Studies
on
Dissociation Constants

by

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Preface.

The work reported in this thesis was carried out at Glasgow University in the Physical Chemistry Department which is under the direction of Professor J. Monteith Robertson.

The author wishes to thank Dr. J.C. Speakman under whose guidance and encouragement the work was performed and the Department of Scientific and Industrial Research for a Maintenance Allowance for part of the time.

Sincere thanks are also due to the late Dr. J.C. James for his help and advice, especially with the section on conductivity.

H.S.D.

Summary.

In the first section the relation between solubility, pH and dissociation constant is applied to the determination of the dissociation constant of p-chloro-, p-bromo-aniline and benzidine by measuring the solubilities at various pHs. With p-chloro- and p-bromo-aniline the value found agreed well with that obtained by potentiometric titration of a solution of the substance, dissolved in standard hydrochloric acid, with caustic soda using a glass electrode. With benzidine the potentiometric titration was carried out successfully but difficulties were encountered in the solubility method.

The second and main section of the work is concerned with measuring the dissociation constant of benzoic acid in mixed solvents, viz. dioxan-water mixtures, by three independent methods:

a) With the conductimetric method it was necessary to make measurements on potassium benzoate and potassium chloride in order to obtain an accurate value of Δ_o , the conductivity at infinite dilution, for benzoic acid. pKs at 25°C. for benzoic acid in dioxan-water mixtures containing 0, 20, 30, 40 and 50% dioxan by weight were obtained by averaging results from measurements on dilute solutions and extrapolating those on more concentrated solutions.

b) E.M.F. measurements were made in the usual type of cell, employing silver-silver chloride and quinhydrone electrodes. Constant results were obtained in aqueous solution but the results in dioxan-water mixtures were less accurate owing to a drift in the E.M.F., presumed to be due to the decomposition of the quinhydrone. A hydrogen electrode was then used in place of the quinhydrone electrode and much more accurate results were obtained employing a platinum surface in the hydrochloric acid solutions and a palladium surface in the benzoic acid solutions.

c) The pHs of exactly half neutralised solutions of benzoic acid, obtained by using the crystalline acid potassium salt, were measured using a calomel reference half cell and a glass electrode in an apparatus designed to give as reproducible a liquid junction as possible. The pH scale was standardised using aqueous phthalate, borax and phosphate buffers and all measured pHs were referred to the standards in water.

A comparison of the methods of obtaining pK from pH measurements was made and extrapolation of a graph of apparent pK against ionic strength is recommended in all solvents used except water, where an average value was found to be satisfactory. There is an appreciable difference between the pK for benzoic acid in dioxan-water mixtures obtained by the pH method and by the conductimetric and E.M.F. methods and, in the discussion, an arbitrary correction, based on measurements of the pH of 0.01M hydrochloric acid in mixed solvents, is suggested in an attempt to improve the agreement. The change in pK with change in solvent is also considered and it is found that, in dioxan-water mixtures containing up to 50% dioxan, the increase in pK can be accounted for entirely by the increased solubility of the benzoic acid.

The <u>third section</u> reports conductimetric measurements of the electrolytic dissociation of magnesium sulphate in water, 10 and 20% dioxan, and 0.1, 0.25, 0.5M aqueous glycine solutions and of lanthanum ferricyanide in 0.1, 0.25, 0.5M aqueous glycine solutions. It is shown that a simple electrostatic explanation will account for the variation of dissociation constant with dielectric constant.

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Electrolytic dissociation has been the subject of much interesting work ever since Arrhenius developed his ionic theory and showed that it could account for electrolytic conductivity and for van 't Hoff's "i factor". Ostwald applied the Law of Mass Action to the equilibrium between the substance and its ions and so calculated the first dissociation constants.

These dissociation constants, calculated by Ostwald, took no account of ionic interaction but formed the basis for the studies which have led to our modern views on the process and extent of dissociation. That the nature and dielectric constant of the solvent have an effect was first suggested by Nernst (1) and Thomson (2) and shown by the work of Hantzsch (3) and others (4), and an explanation in the light of the Brönsted theory (5) was given by Hammett (6). Later, the influence of temperature on dissociation constants, especially in non-aqueous or mixed solvents, was recognised and comprehensive articles on this subject by Everett and Wynne-Jones (7) and by Dippy and Jenkins (8) have been published. A review article by Dippy (9) gives references to all the important work done up to 1941 in non-aqueous and partially aqueous solvents.

There are five general methods available for determining dissociation constants, based on measurements of

a) conductivity, b) emf, c) colour, d) kinetics, e) solubility. The first three methods are fairly generally applicable and give results of high accuracy but use of the last two is more restricted.

It has been claimed (10) that light absorption is the best method for estimating the dissociation constants of weak or moderately strong electrolytes because it is not highly dependent on corrections for the influences of solute ions and neutral molecules, whereas the conductivity method involves assumptions of variations of ionic mobilities. Freezing point, vapour pressure, osmotic pressure and emf methods assume relations between activities and concentrations and some emf methods have also the uncertainties of liquid junction effects. An accuracy of 0.1% in the determination of dissociation constants is stated (11) to be obtained by refined optical methods but general application is limited by two considerations, 1) in light absorption, one, at least, of the ions must absorb light or the complication of an indicator is necessary and the method is then less accurate; 2) in measurement of intensity of Raman radiation, the proportionality between the intensity and the concentration has been investigated for only a very few substances.

The conductivity method as used by McInnes and Shedlovsky (12) gives an accuracy of 0.04% in dissociation constant while Harned and his co-workers (13) claim the same accuracy for their sensitive emf method not involving liquid junctions. Both these methods, however, require specialised technique and expensive apparatus and involve much calculation so are not suited for ordinary use. For this, much use is being made of a glass electrode incorporated in a cell with a liquid junction and the loss of accuracy is compensated by the ease in handling. The use of a glass electrode in non-aqueous and mixed solvent has been much criticised (14,15) and quite large errors have been attributed to it, though, where the aqueous content of the solvent is fairly high, it does give steady and reproducible values (16) which are useful for purposes of comparison. References to recent work using a glass electrode in mixed and non-aqueous solvents are given in a review article by Riddick (17). Colorimetry using visible light and indicators is another rapid, though less accurate, method (the error is upwards of 2% depending on conditions (18)).

The solubility method is limited to substances which are easily separated and estimated quantitatively but is useful for substances which are too insoluble or too weakly dissociated to be suitable for other methods.

A list of references to determinations of dissociation constants in non-aqueous and mixed solvents, since 1941, is given, grouped according to the method of investigation used, conductivity 19-41, emf 21, 36, 42-56, colorimetry 50, 74-91, solubility, kinetics and others 92-104.

In solution, when a substance is in equilibrium with its ions

$$MA \rightleftharpoons M^+ + A^-$$

we can apply the Law of Mass Action and obtain the equilibrium constant

$$K = \frac{[M^+][A^-]}{[MA]} \quad - - - - (1)$$

[ ] indicates concentration.

which, in this particular case, is called the classical dissociation constant. After the introduction of the concept of activity by G.N. Lewis, the concentrations in (1) were replaced by the more accurate activities, giving the thermodynamic dissociation constant

$$K_{therm} = \frac{a_{M^+} \cdot a_{A^-}}{a_{MA}}$$

<u>a</u> is defined by

$$\mu_i = \mu_i^o + RT \log a_i$$

μ = chemical potential

and thus depends on temperature and on the standard state for which $\mu = \mu_0$. The more dilute a solution is the more it tends towards ideal behaviour, where the activity coefficient is 1. Therefore, as the concentration of solute tends towards zero, the activity coefficient tends towards 1, i.e., the activity coefficient of the pure solvent is 1.

Since the concentration of solute can be expressed as molarity, molality or mole fraction, there are three activity coefficients, f on the molarity basis, γ on the molality scale and f_x for the mole fraction. Since each activity coefficient is referred to infinite dilution on its own scale, they differ slightly and so there are three corresponding dissociation constants. In water the difference is negligible but may assume larger proportions in mixed solvents.

Effect of Solvent.

It was early discovered that the same electrolyte, dissolved to the same extent in different solvents did not have the same dissociation constant. This was attributed (1,2) to the fact that the force holding two charged particles together depends on the dielectric constant of the medium

$$F = \frac{q_1 q_2}{r^2 D}$$

and the greater the dielectric constant, the smaller the force and so the greater the dissociation. Experimental evidence for one electrolyte in solvents of the same type but different dielectric constants, e.g., the monohydric alcohols, agreed well but the rule was not generally applicable.

Born (105) considered that the difference between the activity of an ion in water and in another solvent could be calculated from the work done in charging a spherical ion in the two different solvents and obtained the equation

$$\log \gamma_o = \frac{121}{r}\left(\frac{1}{D} - \frac{1}{D^o}\right)$$

for the activity referred to water (γ_o) of an ion of effective radius r from a univalent electrolyte in a solvent of dielectric constant D at 25°C. D^o is the dielectric constant for water at the same temperature. Born's equation is an oversimplification in that it applies rigorously only when each ion can be considered as a separate, spherical unit apart from its surroundings (106). Even in dilute solutions, the ions can scarcely be considered as infinitely distant from each other and so some account must be taken of their interaction.

Like charges attract each other hence on a time average more ions of opposite sign than of similar sign will be found in the neighbourhood of any ion. Each ion can thus be considered as being surrounded by a "cloud" or "ion atmosphere" of oppositely charged particles. Debye and Hückel (107) calculated the size of this atmosphere and also the correction to be applied to the activity of an ion to account for it. They showed that the radius of the ionic atmosphere increases with decreasing ionic strength and with increasing dielectric constant and temperature. One of the assumptions made in developing this theory was that the ionic atmosphere is spherically symmetrical. This is valid so long as the ions are stationary but e.g. in conductivity measurements, this is not usually the case. Onsager (108) appreciated this fact and extended the Debye-Hückel equation to include the effects due to the distortion of the ionic atmosphere and the viscosity of the medium through which it was moving. The dissociation constants obtained by using this extended equation are more accurate but involve a considerable amount of calculation.

Though lack of knowledge of solvent correction makes the earlier results in non-aqueous solvent less accurate, Wynne-Jones (109) discovered that, with certain exceptions, a linear relationship exists between the relative dissociation constant of an acid, referred to benzoic acid for carboxylic acids, and to the pyridinium ion for cationic acids, and the dielectric constant of the medium, $\log K_R \propto \frac{1}{D}$. By extrapolation to infinitely high dielectric constant he obtained what he called the "intrinsic acid strength". The sequence of acid strengths obtained thus was the same as in water and it was concluded that water was not open to criticism as a medium for comparing acid strengths, although cases were known where the order of acid strength was changed on passing from one solvent to another. These, however, were regarded as exceptions and due to effects such as ortho-substitution (110). Intrinsic strengths are useful for relating acid strength to chemical constitution.

The solvents of the acids considered by Wynne-Jones were water, methyl alcohol and ethyl alcohol, and later work by Wooten and Hammett (111) in butanol and Minnick and Kilpatrick (112) in water, methyl alcohol and ethyl alcohol confirmed the relationship though Elliot and Kilpatrick (B3) and Harned (B4) found that results in dioxan-water mixtures disagreed. This was accounted for by assuming that the relationship was valid only for pure solvents of dielectric constant greater than 25.

Investigation (109,113) of the effect of the nature of the solvent revealed the fact that the "proton affinity" of the solvent plays a large part in determining the strength of acids. If a molecule of the solvent can compete successfully with the acid anion for possession of the proton, the dissociation constant is high but where the solvent molecule has little attraction for the proton the dissociation is small and depends mainly on the quantum forces holding the proton and anion together. Thus it was shown (20) that the attraction between the ions of the solute and the molecules of the solvent, i.e., the solvation of the ions, is important. In aqueous solution this solvation sheath is composed of water molecules and in partially aqueous solvents the ions are preferentially solvated by water molecules. As the proportion of non-aqueous constituent increases the composition of the sheath alters and, since the size of the solvent molecule is different from that of the water molecule, the effective size of the solvated ion changes with the solvent (114). This explains why Walden's Rule (115), which assumes that the size of the solvated ion is independent of the solvent, is only very approximate.

