, 19 and 38.5 mm.

[16a] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 79.

[16b] We wish to thank the reviewer of this paper for pointing out this agreement and for various constructive criticisms.

drogen ion and hence must be participated in by biphthalate ions.

Let us assume that the first wave obtained from buffered solutions between *p*H 2.6 and 4.1 containing an excess of barium chloride is due only to the reduction of undissociated molecules of phthalic acid. By taking the wave heights of the first waves from Fig. 6 and by assuming the reduction of phthalic acid to be 96% complete in curve c of Fig. 8 (assumption from Fig. 1) and by making the necessary conversion to get all i_d values in terms of one capillary, the percentage of total phthalate present as undissociated acid can be calculated for the various *p*H values. These values form the basis for the dotted curve in Fig. 1.[17]

Half-wave Potentials.—These have been derived in part by considering anode potential measurements *vs.* the saturated calomel electrode and a probable *IR* correction, but in the main have been derived from the values of the half-wave of cadmium added as a reference ion. A summary of the values is given in Table IV.

TABLE IV

HALF-WAVE POTENTIALS FOR THE PHTHALATE WAVES

Referred to the satd. calomel electrode, temp. approx. 25°.

*p*H	First, or "molecule" wave, volt	Second wave (Ba present), volt
1.5	−1.19	....
2.9	−1.28	....
3.6	−1.32 −1.33 −1.33 −1.35 Av. 1.33	−1.48 −1.48 −1.49 −1.50 Av. −1.49
4.1	Approx. −1.39	−1.53 −1.54

As a rough check on these measurements, it was observed that the half wave potential for maleic acid was −0.93 at *p*H 4.1. Vopicka[10] gives −0.94 at this *p*H relative to the normal calomel electrode which corresponds to −0.966 relative to the saturated calomel electrode.

Analysis of Waves.—The several types of waves were carefully measured and the computed values of log $i/(i_d - i)$ were plotted against the potentials corresponding to the individual *i*-values. The potentials were derived from the applied voltages by making an *IR* correction. The values for 0.059/*n* showing the valence of the reduction were then taken from the reciprocals of the slopes of the lines.[18] The following values were found:

	0.059/*n*
Cadmium waves	0.031 0.035
Phthalic acid	0.033 at *p*H 1.5 0.048 at *p*H 3.6 (cadmium present)
(1) Potassium acid phthalate, *p*H 3.6	0.057 0.056 (single wave, no barium present)
(2) Potassium acid phthalate, *p*H 3.6	Up to half wave 0.053; upper half of wave 0.026; *barium present*
Maleic acid, *p*H 3.6	0.072 0.069

The values for the cadmium waves are higher than the theoretical so presumably the other values are also. The reduction of phthalic acid at *p*H 1.5 appears to have as near the theoretical value as does the cadmium. At *p*H 3.6 the reduction of the phthalic acid has a slope intermediate between that of a bivalent and an univalent process. With barium present at *p*H 3.6 there is a sharp break of the slope at the midpoint. This was observed to be very much more pronounced for potassium acid phthalate and barium with no added buffer, the value being 0.075 for the lower branch and about 0.2 for the upper branch. The slope for maleic acid is very far from the theoretical.

Discussion

The reduction wave for phthalic acid at *p*H 1–2 appears to conform to the standards of a bivalent process. There is no evidence that the process is reversible. The formation of the ***trans*** **δ**-3,5-dihydro acid occurs most readily in acetic acid solution upon reduction with sodium amalgam.[19] One of the 3,5 acids is said to be the chief product upon electrolytic reduction of *o*-phthalic acid.[20] It has not yet been shown in polarographic reductions which of the five dihydroacids or other possible products is formed. The reduction of phthalic anhydride in acid solution is stated to be unsuccessful by the electrolytic method, but possible at 70° in an alkaline solution.[21] The product is phthalide. On the contrary Delfino and Somlo[22] report success in the electrolytic production of phthalide from phthalic acid in neutral or slightly acid solution, with 90% yield. The conditions

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(17) As pointed out by the reviewer, due to the reduction of the undissociated acid, H_2A, if this is the process giving the first wave, the concentration of H_2A at the electrode surface becomes very small and the equilibrium $H^+ + HA^- = H_2A$ should be shifted to the right to produce more H_2A, thus giving a wave greater than that corresponding to the equilibrium concentration of H_2A in the bulk of the liquid, as was observed over part of the *p*H range. However, the presence of a high concentration of barium ion tends to inhibit the formation of undissociated acid because the authors observed that when barium chloride is added to potassium acid phthalate, for example, the *p*H becomes smaller.