The proton affinity of several solvents was studied by Braude and Stern (116) who found that pure water has a very high proton affinity but water in a mixed solvent has an even higher one. This, they suggest, arises from the unusual quasi-crystalline state of liquid water. The proton in pure water is accommodated in the interstices and is equally bonded to the four neighbouring oxygen atoms but in partially aqueous solvent the hydrogen bonding of the water molecules is partly replaced by the weaker hydrogen bonding between organic molecules and the open tetrahedral structure becomes more close packed. The proton is then preferentially surrounded by water molecules which are more closely bound and so reduce the size of the solvation sheath. This results in an increase in the effective proton affinity of the water. As the proportion of organic solvent is increased the water sheath is gradually dispersed till each proton is bound to one water molecule and we have the H_3O^+ ion. At higher concentrations ($>$ 80%) of organic solvent the water begins to be replaced by organic solvent molecules and finally we have ions of the type ROH_2^+.

A recent paper by H.A. Ismailov (117) gives a table showing that the basicity (which is essentially the same as the proton affinity) of a solvent has a much greater effect on dissociation than dielectric constant though the latter cannot be disregarded completely. He proposes that this is due to the formation of an initial addition complex between the undissociated acid and the solvent molecules and that this complex then dissociates. Dissociation should therefore be represented

$$HA + M \rightleftharpoons AHM \rightleftharpoons A^- + HM^+$$

Cryoscopic evidence confirms the existence of addition complexes of the types AHM and AHM_2 for acids but only AHM for phenols in solvents containing hydroxyl groups but in other solvents both acids and phenols give only AHM. This explains the relatively greater increase in strength of acids compared with phenols in the first group of solvents. The differentiating action of solvents is thus due to differences in the constitution and polarity of the addition complexes. This explanation is interesting as it has already been noted that relative acid strength is a function of the acid and the medium (118) and that polar substituents affect the dissociation (119).

From the foregoing discussion it is obvious that, as yet, the process of dissociation is not fully understood but appears to vary according to the system. This presents a difficulty when we try to compare dissociation constants, especially when the solvent is different. The standard free energy change for any process is given by

$-\Delta G^{o} = RT \log K$ where K is the equilibrium constant. When the process is dissociation, K is the dissociation constant (by definition) and thus the figure we obtain as the dissociation constant includes not only the tendency of the substance to dissociate but also effects such as those due to the free energy of solvation of the ions produced. In the case of acids this is due almost entirely to the hydrogen ion and is virtually the proton affinity of the solvent which has been discussed already and is assumed to vary quite considerably. Braude and Stern (116), however, have shown that, in a mixed solvent, except when the proportion of water is low, the solvation is entirely due to water molecules so that no serious error is introduced in comparing dissociation constants in such solvents.

SECTION 1.

SOLUBILITY, pH and DISSOCIATION CONSTANT.

A sparingly soluble acid will increase in solubility as the pH value of the solvent is raised and conversely for a sparingly soluble base. Krebs and Speakman (A1) deduced a relationship between solubility, pH and dissociation constant based on this. The relationship enables solubility to be predicted at different pHs, if the dissociation constant is known, or alternatively, the determination of the dissociation constant from solubility measurements at different pHs.

The work done by Krebs and Speakman was on various sulphonamides (A1,A2) which are amphoteric substances, whereas the work done here has been almost entirely on basic substances.

Krebs and Speakman suggest this method of determining the dissociation constant to be suitable for substances too insoluble or too weakly basic ($K_b < 10^{-11}$) to be dealt with by ordinary means. The substances chosen for this study are p-chloroaniline, $K_b \approx 10^{-11}$, p-bromoaniline, $K_b \approx 10^{-11}$, and benzidine, solubility about 0.002 mol/litre and Ks about 10^{-10} and 10^{-11} respectively.

According to the Lowry-Brønsted theory a base is any substance which can accept a proton (A3,5). Thus on dissolving the base in water, which is amphoteric and here acts as a weak acid, we get

$$H_2O + B \rightleftharpoons BH^+ + OH^-$$

and the dissociation constant of B is given by

$$K_b = \frac{[BH^+]\;[OH^-]}{[B]} \quad \ldots\ldots\ldots \quad (1)$$

Similarly for the conjugate acid, BH^+

$$BH^+ \rightleftharpoons B + H^+$$

and

$$K_a = \frac{[B]\;[H^+]}{[BH^+]} \quad \ldots\ldots\ldots\ldots \quad (2)$$

thus

$$K_aK_b = \frac{[B]\;[H^+]}{[BH^+]} \cdot \frac{[BH^+]\;[OH^-]}{[B]}$$

$$= K_w \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Hence if K_w is known, by finding either K_a or K_b we can evaluate the other.

The stronger the acidity of the solvent, the greater is the tendency for the base to ionise and go into solution, so the solubility of a base which itself is sparingly soluble in water but whose salt is very soluble will increase with decreasing pH.

The solubility, S, at any pH is equal to the total concentration of base, i.e.,

$$S = [B] + [BH^+] \ldots\ldots\ldots \quad (4)$$

At sufficiently low hydrogen ion concentration S falls practically to $S_o = [B]$ and for a weak base K_b about 10^{-10} the solubility at pH 7 or more may be taken as S_o.

A more exact form of (1) is given by allowing for activities, giving

$$K_b = \frac{\{BH^+\}\ \{OH^-\}}{\{B\}}$$

$$= \frac{[BH^+]\ \{OH^-\}\ f_{BH^+}}{[B]\ f_B} \quad \text{when } f = \text{activity coefficient}$$

$$\therefore\ [BH^+] = \frac{K_b\ [B]\ f_B}{\{OH^-\}\ f_{BH^+}}$$

$$= \frac{K_b\ [B]\ f_B\ \{H^+\}}{K_w f_{BH^+}} \quad (\text{here taking } K_w = \{H^+\}\{OH^-\}\ )$$

$$= \frac{K_b\ [B]\ f_B\ \{H^+\}}{f_{BH^+} K_w}$$

substituting in (4)

$$S = S_o + K_b S_o \frac{f_B}{f_{BH^+}} \cdot \frac{\{H^+\}}{K_w}$$

Taking logarithms and putting $-\log \{H^+\} = pH$, $-\log K_b = pK_b$, $-\log K_w = pK_w$,

$$\log\left(\frac{S}{S_o} - 1\right) = pK_w - pK_b - \log \frac{f_{BH^+}}{f_B} - pH \quad \ldots \quad (5)$$

Or,
$$\log\left(\frac{S}{S_o} - 1\right) = \left(pK_a + \log \frac{f_B}{f_{BH^+}}\right) - pH \quad \ldots\ldots \quad (6)$$

$$= pK_a' - pH$$

pK_a' is thus not a true constant as activity varies with concentration.

This is of the form $y = mx + c$, whose graph is a straight line and when $y = 0$, $mx = -c$, or, applying it to our case, $m = -1$ and when $\log\left(\frac{S}{S_o} - 1\right) = 0$, $pH = pK_a'$, thus in the graph of $\log\left(\frac{S}{S_o} - 1\right)$ against pH, the line, which has gradient -1, cuts the pH-axis to make an intercept equal to pK_a' whence pK_b' can be calculated. This value differs from pK_b by $\log \frac{f_{BH^+}}{f_B}$ but this will be approximately constant and fairly small when a constant and low ionic strength is maintained. By making use of assumptions made in connection with the standardisation of pH in terms of the hydrogen ion activity, it can be estimated (A4,A5).

A diacidic base is considered as ionising in two stages

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$BH^+ + H_2O \rightleftharpoons BH_2^{++} + OH^-$$

K_{b1} is thus the same as K_b for a monoacidic base and

$$K_{b2} = \frac{\{BH_2^{++}\}\{OH^-\}}{\{BH^+\}}$$

If K_1 is the constant for the first stage of ionisation, be it acidic or basic, and the form which is the stronger acid will be the weaker base

$$\text{from (3),} \quad K_{a1}K_{b2} = K_w$$

$$\therefore \log K_{b2} = \log K_w - \log K_{a1}$$

$$\therefore pK_{b2} = pK_w - pK_{a1}$$

$$\text{and } pK_{b1} = pK_w - pK_{a2}$$

$$K_{a2} = \frac{\{H^+\}[BH^+]f_{BH^+}}{[B]\,f_B} \quad \text{and} \quad K_{a1} = \frac{\{H^+\}[BH_2^{++}]\,f_{BH_2^{++}}}{[BH^+]\,f_{BH^+}}$$

$$K_{a1}K_{a2} = \frac{\{H^+\}^2[BH_2^{++}]\,f_{BH_2^{++}}}{[B]\,f_B}$$

$$S = [B] + [BH^+] + [BH_2^{++}]$$

$$= [B] + \frac{K_{a2}[B]\ f_B}{\{H^+\}\ f_{BH^+}} + \frac{K_{a1}K_{a2}[B]f_B}{\{H^+\}^2\ f_{BH_2^{++}}}$$

$$\frac{S - S_o}{S_o} = \frac{K_{a2}f_B}{\{H^+\}}\left(\frac{1}{f_{BH^+}} + \frac{K_{a1}}{\{H^+\}f_{BH_2^{++}}}\right)$$

If $K_{a1} \ll \{H^+\}f_{BH_2^{++}}$, the second term is negligible compared with $\frac{1}{f_{BH^+}}$ and the equation is the same as that for a monoacidic base and if $K_{a1} \gg \{H^+\}f_{BH_2^{++}}$, $\frac{1}{f_{BH^+}}$ can be neglected and the equation becomes

$$\frac{S}{S_o} - 1 = \frac{K_{a1}K_{a2}f_B}{\{H^+\}^2 f_{BH_2^{++}}}$$

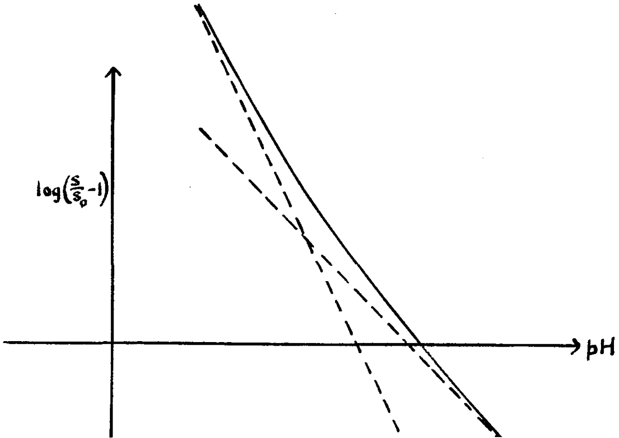
Substituting as before,

$$\log\left(\frac{S}{S_o} - 1\right) = 2pH - pK_{a1} - pK_{a2} + \log\frac{f_{BH_2^{++}}}{f_B}$$

or $\log\left(\frac{S}{S_o} - 1\right) = 2pH - pK'_{a1} - pK'_{a2}$

In this case the graph will have a gradient of -2 and will cut the pH-axis where $pK'_{a1} + pK'_{a2} = 2pH$.

In practice the graph is a curve whose extremities approach the theoretical slopes, as shown below,



and it is necessary to extrapolate back to find where the ideal graph would cut the axis.

The activity correction again can be estimated and at constant I, will be a constant.

For comparison of results pK_b was also found by an entirely independent method, viz. potentiometric titration. Owing to the weakness and insolubility of these bases in water, it was found more convenient to titrate the conjugate acid (anilinium type) rather than the free base. This means that again it is actually pK_a which is measured but this time the activity correction is applied during the calculation. The method of calculation for a monobasic acid is given by Glasstone (A6) and is briefly:

$$K_a = \frac{\{H^+\}\{B\}}{\{HB^+\}} = \frac{\{H^+\}[B]f_B}{[HB^+]\ f_{BH^+}}$$

Consider the base as being dissolved in excess of strong acid H^+X^- of total concentration <u>h</u>, and being titrated with strong base M^+OH^- of total concentration <u>b</u>, at any stage of the titration,

$h = [X^-]$ since HX is completely dissociated
$b = [M^+]$ " MOH " " "
$a =$ total base $= [B] + [HB^+]$

For electroneutrality, at every stage the number of positive charges must be equal to the number of negative charges, i.e.,

$$[M^+] + [H^+] + [BH^+] = [X^-] + [OH^-]$$

On the acid side of pH 7, $[OH^-]$ can be taken as negligible

$$\therefore \quad [BH^+] = h - b - [H^+]$$

$$[B] = a - [BH^+] = a - (h - b - [H^+])$$

$$\therefore \quad K_a \doteq \frac{\{H^+\}\,[a - (h - b - [H^+])]\,f_B}{(h - b - [H^+])\,f_{BH^+}} \quad \ldots\ldots \quad (7)$$

In this case it is sufficient to take $\{H^+\}$ and $[H^+]$ to be equal; and $f_B = 1$. f_{BH^+} (or f_1) is obtained from the Debye-Hückel Limiting Law

$$-\log f_1 = 0.5\sqrt{I} \qquad \text{where } I = \tfrac{1}{2}\sum cz^2 \qquad (107)$$

During titration of a cationic acid,

$$BH^+ + M^+ + OH^- \longrightarrow B + M^+ + H_2O$$

BH^+ is merely replaced by M^+, so that the concentration of positive, and also of negative, ions remains constant, hence I is a constant and = h, thus

$$-\log f_1 = 0.5\sqrt{h}$$

For a cationic, dibasic acid, the method has not previously been set out but is similar to that given by J.C. Speakman for a neutral dibasic acid (A7). A dibasic acid ionises in two stages and we assume the first stage completed before the second stage begins. The two dissociation constants are denoted by K_{a1} and K_{a2}, K_1 and K_2 for short.

1st stage, $BH_2^{++} \rightleftharpoons H^+ + BH^+$

$$K_1 = \frac{\{H^+\}\,[BH^+]\,f_1}{[BH_2^{++}]\,f_2} \quad \ldots\ldots \quad (8)$$

2nd stage, $BH^+ \rightleftharpoons H^+ + B$

$$K_2 = \frac{\{H^+\}\,[B]\,f_o}{[BH^+]\,f_1} \quad \ldots\ldots \quad (9)$$

$\underline{h}$ and $\underline{b}$ are the same as before.

a = total $[B] = [BH_2^{++}] + [BH^+] + [B]$

For electroneutrality,

$$[H^+] + [M^+] + [BH^+] + 2[BH_2^{++}] = [X^-] + [OH^-]$$

Again $[OH^-]$ is negligible,

$$\therefore\ b + [H^+] - [X^-] = -2\,[BH_2^{++}] - [BH^+]$$

Let $L = [BH^+] + 2[B] = 2a - (h - b - [H^+])$

$M = [BH_2^{++}] - [B] = (h - b - [H^+]) - a$

$N = 2[BH_2^{++}] + [BH^+] = h - b - [H^+]$

From (8) (9)

$$K_1K_2 = \frac{\{H^+\}\,[BH^+]\,f_1}{[BH_2^{++}]\,f_2} \cdot \frac{\{H^+\}\,[B]\,f_o}{[BH^+]\,f_1}$$

$$= \frac{\{H^+\}^2\,[B]\,f_o}{[BH_2^{++}]\,f_2}$$

Multiplying top and bottom by the same quantity, $(2[BH_2^{++}] + [BH^+])$

$$K_1K_2 = \frac{\{H^+\}^2\,[B]\,f_o\,(2[BH_2^{++}] + [BH^+])}{[BH_2^{++}]\,f_2\,(2\,[BH_2^{++}] + [BH^+])}$$

$$= \frac{\{H^+\}^2 f_o\,(2[B]\,[BH_2^{++}] + [B]\,[BH^+] + [BH_2^{++}]\,[BH^+] - [BH_2^{++}]\,[BH^+])}{f_2\,[BH_2^{++}]\,(2[BH_2^{++}] + [BH^+])}$$

$$= \frac{\{H^+\}^2 f_o \left\{ [BH_2^{++}] \ (2[B] + [BH^+]) - [BH^+] \ ([BH_2^{++}] - [B]) \right\}}{f_2 [BH_2^{++}] \ (2[BH_2^{++}] + [BH^+])}$$

$$= \frac{\{H^+\}^2 (2[B] + [BH^+]) f_o}{(2[BH_2^{++}] + [BH^+] f_2} - \{H^+\} \Big/ \left(\frac{\{H^+\} [BH^+] f_1}{[H_2B^{++}] f_2} \right) \frac{([BH_2^{++}] - [B]) f_o f_2}{(2[BH_2^{++}] + [BH^+]) f_2 f_1}$$

$$\therefore K_1 K_2 = \frac{\{H^+\}^2 L \ f_o}{N \ f_2} - \frac{\{H^+\} \ K_1 M \ f_o}{N \ f_1}$$

$$\text{or} \quad \frac{\{H^+\}^2 \ L \ f_o}{N \ f_2} = \frac{\{H^+\} \ K_1 M \ f_o}{N \ f_1} + K_1 K_2$$

which may be written shortly as $X = K_1 Y + K_1 K_2$. When, therefore, values for X and Y are obtained from experimental results, the graph of X against Y has gradient K_1 and makes an intercept on the Y-axis at $-K_2$.

The estimation of f_o and f_1 is the same as before and further from the Debye-Hückel Law f_2 is obtained from:-

$$-\log f_2 = 2.0 \sqrt{I}$$

If the dihydrochloride of the base is used

$$h = 2a$$

$$\text{and } L = b - [H^+]$$

$$M = a - b - [H^+]$$

$$N = 2a - b - [H^+]$$

In calculating I for a dibasic acid, up to half neutralisation the first stage of dissociation is taking place and $BH_2^{++} + X^- + M^+ + OH^- \longrightarrow BH^+ + X^- + M^+ + H_2O$

$$\therefore [M^+] = b$$

$$[BH^+] = b$$

$$[BH_2^{++}] = a - b$$

$$[X^-] = h$$

$$\therefore \quad I = \tfrac{1}{2}\{b + b + h + 4(a - b)\}$$

$$= \frac{h}{2} + 2a - b$$

During the second half of neutralisation we have

$$BH^+ + X^- + M^+ + OH^- \longrightarrow B + X^- + M^+ + H_2O$$

which is the same as for a monobasic cationic acid. I is constant and equal to h.

EXPERIMENTAL

Distilled water was used throughout.

For p-chloroaniline, p-bromoaniline and benzidine by the potentiometric titration method, a temperature of 20°C. was used but the later work, pKs of benzidine from solubility measurements, was carried out at 25°C. to facilitate utilisation of the data available in the literature.

Commercial p-chloroaniline was purified by boiling a solution in aqueous alcohol twice with animal charcoal and recrystallising the product again from aqueous alcohol m.p. 69.5° - 70°C.

p-bromoaniline was recrystallised from petroleum ether (B.P. 60° - 80°C.). m.p. 65° - 66°C.

Benzidine was purified by recrystallisation from hot water. The final crystallisation was allowed to take place below about 70°C. and crystals obtained thus contain one molecule of water of crystallisation per molecule of benzidine. (A8). The dihydrochloride was obtained by dissolving some of the purified benzidine in dilute HCl and then increasing the concentration of HCl, as the hydrochloride is less soluble in concentrated HCl than in water(A9).

In all cases, buffer solutions were made up by adding sodium hydroxide to an acid or mixture of acids to give the required pH (A10). The acid solutions were N/10 and the mixture, viz. phosphoric and acetic acids was 0.04M to each acid.

N sodium chloride was added to the p-chloro- and p-bromo-aniline solutions to keep the ionic strength constant, allowing for the ions produced on dissociation of the base in solution. With the benzidine in phosphoric-acetic buffer it was calculated that the ionic strength was already slightly greater than 0.1M, and since the regulation of ionic strength in the previous cases had caused no appreciable change in apparent pK, it was omitted.

The solubility of the bases at low pH was sufficient to raise the pH by more than 1 unit, so pure N/10 acid was used to obtain pH 3 - 4.

A saturated solution of the base was made by stirring, mechanically, a quantity of the solid base in buffer solution for the required time (found by drawing a solubility/time curve and allowing half an hour beyond what was found to be the time required to reach saturation). The solution was filtered quickly and the solubility of the p-chloro- or p-bromo-aniline estimated by the well-known method of bromometric titration, using N/10 $KBrO_3$, KBr solution and 0.03N sodium thiosulphate.

The pH of the same saturated solution was measured with a glass electrode, standardised by the buffer solutions recommended by Hitchcock and Taylor (A11).

A method of estimating benzidine in solution was titration of the solution, made acid with HCl, with standard sodium nitrite solution (about 0.2N) until after standing for 5 minutes a drop of the solution gave a blue colour with starch-iodide paper (A12,A13). The nitrite solution was standardised by running a known volume into a known volume (excess) of warm potassium permanganate solution, heating the solution to about 80°C. and adding more than sufficient standard oxalic acid solution to decolourise the permanganate and finally titrating the solution with permanganate in the usual way to an end point (A14).

The solubility of benzidine in water or buffer of pH about 7 is so small that 50 cc. or 75 cc. solution gave a titration of 1.6 cc. or 2.4 cc. and the accuracy of this method is obviously not sufficient.

The colorimetric method due to Bratton and Marshall (A15) and recommended by Klein (A16) was then used. A stock solution was made by dissolving 2.0360 g. benzidine in 50 cc. 0.2N HCl and diluting by 1000 with water. 5 cc. of this solution were then treated along with the test solutions and the colour of it used as the standard. As read on the Spekker absorptiometer the solution was 0.000001583M and gave a deflection of about 400 from water.

The time allowed between the various stages was found to be critical and the following schedule was adopted:
To the test or standard solution in a 50 cc. standard flask 1 cc. 0.5N HCl was added. To this solution, cooled in ice, 1 cc. 0.1% $NaNO_2$ was added, the flask shaken and allowed to stand 2½ - 3 minutes. The flask was then removed from the ice-bath and 1 cc. 20% urea solution added. After shaking, the inside of the flask was washed down with water and allowed to stand 5 minutes. 1 cc. 0.1% aqueous N-1-naphthyl ethylenediamine dihydrochloride was added and after 20 minutes the contents of flask were diluted to the mark. The readings on the Spekker absorptiometer were then taken in less than 2 hours.

The reason for the initial addition of HCl is that the dyestuff produced is an indicator, being purple in acid, pH < 4, yellow-amber at pH 4-10 and pink at pH > 10.

The peak of the absorption band of the purple solution was found to be about 5700, so the Spekker was used with filter No. 606.

The potentiometric titration was carried out by adding N/10 caustic soda (carbonate free) to an accurately known amount of substance dissolved in an accurately known amount of N HCl, diluted to the required volume. Measurements of pH again were made with a glass electrode as before.

The pH of the buffers is known (A11), viz. 4.64 at 20°C. and 4.65 at 25°C. for acetate (0.1N) and 9.22 at 20°C. and 9.18 at 25°C. for borax (0.05M). Thus from the potentiometric readings $\frac{\Delta E}{\Delta pH}$ can be calculated and the potentiometer readings converted to pHs, taking the pH of the acetate buffer as the standard. From this $\{H^+\}$ can be calculated. h and a are known from the amounts of base and acid from which the solution is made. b is found from the fact that at the equivalence point b = h and so at any stage in titration b is the fraction of h that the volume of caustic soda added at that point is of the volume added at the equivalence point. K_a can now be obtained by substitution of these values in equation (7).

RESULTS

p-chloroaniline.