(18) Heyrovsky and Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **7**, 198 (1935); *cf.* Kolthoff and Lingane, ref. 15, pp. 184–195.

(19) Bernthsen and Sudborough, "Organic Chemistry," D. Van Nostrand Co., New York, 1922, reprinted 1931, p. 498; based on work of A. Baeyer, *Ann.*, **269**, 147 (1892).

(20) F. Somlo, *Z. Elektrochem.*, **35**, 769 (1929).

(21) B. Sakurai, *Bull. Chem. Soc.* (Japan), **7**, 127, 130 (1932); C. A., **26**, 3996–7 (1932).

(22) P. Delfino and F. Somlo, through *C. A.*, **30**, 2855 (1939), from IX, *Congr. intern. quim. pura aplicada*, **4**, 360 (1934).

that are best for the polarographic reduction (*p*H 1–2) would appear to favor the formation of one of the dihydroacids rather than phthalide.

A few experiments were made with terephthalic acid or with sodium terephthalate. When 0.01 *M* sodium terephthalate was added to an equal volume of a buffer of *p*H 3.6, most of the acid precipitated but the curve showed a small wave (about 3 mm. = 0.4 microampere). At *p*H 8 either with or without barium present there was only a faint indication of a wave—so faint that it could not be ascribed to the terephthalate.

Summary

A polarographic study has been made of the reduction of *o*-phthalic acid and its salts over the *p*H range 1–8, and the following are the principal findings.

1. The distribution of total phthalate between the forms: undissociated molecules, biphthalate ions, and phthalate ions has been calculated from *p*H 0–8 and the polarographic results have been interpreted with reference to the theoretical distribution.
2. Three reproducible polarographic waves due to phthalate are produced in unbuffered solutions near *p*H 4 with multivalent cations present. In the absence of the latter, the first wave obtained is always of a composite nature.
3. Although the number of the waves and the heights of the waves obtained from phthalates depend on the *p*H of the buffer used, the wave heights from buffered solutions can be used for quantitative studies.
4. The effect of small successive additions of barium chloride, barium acetate, calcium chloride, and lanthanum chloride to well-buffered phthalate at *p*H 3.6 diminishes the first wave systematically but not linearly.
5. The amount of undissociated phthalic acid that is derived from the polarographic measurements agrees roughly with the theoretical distribution of the undissociated form as a function of *p*H (Fig. 1).
6. Approximate half wave potentials have been noted for the phthalate waves at various *p*H values.
7. The slopes of typical curves have been analyzed by constructing the plot of log $i/(i_d - i)$ against reduction potential. The reduction of the acid at *p*H 1–2 gives a graph of the same slope as cadmium. The other phthalate waves are apparently of composite nature. The maleic acid wave gives a graph that deviates from the theoretical slope.

PRINCETON, NEW JERSEY RECEIVED AUGUST 14, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Apparent Volumes of Individual Ions in Aqueous Solution[1]

BY KASIMIR FAJANS AND OLIVER JOHNSON

Introduction

The apparent molar volume of electrolytes at infinite dilution (Φ_0) is one of the properties which can be expected to be exactly additive for a given solvent at definite temperature and pressure. The partition of these values into the apparent volumes of individual ions is of special interest because this is the only kind of volume of individual ions to which exactly defined values can be assigned.

According to the wave mechanical picture of a free atom or ion, the density of its electron distribution diminishes asymptotically as a function of the distance from the nucleus[2]; thus it is not possible to assign a definite radius or volume to a free ion. Within a molecule, crystal, or solution, the electronic system of an ion interpenetrates that of the oppositely charged ions or of the solvent molecules. Therefore the partition of lattice distances or crystal volumes into ionic radii[2] or volumes[3] can be performed only when some appropriate definitions or assumptions are made.[4] The fact that interionic distances in molecules and crystals and the volumes of crystals show systematic deviations from additivity[5] leads to the same result. However, the value of the volume which an ion at infinite dilution adds to

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(1) Presented in part at the 102nd Meeting of the American Chemical Society, September 11, 1941.

(2) See, *e. g.*, L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940.

(3) W. Biltz, "Raumchemie der Festen Stoffe," Verlag Leopold Voss, Leipzig, 1934.

(4) See the criticism [K. Fajans, *Z. physik. Chem.*, **B24**, 125 (1934)] of Wasastjerna's derivation of ionic crystal radii.

(5) K. Fajans, *J. Chem. Phys.*, **9**, 281–283, 379 (1941).