After several determinations the value 0.0198 mole/litre was assigned to S_o, the solubility at pH 7 or more.

The ionic strength after saturation at pH7 was calculated to be approximately 0.1 so the ionic strength was maintained at this value throughout. Values of the solubility at various pHs were then found, $\log\left(\frac{S}{S_o} - 1\right)$ plotted against pH and the line with gradient -1 drawn as shown in figure A1.

From the graph, $pK_a' = 4.16$

$\therefore \; pK_b' = 10.01$ (pK_w at $20^\circ C = 14.17$)

Correcting for estimation of activities,

from (5) $pK_b + \log \frac{f_{BH^+}}{f_B} = pK_b'$

$$\therefore \; pK_b = pK_b' - \log \frac{f_{BH^+}}{f_B}$$

$$-\log f_{BH^+} = 0.5\sqrt{0.1}$$

$$\therefore \; -\log f_{BH^+} = +0.16$$

$$\therefore \; pK_b = 10.17$$

$$\therefore \; pK_a = 4.00.$$

Potentiometric Titration Method. A solution containing about 0.2 - 0.25 g. p-chloroaniline and 2.5 cc. N HCl in a 100 cc. solution was made up and 10 cc. diluted to 40 cc. for use, that concentration being of the same order as that which would be obtained by the method of saturation in buffer solution. A specimen calculation is given in Table A1.

Four determinations gave the values for pK_b 10.27, 10.27, 10.26, 10.27, i.e., $pK_a = 3.90$.

Farmer and Warth (A17) obtained the value of 4.07 for

pK_a at 25°C. and Flürscheim (A18) obtained the value 3.93 for pK_a at 25°C. (using K_w at 25°C = 1.18×10^{-14}) by the distribution method. Hall (A19) gives a method of correcting values of pK_h for change in temperature but owing to the other differences here, e.g., the value of K_w, this correction is not significant.

p-bromoaniline.

Four hours was again found to be sufficient time for saturation.

The procedure described for p-chloroaniline was repeated using p-bromoaniline.

S_o was assigned the value of 0.0142 mole/litre.

From the graph, figure A2,

$$pK_a' = 4.01$$

$$\therefore \quad pK_b' = 10.16.$$

Applying the activity correction as before,

$$pK_a = 3.85 \text{ and } pK_b = 10.22.$$

Potentiometric Titration Method. A solution similar to the one for the potentiometric titration of p-chloroaniline was used. An extract from the results is given Table A2.

Two determinations gave the values 10.24 and 10.22 for pK_b. For p-bromoaniline, Flürscheim (A18) obtained the value 3.87 for pK_a at 25°C. and Farmer and Warth (A17) the value 3.94 for pK_a again at 25°C.

In applying the activity correction the simple Debye-Hückel equation for dilute solutions was used but as the solutions were of concentration 0.1M and thus rather too concentrated for this equation to be adequate, the amount subtracted from pK_a' will be slightly too large and the values of pK_a will tend to be low. At present the data required to use the more exact equation are not available.

The results are in good agreement with previous ones and, as neither of the workers referred to were in a position to make activity corrections, the results obtained here should be more accurate. Also the results obtained here by the two different methods agree closely, especially those for p-bromoaniline.

Benzidine.

Potentiometric Titration Method. The first time the dihydrochloride was used in about the same concentration as for previous experiments, and the results were inaccurate owing to the benzidine crystallising out when the equivalence point was approached.

Two titrations were then done on the free base dissolved in acid solution. About 0.2 g. benzidine.H_2O was dissolved in about 2.5 cc. N HCl and the solution diluted to 100 cc. 10 cc. of this solution were diluted to 40 cc.

for use. The calculation given previously was tabulated as shown in Table A3. The critical points of the graph were found all to lie in the second half of the neutralisation where the ionic strength is constant, hence f_1 and f_2 are also constant.

From the graph, figure A3,

$$K_{a2} = 1.05 \times 10^{-5}$$

$$K_{a1} = \frac{2.45 \times 10^{-9}}{1.05 \times 10^{-5}}$$

$$\therefore K_{a1} = 2.33 \times 10^{-4}$$

$$\therefore pK_{a1} = 3.63 \; ; \quad pK_{a2} = 4.98$$

$$\therefore pK_{b1} = 9.19 \text{ and } pK_{b2} = 10.54.$$

The second titration gave $pK_{b1} = 9.20$ and $pK_{b2} = 10.51$.

A further titration was done on 20 cc. (diluted to 40 cc.) of about 0.14 g. benzidine dihydrochloride in 100 cc. and the values $pK_{b1} = 9.18$ and $pK_{b2} = 10.44$ were obtained.

Landolt-Börnstein's Tabellen quote a single value of $K_b = 1.6 \times 10^{-9}$ corresponding to $pK_b = 8.80$ at 20°C. given by Pring, and $K_{b1} = 9.3 \times 10^{-10}$ and $K_{b2} = 5.6 \times 10^{-11}$ at 30°C., corresponding to $pK_{b1} = 9.03$ and $pK_{b2} = 10.25$ by Clark, Cohen and Gibbs. As before the values given here should be more accurate than those of previous workers.

Solubility Method. As before it was necessary first to determine the S_0 value but this proved to be unexpectedly difficult. The results were not as consistent as previously and the doubt as to the true value for S_0 cast suspicion on any other solubility determinations. However, other measurements were made at lower pHs, supplied by the phosphate-acetate buffer, and these seemed to indicate an extremely low solubility at pHs around 4.5. Inspection revealed that the appearance of the solid residue after stirring was slightly different from the original appearance of the benzidine. At this pH stage, the phosphate ions should be almost entirely H_2PO_4' and so a saturated aqueous solution of benzidine was mixed with aqueous KH_2PO_4, and a precipitate, similar in appearance to the residue, was obtained. Analysis of the residue gave benzidine, colorimetrically as already described, 66.9% and H_2PO_4', precipitated and weighed as magnesium ammonium phosphate hexahydrate, 34.8% and 33.7%. The formula $NH_2C_6H_4C_6H_4NH_3^{\cdot}H_2PO_4'$ requires benzidine 65.3% and H_2PO_4' 34.4% so the residue was assumed to be benzidine dihydrogen phosphate.

Succinate buffer, which was then tried, gave similar trouble and it was presumed that benzidine also gives an insoluble succinate.

With acetate buffer increased solubility was noted with decreasing pH and the trend was in approximately the correct direction but unfortunately with this buffer it was impossible to get solutions of pH < 4, even using solutions of N/10 acetic acid.

A graph of the form in which benzidine would be present at various pHs was worked out from the equations given by Smith (A20) and using the dissociation constants obtained by potentiometric titration (figure A4). This was mainly to give an indication of the ionic strength of the solutions under observation and also to give some idea of how low a pH would be required for the solubility-pH graph to approach a gradient of -2.

A hydrochloric acid-sodium chloride buffer was then used. Again an increased solubility of benzidine was found with decreasing pH but once more a bar was encountered about pH 4 and any measurements obtained at lower pH were very erratic.

N/10 formic acid was also tried as solvent with no better result.

No satisfactory explanation can at present be given either for the inconsistency in the S_o determinations, which seemed unreliable even in water, or for the difficulty in getting values for S below pH 4.

An experiment was tried out in which benzidine was stirred in N/10 HCl solution and the pH measured at intervals.

The initial pH of 1.13 rose to 2.77 after 35 minutes and remained substantially constant for $1\frac{1}{2}$ hours. This may indicate that benzidine was going into solution and benzidine hydrochloride separating out so that, in fact, the solubility of benzidine hydrochloride in HCl was being measured, and this is known to decrease with increasing concentration of HCl (A9).

Also the benzidine as used contains 1 molecule of water of crystallisation and this might cause trouble if a transition was involved as well as the ordinary process of solution. However, the literature seems to indicate 70°C. as nearer the transition temperature and the temperature here was constant at 25°C. (A8).

In figure A5, $\log\left(\frac{S}{S_o} - 1\right)$ has been plotted against pH as far as possible. The value used for S_o, 0.00196 mole/litre, is the average of 32 determinations in water, hydrochloride and phosphate-acetate buffers in which the final pH was greater than 7. Lines, of gradients -1 and -2, have been drawn and these cut the pH-axis at 5.0 and 4.6_5 respectively, giving $pK_{a2} = 5.0$ and $pK_{a1} = 4.3$ and so $pK_{b1} = 9.2$ and $pK_{b2} = 9.9$. As expected pK_{b2} is very much lower than the potentiometric value but pK_{b1} is in good agreement.

The position is, therefore, that in acetate and hydrochloride buffers an increase in solubility with decreasing pH is found and the solubility-pH graph has a slope of approximately -1, cutting the pH-axis about pH 5, the uncertainty being caused by an uncertainty as to the true S_o value on which depends the accuracy of the pK obtained. Below pH 4 no accurate figures have so far been obtained and so the final gradient of the graph is yet unconfirmed.

Preliminary investigations were carried out on 4-nitro-resorcinol to ascertain if it was suitable for use as a dibasic acid. The dissociation constants are not known very accurately but its solubility is of about the right order.

4-nitroso-resorcinol was prepared according to Henrich (A21) and then oxidised with alkaline hydrogen peroxide (A22), the precautions given by Gilbert, Laxton and Prideaux (A23) being observed. Only a very small quantity of the hemihydrate, m.p. 82°C. was obtained.

The method recommended by Astle and Stevenson (A24) was then tried. This is due to Kauffman and Kugel (A25) and was found to be more successful.

21.2 g. sodium carbonate was added to 11 g. resorcinol dissolved in 310 cc. water. 15.4 g. benzoyl chloride was added and the mixture shaken vigorously until small hard pellets of the monobenzoate were formed. After recrystallisation from benzene, 1 part of the monobenzoate was dissolved in 10 parts glacial acetic acid and 1 part concentrated nitric acid added. When the reaction was over the mixture was diluted with the same volume of water and the product filtered, dried on a water-bath and extracted with chloroform. The residue, after recrystallisation from 50% alcohol and charcoal, was pure white. The nitromonobenzoate was hydrolysed by heating it for a short time with 10% sodium hydroxide solution and the solid obtained on acidification of the solution with HCl recrystallised from carbon tetrachloride to remove benzoic acid.

Potentiometric titration was carried out and as the graph of pH against cc. NaOH added showed two end points, the pKs were worked out separately as for two monobasic acids. Four titrations gave the values 6.23, 6.74, 6.19, 6.21 for pK_1 and 9.40, 9.50, 9.35, 9.40 for pK_2. This indicates a value of about 6.2_1 for pK_1 and 9.3_9 for pK_2.

Gilbert, Laxton and Prideaux (A23) obtained a pK = 5.98 by a conductivity method and a pK of 8.81 by a colorimetric method. Bader (A26) gives $K = 1.2 \times 10^{-5}$, i.e., pK = 5.92.

A suitable method of estimating 4-nitroso-resorcinol in solution was not found.

SECTION 2.

DISSOCIATION CONSTANTS IN MIXED SOLVENTS BY DIFFERENT METHODS.

As mentioned in the introduction, measurements of dissociation constants for acids in non-aqueous and in mixed solvents are of interest for the information they provide as to solvent nature and acid strength. In particular, considerable importance has attached in recent years to the variation of the relative strengths of acids with the dielectric constant of the medium. This raises the problem of whether the change in pK is due mainly to the change in dielectric constant or to some other effect. Also it is necessary to know the reliability of the pKs obtained by different methods in order to make a fair comparison, i.e., if it is valid to compare pK in mixed solvent obtained by conductivity with the apparent pK from measurement of pH in a cell involving a liquid junction and with a glass electrode standardised by aqueous buffers.

Knowledge of the variation of dissociation constant with solution composition is also of interest in connection with dissociation constant data for acids which are insoluble, or very sparingly soluble, in water. In such cases the dissociation constant is normally determined in non-aqueous or mixed solvent and a dissociation constant in water obtained by extrapolation. Lynch and La Mer (B5) found that, for acetic, propionic, butyric and benzoic acids in dioxan-water mixtures, a linear plot was obtained in a graph of pK against the reciprocal of the dielectric constant.

Cavill, Gibson and Nyholm (54), using p-alkoxybenzoic acids in acetone-water mixtures, plotted apparent pK against $x^{1.28}$, where $\underline{x}$ was the percentage acetone. The work done in both of these papers, however, was complicated by the presence of considerable quantities of lithium chloride and in the latter case measurements were made on a glass electrode, which has been stated to be unreliable in mixed solvent.

A certain discrepancy exists in dissociation constants as obtained by different methods, especially where the percentage of water is low. Dippy states (9) that Kilpatrick reports two different values of pK for substituted benzoic acids obtained by different procedures. Saxton and Darken (B6) obtained a consistent value for formic acid and could not explain the difference between their value and that of Harned and Embree (B7), except that it was done by a different method.

It was therefore decided to carry out a series of determinations of dissociation constant of benzoic acid in mixed solvent, viz. dioxan-water mixtures, by different methods, conductimetric, E.M.F. and pH, and compare the results obtained. The pH method is the most convenient to use but also the least accurate owing to the difficulty of the liquid-liquid junction potential and of the solvent error of the glass electrode. According to Dole's theory (B9) a correction based on the activity of the water in the solvent can be applied to the measured pH to allow for the effect of change of solvent on the glass electrode but recently Dole's theory has been criticised (B8) and opinion is now divided, Dole maintaining that the correction is applicable (B10) while others (23,65,70,73,E4) prefer to leave the pH as measured. It was hoped that from the comparison of results obtained by the different methods some opinion could be expressed on this matter.

Part 1.

Conductimetric Method.

The method of obtaining dissociation constants from conductivity measurements has its origin in Ostwald's Dilution Law

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad \text{where } \alpha \text{ is the degree of dissociation.}$$

After the development of the theory of strong electrolytes it was found necessary to modify Ostwald's original equation and use a slightly lower value than Λ_0. Λ_x, as it was designated, can be calculated from the Onsager equation as is described later. Thus $\alpha = \frac{\Lambda}{\Lambda_x}$

The classical dissociation constant, $K_{cl} = \frac{\alpha^2 c}{1 - \alpha}$ has now been replaced by the thermodynamic dissociation constant, $K_T = \frac{\alpha^2 c}{1 - \alpha} . \frac{f_\pm^2}{f_u}$. It is possible to estimate the activity of the ions, $f_\pm$, in very dilute solution by means of the Debye-Hückel equation

$$-\log f_\pm = \frac{1.8245 \times 10^6 z_i^2 \sqrt{I}}{(DT)^{3/2}}$$

and the activity of the neutral molecules, f_u, which is very nearly unity, has been allowed for by plotting pK_c, the negative logarithm of the dissociation constant as calculated, against c_u, the concentration of undissociated molecules, and extrapolating to zero c_u (B30).

In order to obtain an accurate Λ_0 value for benzoic acid, it was found necessary to evaluate Λ_0 for HCl, KCl and potassium benzoate and to use the relationship

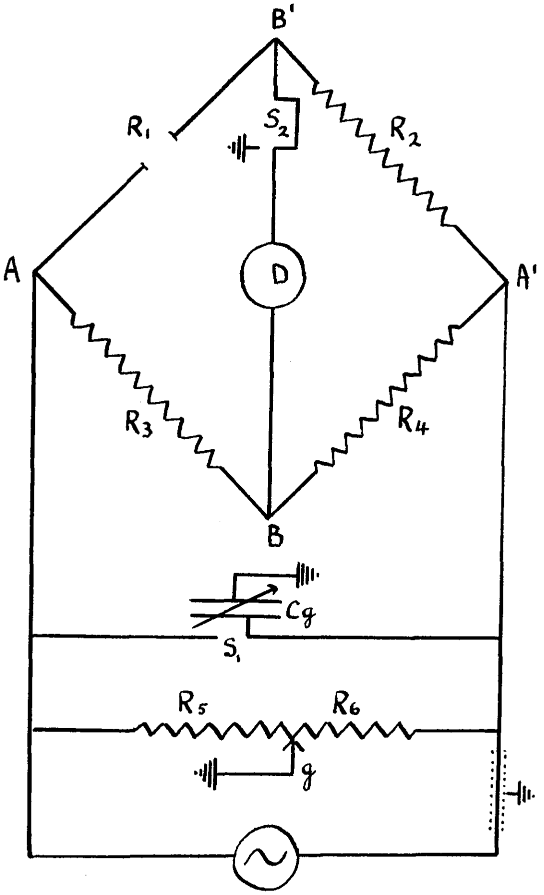
$$\Lambda_{o\,HBz} = \Lambda_{o\,HCl} + \Lambda_{o\,KBz} - \Lambda_{o\,KCl}$$

Measurements on the benzoic acid itself then made possible the calculation of pK.

Conductivity measurements give an accurate value for pK, but the method is tedious and the apparatus required is elaborate.

Conductivity measurements were made on a screened A.C. bridge of the type described by Jones and Josephs (B11) and by Shedlovsky (B12), the precautions recommended for minimising effects due to the inductance and capacity of various parts of the bridge network being followed.

The circuit was essentially as shown in the diagram (p.42). R_1 was the cell. R_2 was a Sullivan non-reactive resistance box, reading from 10,000 to 0.1 ohm. The ratio arms, R_3 and R_4 were supplied by a 100 ohm, Sullivan non-reactive slide resistance, the total resistance being subdivided into 10^5 parts by means of two concentric dials. The amplifier was a two stage, high gain, mains operated model and measurements were normally made at 1000 and 3000 cycles per second. The oscillator, a mains operated, Hartley type giving frequencies from 1000 to 10,000 cycles per second, was placed about 12 feet from the bridge to



prevent interaction. The leads, which were screened and grounded, connected the oscillator to the bridge via a Sullivan, balanced and screened transformer, designed to screen effectively the supply source from the bridge without upsetting the balance of the latter to earth. It is preferable to have the bridge earthed especially if other electrical apparatus is present in the room (B12) but this must be done carefully or errors due to leakage currents to earth may be introduced. The sharpness of the sound minimum in the detector is improved by earthing but the telephone earpiece must be at ground potential or the capacity between the telephone coils and the operator will cause a leakage of current. Jones and Josephs (B11) describe a modified Wagner earth which is very satisfactory. In the diagram this is represented by resistances R_5, R_6, the contact g, and the variable condenser C_g. The condenser was connected by switch S_1 to either A or A'. The bridge was balanced in the usual way and then the detector, D, was connected to ground by switch S_2. B was brought to ground potential by adjusting the contact g and the condenser C_g. The bridge was again balanced in the usual way and if the change in R_2 was appreciable the process was repeated.

Connections to the cell were made by taking leads from the electrodes to two mercury cups supported in the thermostat. This prevented heat interchange to the room from the cell.

Any resistance effect due to the leads from the mercury cups to the bridge was allowed for by having an equal length of identical wire connecting the resistance box R_2 to the circuit.

A Sullivan decade stable mica condenser, reading from 0 to 0.01 μF, could be connected across R_2 or the cell in order to compensate for capacity effects in the arms of the bridge. The connections to the cell and the resistance box could be interchanged by means of a commutator of the rocking type.

When water or solutions of high resistance were being measured, a shunt was necessary across the cell. This was supplied by a 10,000 ohm standard resistance.

Temperature Control.

As it has been stated that the use of water may introduce considerable errors (B11), the cell was supported in an oil-filled thermostat. The temperature of the bath was kept uniform by an electrically driven paddle system, and constant to 25°C. ±0.005°C. by means of a toluene-mercury spiral regulator, operating a 60 watt carbon filament lamp through a vacuum relay. The thermometer used was standardised against a thermometer which had been recently calibrated at the National Physical Laboratories.

Weight Measurements.

Small weighings were carried out on a balance made by Thomson, Skinner and Hamilton Ltd., Glasgow, while loads of over 50 g. were weighed on a larger Sartorius balance, sensitive to 0.001 g. The micro-weighings were carried out on an Oertling micro-balance which was kept in a thermostatically controlled room. On this balance up to 10 mg. could be weighed out accurately to 0.005 mg. by difference using counterpoises. The weights for use on the other two balances were calibrated by the method of Richards (B13).

Conductivity Cells.

Two cells, both of the Hartley-Barrett type (B14) were used, one of fused silica and one of Pyrex glass. The silica cell had a capacity of about 300 cc. and the electrodes, which were platinum coated lightly with platinum black, were placed about 3 mm. apart. It was used in benzoic acid determinations. The Pyrex cell had a greater capacity, about 425 cc., and the electrodes of bright platinum were spaced about 1 cm. apart. It was used for potassium benzoate and potassium chloride. The top of both cells carried the electrode supports, a side tube closed by a three-way tap through which pure air could be blown into the cell, and an opening, closed by a ground glass cap, to allow the additions of stock solution from a weight burette.

Preparation of Conductivity Water.

Conductivity water was prepared in a still of the type described by Bourdillon (B15) with certain modifications.

Tap water (1°H) was boiled in a copper boiler containing a little potassium bisulphate. The steam, after passing downwards through a long spiral, swirled through a spray trap and up into a vertical, block tin pipe, through which was passing a stream of pure air to remove the carbon dioxide. At the top of the pipe there was a cold water condenser which condensed the steam so that it ran back down the pipe and collected at the bottom, whence it could be run off into a well-seasoned Pyrex storage flask, fitted with a soda lime guard tower. A side arm allowed water to be run direct from the bottom of the column into the cell. This was done in all measurements in water but for making up mixed solvent water from the flask was used.

The stream of air was obtained by purifying laboratory compressed air. This was effected by passing the compressed air through a cotton wool filter, three bubblers containing half strength sulphuric acid to remove NH_3 and up three towers packed with glass beads and containing 10% caustic soda. Finally it passed through a spray trap, a cotton wool filter and filter paper held between spirally grooved metal discs.

The specific conductivity of the water was usually of the order of 0.2 - 0.4 gemmhos.

Introduction and Measurement of Solvent.

The cell was dried by rinsing it with acetone and blowing a current of pure air through it and then weighed.

In the case of water, it was run directly from the still into the cell, which was rinsed several times and finally filled.

Mixed solvent was made up by blowing, with pure air, an approximate amount of pure solvent into a cleaned, steamed, dried and weighed Pyrex flask. This was then weighed accurately and the calculated amount of conductivity water added, in the main direct from the storage flask but the last 10 g. or so from a dropper. The solvent composition was always within 1 in 30,000 by weight. A stream of pure air was used to blow the solvent over into the cell, which was rinsed several times before being filled. After being re-weighed, the cell was placed in the thermostat and shaken gently at intervals until the resistance became constant.

Preparation of Stock Solution.

A sample of the solid substance in a small glass tube was weighed, by difference, into a clean, steamed and weighed Pyrex flask. A suitable amount of water was run in, or mixed solvent blown over, and the flask and contents re-weighed. Stock solutions were prepared fresh each day measurements were being made.

Measurements.

From a weight burette with a long narrow stem, the stock solution was added to the solvent in the cell in portions never less than 1 g. The cell was gently rocked until the resistance became constant. This usually took 30 - 40 minutes. Five or six points were normally taken on one run. Finally the cell was dried and weighed and if any decrease in weight had occurred the average weight of the solution was used in the calculation. (Decrease was rarely more than 1 in 3,000.).

Cell Constant Determinations.

A.R. potassium chloride was recrystallised three times from conductivity water and dried in an electric oven. Just before use, samples were heated to dull redness in a platinum dish and cooled in a desiccator.

The cells were standardised by carrying out several series of measurements with potassium chloride solutions, giving resistances over the range of resistances which would be measured. Conductivities were corrected, where necessary, for interionic attraction effects (B16). The cell constant was then found by comparing each measured value with the conductivity values derived by Shedlovsky (B17) at the same concentrations, calculating them from the interpolation formula (B18)

$$\Delta = 149.92 - 93.85\sqrt{c} + 50c$$

which agrees with the data of Shedlovsky (corrected to the Jones and Bradshaw standard) to an average deviation of 0.05 conductivity unit. 20 determinations for the silica cell gave 0.04092 ± 0.02% and 15 determinations for the Pyrex cell gave 0.10044 ± 0.08%.

Densities, Viscosities and Dielectric Constants.

The densities of the strong solutions used in the calculations were obtained from a graph of density, as measured for each solution by means of a Sprengel pyknometer, against concentration.

For the weak solutions ($c < 0.003M$) the density of the pure solvent was used as obtained from the data of Geddes (B19) and of Hovorka (B20).

The viscosities required were obtained from the work of Geddes (B19) and of Owen and Waters (B21).

Values of the dielectric constants for the solutions could be found by interpolating those given by Åkerlöf and Short (B22).

Purification of Materials.

May and Baker dioxan was refluxed with metallic sodium for several days in an all glass apparatus carrying a $CaCl_2$ guard tube. It was then distilled and the process repeated until the sodium remained bright after several hours' boiling. It was finally distilled and stored in a Pyrex flask, stoppered and protected by a bottle fitting on to the neck of the flask by a rubber ring.

A.R. benzoic acid was recrystallised three times from conductivity water and finally sublimed. It was ground and left in a desiccator over night before use.

Potassium benzoate was prepared by dissolving A.R. potassium carbonate in conductivity water and gradually adding the calculated quantity of A.R. benzoic acid to the warm solution, the potassium benzoate being obtained by evaporation of the solution to small bulk on a water bath.

The crystals obtained were dried at 110°C. recrystallised twice from 95% alcohol and dried again at 110°C. (B22).

To ascertain if the crystals were anhydrous, an estimation of the potassium content of the salt was carried out by converting it to K_2SO_4 and weighing as such (B24). About 0.1 g. potassium benzoate was weighed into a platinum crucible and ignited in air until all the organic matter had been oxidised away. After cooling, one or two drops pure concentrated H_2SO_4 were added, the crucible was heated to dull redness, cooled and weighed. A little solid ammonium carbonate was sprinkled over the residue and the crucible ignited again to decompose any bisulphate formed. Two estimations gave the potassium content as 24.29% and 24.34% compared with the theoretical of 24.44%. As a check on the method of analysis, a sample of pure potassium hydrogen benzoate was treated as above and the percentage potassium was found to be 13.67% (Theoretical 13.86%).

The potassium benzoate was also ground and left over night in a desiccator before use.

The purification of the potassium chloride has been described under cell constant determination.

Λ_0, the Conductivity at Infinite Dilution.

Methods for the extrapolation of conductivity data for weak electrolytes have been given by Fuoss and Kraus

(B25), Shedlovsky (B26) and Davies (B27). Application of these methods to the present data in aqueous solution gave values for Λ_o in good agreement with one another and with that obtained from independent mobility data (B17,B23). With mixed solvent, however, marked curvature of the extrapolation plot was observed in all cases and it was not possible to obtain an accurate value by these methods.

In order to obtain an independent value of Λ_o from the mobilities of the hydrogen and benzoate ions, it was necessary to carry out measurements on KCl and potassium benzoate in mixed solvent. Hydrolysis of potassium benzoate solutions was repressed by adding the number of milligrams of benzoic acid calculated to maintain the pH of the solution at 7. At the end of the run, the pH was checked on a glass electrode set up and found to be within 0.5 unit of pH 7. Λ_0 could then be obtained from the relationship

$$\Lambda_{oHBz} = \Lambda_{oHCl} + \Lambda_{oKBz} - \Lambda_{oKCl}$$

The values for HCl were obtained from the data of Owen and Waters (B21), those for potassium benzoate in water from Brockman and Kilpatrick (B23) and those for KCl in water from Shedlovsky (B17).

In the present work on KCl and potassium benzoate in mixed solvent, $\Lambda + b\sqrt{c}$ (where b is the Onsager slope (108)) was plotted against $\sqrt{c}$ and extrapolated back to zero c. Table B3 gives Λ at round concentrations for potassium benzoate and Table B4 for KCl.

The Λ_o values for HCl, KCl and potassium benzoate and the derived Λ_o values for benzoic acid are summarised in Table B2.

Dissociation Constant.

The thermodynamic dissociation constant for a weak acid is given by

$$K = \frac{\alpha^2 c}{1 - \alpha} \cdot \frac{f_{\pm}^{\,2}}{f_u} \quad . \; . \; . \; . \; . \; (1)$$

where α is the degree of dissociation, c the molar concentration, $f_{\pm}$ the mean activity coefficient and f_u the activity coefficient for undissociated molecules. No attempt has been made here to distinguish between the contributions to the activity made by the positive and negative ions respectively. In the emf and pH work it was necessary to make this distinction in accordance with the definition of pH as hydrogen ion activity, hence in these sections f_o, for undissociated molecules, and f_1, f_2 for univalent and bivalent ions respectively, were used.

α may be obtained from the Onsager equation, the general form of which is

$$\Lambda = \Lambda_o - \left[\frac{2.8007 \times 10^6 z_1 z_2}{(DT)^{3/2}} \Lambda_o \frac{q}{1 + \sqrt{q}} + \frac{41.179(z_1 + z_2)}{\eta (DT)^{\frac{1}{2}}} \right] \sqrt{I}$$

where $q = \dfrac{z_1 z_2(\Lambda_1^\circ + \Lambda_2^\circ)}{(z_1 + z_2)(z_1 \Lambda_2^\circ + z_2 \Lambda_1^\circ)}$

z_1 and z_2 are the valencies of the two ions while Λ_1° and Λ_2° are their limiting ionic conductivities. For a 1:1 electrolyte at 25°C., employing the most recent values of the constants, due to Birge (B28), the equation becomes

$$\Lambda_x = \Lambda_o - \left[\frac{159.33}{D^{3/2}} \Lambda_o + \frac{4.7696}{D^{\frac{1}{2}} \eta}\right] \sqrt{\alpha c}$$

Λ_x was obtained by successive approximations and α was taken as $\dfrac{\Lambda}{\Lambda_x}$

At high dilutions ($< 0.003N$) f_u, the activity coefficient of a neutral molecule, may be taken as unity and values for $f_\pm$ can be derived from the limiting Debye-Hückel equation (107)

$$- \log f = \frac{1.8245 \times 10^6 z_i^2 \sqrt{I}}{(DT)^{3/2}}$$

which for a 1:1 electrolyte at 25°C. becomes

$$- \log f = \frac{354.38 \sqrt{c_i}}{D^{3/2}}$$

In Tables B5-B9, pK, the negative logarithm of the dissociation constant, is given. pK' is the value given by equation (1) without allowing for $\dfrac{f_\pm^2}{f_u}$ and pK_c the value corrected for activity. The mean of the pK_c values is given as pK.

In the case of the stronger solutions ($c > 0.003$) a further refinement was required. At such concentrations, there is an apparent decrease in dissociation constant and this has been attributed to the "medium effect" of the neutral molecules, i.e., it is not correct to take f_u as unity. Saxton and co-workers (B6,B30) assumed this to be a linear function of c_u and used the equation

$$\log k_A - 1.013\sqrt{c_i} = \log K_A - \beta c_u$$

for solutions in water. 1.013 is 2A or twice the Debye-Hückel limiting slope. For this work the equation is therefore

$$pK_c + 2A\sqrt{c_i} = pK + \beta c_u$$

The left side of the equation was plotted against c_u and extrapolated to zero c_u. This value was taken as the true pK.

The results by the two methods are summarised in Table B11. Agreement is good, the average deviation being of the order of 0.003 pK unit.

In figure B7, $\Delta_o \eta$ for KCl, potassium benzoate and benzoic acid has been plotted against percentage dioxan. Walden has suggested that $\Delta_o \eta$ should be constant for large organic ions in different solvents but with simple ions this has been found not to be true and the discrepancy is usually said to be due to the differences in the extent of solvation of the ions in various solvents. The graphs here all show an initial rise, followed by a steady fall as the percentage dioxan increases. Connell, Butler and Hamilton (B29) obtained a graph of similar shape for KI in ethanol-water mixtures. Various explanations have been given. Butler suggests the initial rise is due to a) frictional resistance between an ion entirely solvated by water and the mixed solvent being less than that corresponding to the bulk viscosity of the latter, and b) the viscosity of the solvent just outside the solvation sphere being less than that at a distance from the ion, because of the salting out of the organic solvent. Recent spectrophotometric work on cationic acid behaviour in mixed solvents by Braude and Stern (116) has shown that the proton affinity of water is increased by addition of dioxan, ethanol or acetone, this effect being ascribed to the lattice-breaking action of the organic solvent on the water structure, leading to an increase in the stability of the hydroxonium ion H_3O^+. It is probable that the cation affinity of water is similarly increased and that such an increase in hydration energy is responsible for the observed initial increase in $\Lambda_0\eta$. As the proportion of organic solvent is increased, the aqueous solvation shell is gradually dispersed and $\Lambda_0\eta$ decreases.

In figure B7 values for β for benzoic acid in dioxan-water mixtures have been plotted against percentage dioxan. It is of interest to note that the values of β and of $\Delta_0 \eta$ for benzoic acid both show maxima at about the same solvent composition. The maximum in β presumably indicates that the medium effect of benzoic acid on its ions is greatest at this point but the exact theoretical significance of this quantity is still uncertain.

Part 2.

E.M.F. Method.

This method also gives accurate values of pK. Theoretically the cell used can be represented by

$$Ag\text{-}AgCl/HBz.KBz.KCl/QH\text{-}Pt\text{-}QH/HCl(a_2 = 1.0)/AgCl\text{-}Ag$$

(Strictly speaking the quinhydrone is in solution and so should be represented with the other constituents of the solution but as the quinhydrone is an integral part of the electrode rather than of the solution under observation it has been written as part of the electrode.)

This is essentially a concentration cell with HCl such that the hydrogen chloride activity on the right side is 1, and that on the left side is given by

$$a_{H^+} \times a_{Cl^-} = a_2$$

a_{H^+} is governed by the dissociation of the benzoic acid, while a_{Cl^-} depends on the concentration of KCl.

Considering each side of the cell separately, on the left side,

$$E_I = E_o - k \log m_{H^+}\gamma_{H^+}m_{Cl^-}\gamma_{Cl^-} \quad \cdots\cdots (1)$$

Similarly, on the right side,

$$E_{II} = E_o - k \log a_{H^+}a_{Cl^-}$$

But when $a_{H^+}a_{Cl^-} = 1$, $k \log a_{H^+}a_{Cl^-} = 0$

$$\therefore \; E_{II} = E_o$$

and hence E_o can be evaluated.

The thermodynamic dissociation constant can be written as

$$K = \frac{m_{H^+}\gamma_{H^+}m_{Bz^-}\gamma_{Bz^-}}{m_{HBz}\gamma_{HBz}}$$

Substituting for m_{H^+} in (1) and re-arranging

$$pK = \frac{E - E_o}{k} + \log \frac{m_{Cl^-}m_{HBz}}{m_{Bz^-}} + \log \frac{\gamma_{Cl^-}\gamma_{HBz}}{\gamma_{Bz^-}}$$

In practice, E_o was found by measuring the emf. of the right side of the cell with several concentrations of HCl and extrapolating towards zero HCl, where activity coefficients approach unity. Allowance had to be made for the activity of the ions at the measured concentrations.

E for the left side was then obtained by measuring the emf. of the half cell containing a solution of benzoic acid, its potassium salt and KCl of known concentrations.

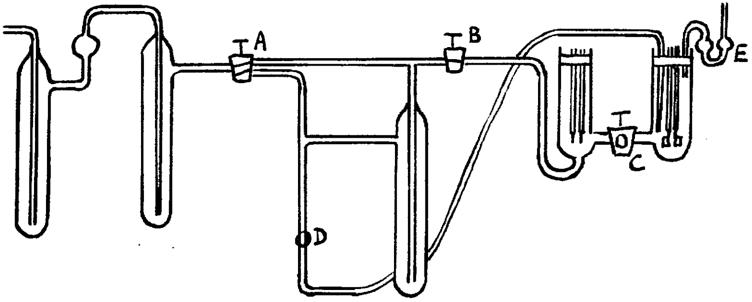
The customary procedure is to begin with a solution of the acid and potassium chloride and to form the potassium salt of the acid by partial titration with potassium hydroxide. Recently Speakman and Smith (C20) have recommended the use of the crystalline acid salts of organic acids as pH standards. These salts can also be used very conveniently to give solutions of the acid exactly half neutralised by a strong base. With such solutions m_{HA} is almost exactly equal to m_{A^-} and the calculation is considerably simplified. Several different concentrations of potassium hydrogen benzoate were used and the pKs calculated.

The whole process was repeated for each different solvent mixture.

The cell used was of the customary H-type and can be represented as

Ag-AgCl/solution/quinhydrone-Pt

Contact between the limbs could be established through a wide-bored tap, which normally was kept closed to minimise diffusion of the quinhydrone to the Ag-AgCl electrodes.

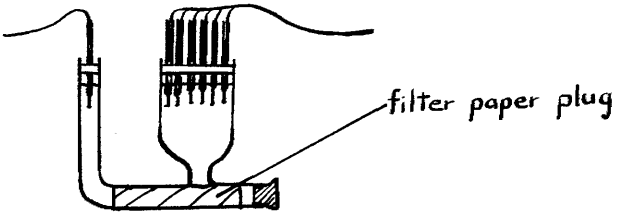


The liquid in E was in all cases the solvent being used at the time. Nitrogen was bubbled through the test solution for about 10 minutes and also blown through the cell several times. The solution was blown over into the cell, with tap C open, until all the electrodes were immersed. Taps B and C were closed and D opened intermittently to stir the contents of the quinhydrone limb of the cell and hasten equilibrium. After about 20 minutes, readings were taken on a Cambridge Slide Wire Potentiometer connected to a lamp and scale galvanometer. The circuit was standardised using a substandard Weston cell checked against several standard cells recently calibrated at the National Physical Laboratories. Each Ag-AgCl electrode could be compared independently with each Pt electrode in turn, giving four readings in all.

The cell was immersed in a water-filled thermostat, stirred by an electrically driven paddle system. The temperature was kept constant at 25°C. ±0.01°C. by means of a 100 watt lamp operated through a Sun-Vic relay. The thermometer was checked against one recently calibrated at the National Physical Laboratories.

The platinum electrodes were bright platinum foil, contact with the mercury in the connections being made through sealed in Pt wire. The electrodes were cleaned by being heated in chromic acid for a few minutes, washed with distilled water, heated to redness in an alcohol flame and stored for at least two days in distilled water (C1).

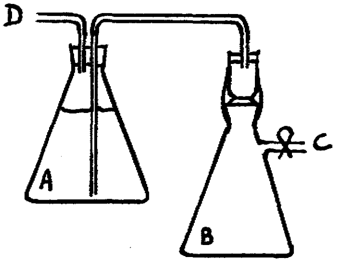
The Ag-AgCl electrodes were made by the method of Brown (C2). The plating solution contained 10 g. per litre distilled water of potassium silver cyanide made by adding excess silver cyanide to a hot, filtered 20% solution of potassium cyanide, stirring for half an hour, filtering, cooling and recrystallising the product from distilled water. Just before use sufficient dilute silver nitrate solution to produce a faint cloud was added, the solid allowed to settle and the supernatant liquid decanted off. This ensured that no free cyanide was present in the solution. About 1.5 cm. Pt wire was sealed through glass and cleaned by boiling in concentrated nitric acid and leaving overnight in distilled water. Six electrodes were plated at a time by passing a total current of 2 milliamps for about 4 hours through the plating solution using the six electrodes as cathode and a Pt electrode as anode. Diffusion of cyanide ions to the cathode was minimised by using a vessel as shown



After being washed overnight in distilled water, the electrodes were chloridized by being made the anode in 0.1 N HCl for half an hour with a current of 2 milliamps passing. After again being left overnight in distilled water the electrodes were ready for use.

The gold electrode used was a thick piece of gold wire, rounded at the end. It was boiled for a minute or two in concentrated nitric acid, washed and heated to dull redness in an alcohol flame each time before use.

Quinhydrone of A.R. quality was recrystallised from conductivity water in an atmosphere of nitrogen. The apparatus was as shown.



With a stream of nitrogen passing through it, conductivity water was boiled in a Pyrex flask A for 10 minutes and cooled to below 75°C. (C3). The quinhydrone was added to A and the whole apparatus swept through with nitrogen which, till now, entered at C. The clip was closed and the nitrogen supply connected to D. A suction pump was applied at C and the flow of nitrogen regulated to keep the solution blowing over at the rate at which it was sucked through the sintered glass filter. The clip C was then closed and the quinhydrone allowed to crystallise out in an atmosphere of nitrogen. The crystals were washed twice by decantation with conductivity water and finally dried for several days over phosphorus pentoxide in a desiccator filled with nitrogen.

Standard hydrochloric acid was prepared from constant boiling acid distilled in an all glass apparatus. The densities given by Foulk and Hollingworth (C4) were used. All measurements were done by weight. As a check the acid was titrated against anhydrous sodium carbonate using screened methyl red as indicator and the factor so obtained converted to a weight basis for comparison (C5). All volumes were corrected to in vacuo and the results agreed to within 0.3%.

Potassium hydrogen benzoate was prepared by mixing the theoretical quantities of A.R. benzoic acid and potassium hydroxide pellets dissolved in hot alcohol and allowing the solution to cool. The product was then recrystallised from alcohol (C6,C7). A potassium estimation was carried out as already described. Found, 13.79% and 13.85%. Theoretical, 13.86%.

The KCl was the same as was used previously.

The cylinder nitrogen was purified by bubbling up a column containing glass beads and alkaline sodium hydrosulphite, with sodium anthraquinone β-sulphonic acid as a catalyst (C8), to remove oxygen and a column containing the solvent being used in the cell. Later it was noticed that a blackening was produced if lead acetate was added to the solvent column so, as previous workers had found the traces of oxygen to have no adverse effect (111), the nitrogen was passed only through the solvent column.

Evaluation of E^o, the standard electrode potential.

Solutions of HCl in water and in dioxan-water mixtures were used in the cell described and the emf found at several concentrations of HCl in each solvent.

The emf is given by

$$E - \frac{\nu RT}{NF} \ln m_{\pm} = E^o + \frac{\nu RT}{NF} \ln \gamma_{\pm}$$

where ν = no. of ions produced by one molecule.

$m_{\pm} = m \left[\nu_+^{\nu_+} - \nu_-^{\nu_-}\right]^{\frac{1}{\nu}}$ and $\underline{m}$ is the molality.

$E^o = E$ when mean activity or product $m\gamma$ is unity.

$\gamma_{\pm}$ = mean activity coefficient of the ions.

Since it is extremely difficult to get accurate measurements at low enough concentrations for $\gamma_{\pm}$ to be taken as 1, Hitchcock (C9) has modified the equation making use of the Debye-Hückel theory to allow measurements to be made at higher concentrations and extrapolated back to zero concentration. The equation is

$$\left[E - \frac{\nu RT}{NF} \ln m_{\pm} + \frac{\nu RT}{NF} A\sqrt{\Gamma}\right] = E^o + \frac{\nu RT}{NF} B'm$$

where A is the Debye-Hückel-limiting slope

and Γ is the ional concentration

and B' is the additional constant from the Debye-Hückel equation.

Or $E - 2k \log m_{\pm} + 2kA\sqrt{\Gamma} = E^o + 2kB'm$

where $k = \frac{2.3RT}{NF}$

hence if the left hand side is plotted against m, E^{o} can be found by extrapolation.

The graph, however, shows curvature when the value of m is small and this is probably due to the inadequacy of using $\log \gamma = -A'\sqrt{m} + B'm$ for the Debye-Hückel equation. Brown and McInnes (C10) substituted the more accurate form of the Debye-Hückel equation $\log\gamma = -\frac{A'\sqrt{m}}{1 + \beta' a_i \sqrt{m}}$ and obtained the expression

$$E + 2k \log m - 2k A'\sqrt{m} = E^{0} - \beta' a_i \sqrt{m}\left[E - E^{o} + 2k \log m\right] \quad ..(A)$$

The plot of the left hand side of the equation against $\sqrt{m}\left[E - E^{o} + 2k \log m\right]$ gives a straight line over the lower concentration region, cutting the axis at E^{o} and having a slope of $-\beta' a_i$. β' is the appropriate Debye-Hückel constant and a_i is the distance of closest approach of the ions. The Brown-McInnes plot leads to a slightly higher value of E^{o} than the Hitchcock plot but should be more accurate (C11).

Evaluation of pK.

The emf of solutions containing potassium hydrogen benzoate and KCl in water or in mixed solvent was measured at several concentrations of potassium hydrogen benzoate and KCl. pK could then be calculated from the equation (C12).

$$E^o - E + \frac{RT}{F}\ln\frac{m_{HBz}m_{Cl^-}}{m_{Bz^-}} = -\frac{RT}{F}\ln K - \frac{RT}{F}\ln\frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{HBz}}{\gamma_{H^+}\gamma_{Bz^-}}$$

$$\text{or} \quad pK = \frac{E^o - E}{k} + \log\frac{[HBz][Cl^-]}{[Bz^-]} + \log\frac{\gamma_{HBz}\gamma_{Cl^-}}{\gamma_{Bz^-}}$$

Allowance for the ionisation of benzoic acid, which affects $[HBz]$ and $[Bz^-]$, can be made by using a method of successive approximations, each time making use of the pK from the previous calculation. Usually one approximation was found to be sufficient.

$$\text{If } pK' = \frac{E^o - E}{k} + \log\frac{[HBz][Cl^-]}{[Bz^-]}$$

then pK' approached pK as the ionic strength approached zero since the activity coefficient approached 1 as the ionic strength decreased. As the products $\gamma_{H^+}\gamma_{Cl^-}$ and $\gamma_{H^+}\gamma_{Bz^-}$ tended to cancel each other and the activity coefficient for a non-electrolyte such as γ_{HBz}, had been found to be roughly a linear function of the ionic strength (C13), pK could be found by extrapolation of a plot of pK' against ionic strength. In water however the experimental error was larger than the correction and pK was therefore taken as the average of the pK' values.

In aqueous solution steady readings were obtained after 20 - 30 minutes and no change was noticed in periods of more than an hour. The extrapolation gave an E^o value for the cell which agreed to 0.0001 v. with that obtained by Harned and Wright (C3).

With 20% dioxan a drift was noticed, the emf reading decreasing with time. Attempts were then made to improve the constancy of the readings. One of the platinum electrodes was replaced by a gold electrode and the readings on the two electrodes compared. Immediately on immersion the disparity was several millivolts but this rapidly diminished, the reading with the platinum electrode falling and that with the gold electrode rising. In 1½ - 2 hours the readings agreed and thereafter the readings fell with time at about the same rate, the platinum sometimes falling very slightly faster than the gold. After several hours the gold electrode became less sensitive and had to be re-cleaned. Removal of either the platinum and gold electrodes or the Ag-AgCl electrodes for cleaning or replacing did not seem to interfere with the results. Replacement of any electrode by a completely new one made no difference to the readings after about 10 minutes had been allowed for the electrode to settle down. Harned and Morrison (C14) state that the values in 20% dioxan were not as constant as in other dioxan-water mixtures and took the precaution of having no rubber in their apparatus. Wooten and Hammett (111), however, used rubber stoppers with no ill effects and so, though rubber stoppers were employed in this apparatus, care was taken that they never came in contact with any of the solutions. Wooten and Hammett recommended that nitrogen be passed over the solution instead of through it and so the stirring of the quinhydrone limb with nitrogen was discontinued and a mechanical paddle used instead. This was found to improve the constancy of the readings and it was then that the purification of the nitrogen to free it from oxygen was stopped, as it seemed that other contamination of the gas was occurring.

The drift was still quite definite though less than before and so extrapolation to zero time of an emf-time graph was tried. Usually the value obtained by extrapolation was about 0.5 millivolt higher than that obtained by averaging the readings taken over a period of 1½ - 2 hours, half an hour having been allowed for the system to come to equilibrium.

40% dioxan was now used and it was found that a solution which had stood for several days before being used drifted much more rapidly than one which was freshly made up. Dioxan is known to be decomposed by atmospheric oxygen and by concentrated HCl (C15) so probably even at the low concentrations of acid involved here the combined action had a perceptible effect.

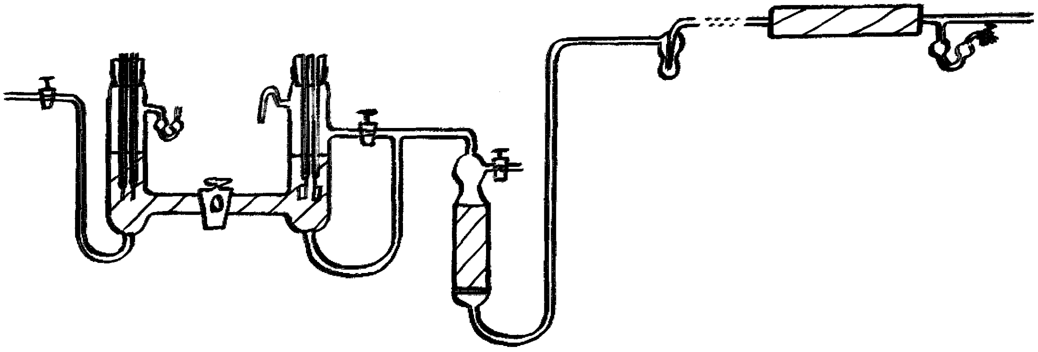
Drift tending to lower the measured potential has also been attributed to decomposition of quinhydrone in buffer solution. In acetate buffer it occurs after 20 hours in the dark but is accelerated by daylight (C1).

In aqueous solution a slight darkening of the solution containing the quinhydrone was noticeable after several hours but, as the emf had reached a constant value well before that time, it was not serious. However, as the percentage dioxan in the solvent was increased, the darkening became both deeper and more rapid until in the worst instance, $KHBz_2$ in 50% dioxan, it began to appear almost at once and after about half an hour the solution was dark brown. The slight drift which was noticed in 20% dioxan became greater until with $KHBz_2$ in 50% dioxan it was of the order of 10 mv. per hour. In an attempt to minimise the error, the cell and its contents were allowed to come to equilibrium in the thermostat before the quinhydrone was added. Readings were commenced immediately and taken every few minutes. During the first 10 minutes or so, the value of E showed a gradual increase but after that the usual downward drift was apparent. Extrapolation to zero time gave a value of E about 1.0 - 1.5 mv. higher than the maximum measured value, and the discrepancy between two platinum electrodes, which agreed in aqueous solution, varied from a few tenths of a mv. to about 2 mv. It would thus appear that a quinhydrone electrode is not suitable for use in dioxan-water mixtures.

A chloranil electrode was tried but showed only slightly less variation in 50% dioxan.

The results obtained with the quinhydrone electrode are given in tables C1 - C5 of the appendix. Their reliability decreases with increasing proportion of dioxan in the solvent.

It was then decided that a hydrogen electrode should be used and the apparatus was modified accordingly. All rubber tubing was replaced by glass or polyvinylchloride tubing. All joints were ground glass cone and socket type and Pyrex glass was used throughout the new part of the apparatus, which is shown in the diagram.



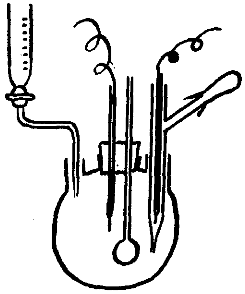
Only the Ag-AgCl electrodes were sealed into soda glass tubes supported by a rubber stopper as previously. Dow Corning Silicone grease was used to lubricate the taps.

The making of the Ag-AgCl electrodes has already been described (C2).

The platinum electrodes were platinum foil welded on to platinum wire which was pinch sealed through Pyrex glass tubes. The electrodes were cleaned in chromic acid, washed with distilled water and heated to dull redness in an alcohol flame before being plated by electrolysis of a 2% platinic chloride solution in $2\bar{N}$ hydrochloric acid for 10 - 20 minutes at a current density of 10 - 20 ma/cm^2 (C11). After being washed for 48 hours, the electrodes were stored in distilled water till required and when not in use. In dioxan-water mixtures, freshly plated electrodes were found to come to equilibrium more quickly than ones which had previously been used in dioxan-water and with constant use the settling time became progressively longer though the final value reached, agreed well with that reached in much less time with a freshly-plated electrode. Prolonged washing with distilled water restored their original speed of settling but in practice it was more convenient to clean and replate the electrodes.

Cylinder nitrogen was passed through only a column of the pure solvent before being used but cylinder hydrogen was passed over platinised asbestos (C16) heated to 500°C. in a Pyrex tube before being led into the presaturator which was fitted with a sintered glass disc to keep the bubble size small and so improve the contact between the gas and the solution. The presaturator and its connections to the cell were immersed in the thermostat. The connections were such that the hydrogen could be passed over the solution while readings were being taken but normally bubbled through the solution.

The materials were the same as those used previously. The HCl solution was restandardised on a weight basis by the method of differential titration as recommended by Ives (C11). Standard silver nitrate was made up by weight approximately $0.1\bar{M}$, and the factor checked by differential titration against purified KCl. The apparatus is shown in sketch



The glass paddle was mechanically driven and during titration the whole apparatus was enveloped by a black cloth to prevent photo-decomposition of the precipitated AgCl. Both electrodes were Ag-AgCl electrodes made as already described. The HCl solution was weighed into the flask and an appropriate amount of distilled water added. The bulk of the $AgNO_3$ solution was added from a weight burette and, after adequate stirring, the end point was approached by adding, from a microburette, small equal portions of a $AgNO_3$ solution made by diluting a known weight of the standard $AgNO_3$ solution to a definite volume so that 1 ml. of the diluted solution contained approximately 0.1 g. of the standard $AgNO_3$ solution. The electrode compartment was emptied and refilled several times after each addition of $AgNO_3$ to bring the reading to zero. $\frac{dE}{dV}$ for each point was then plotted against volume added up to that point and a graph of the usual type showing a maximum at the end point was obtained. The factor calculated differed by less than 0.1% from the original factor used for the acid.

All solutions were made up by weight just before use. Nitrogen was bubbled through the two halves of the cell before the cell and the presaturator in the hydrogen train were filled by blowing the test solution over with nitrogen. The centre tap was kept closed except while readings were actually being taken and during that time the nitrogen bypassed the cell and the hydrogen passed over instead of through the solution. In this way, mixing of the solutions in the two halves of the cell was kept to a minimum.

All readings were corrected to a pressure of 1 atmosphere of hydrogen, allowance being made for the depth of delivery of the hydrogen bubbles (C11).

E^o and a_i were calculated in the same way as for the quinhydrone electrode system. The values of a_i were used to obtain the "extended terms" of the Debye-Hückel equation as given by Gronwall, La Mer and Sandved in their tables for symmetrical valency types of electrolytes (C17). The left hand side of equation A became

$$E + 2k \log m - 2kA'\sqrt{m} + 2k\left[\left(\tfrac{1}{2}X_3(\kappa a) - 2Y_3(\kappa a)\right) + \left(\tfrac{1}{2}X_5(\kappa a) - 4Y_5(\kappa a)\right)\right],$$

the values for the last term being read from the tables. The correction was negligible in aqueous solution but increased with increasing percentage of dioxan to about 0.0004 v. in 50% dioxan.

Measurements of emf were made on solutions of several concentrations of potassium hydrogen benzoate and potassium chloride, present in approximately equimolar amounts in water and dioxan-water mixtures and pK' calculated as before. In 50% dioxan the plot of pK' against ionic strength gave a reasonably accurate line for extrapolation. In 40% dioxan there appeared some scatter among the weaker points and in 30% dioxan the scatter was too great to permit an extrapolation with any degree of accuracy.

Previous workers found difficulty in using organic acids with a hydrogen electrode employing a platinum surface (C18), but discovered that platinum plated with palladium gave more satisfactory results. This has been attributed to the lower catalytic activity of the palladium (C19). In aqueous HCl, it has been shown (C18), that the platinum and palladium plated electrodes give identical emf readings so there should be no difference in E^o for the cell.

The platinum foil electrodes were heated to red-heat in an alcohol flame and then made the cathode in the electrolysis of a solution of 6 g. $PdCl_2$ in 100 cc. $^N/_{10}$ HCl for 30 seconds with a current of about 200 milliamps passing. After having been washed for 48 hours in distilled water, the electrodes were stored in distilled water as before.

These palladium-plated electrodes took much longer to come to equilibrium, about 3 hours in water and longer as the percentage dioxan in the solvent increased, but the scatter of the points on the graph was very much reduced and extrapolation was possible.

The results are given in Tables C6 - C10.

Part 3

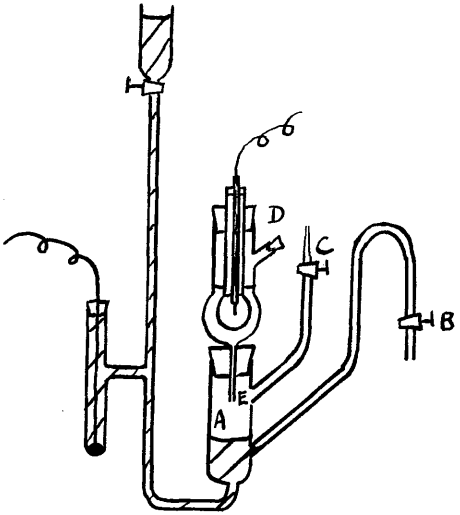
pH Method.

Though less accurate than the two preceding methods, owing to the presence of a liquid junction and a glass electrode, this method is useful because of the availability of the apparatus required and the comparative ease of calculation.

pH was originally defined by Sørensen as the negative logarithm of the hydrogen ion concentration but, in modern theory, concentration has been replaced by the more exact activity and pH is generally taken as - log $a_{H_3O^+}$. The activity of a single ion cannot be determined exactly and so it is not possible to obtain an absolute pH scale. For practical purposes a pH scale has been standardised by measuring the pH of buffer solutions of acids whose dissociation constants have been exactly determined. Hitchcock and Taylor (A11) and Bates (D2) recommend several such buffer solutions which give reproducible results and can be used to standardise this conventional pH scale.

The use of mixed or non-aqueous solutions presents a difficulty as the H_3O^+ activity will vary with the solvent. Ideally the pH scale should be standardised for each solvent as it has been for water but this would require as a preliminary the exact measurement of the dissociation constant of several suitable acids in each solvent and the work involved would be considerable. Some workers (16,31) have made up the buffer solutions in the solvent being used and assumed that the pH obtained is the same as that of the buffer in water. Their scale is thus based on the pH of a solution whose pH is not known and there is no basis for comparison of pH in different solvents. The other expedient, the one which has been used in the present work, is to standardise the scale with the aqueous buffers and to refer all the measured pHs to that scale. The values obtained will deviate more and more from the true pH as the difference between the activity of the hydrogen ion in the solvent and in water increases but they are all referred to a known pH and can be compared. This method has been used especially when it was desired to extrapolate the results to zero concentration of organic solvent (73).

A liquid-liquid junction is always a source of uncertainty since the potential developed at it cannot be calculated accurately. The alternative usually adopted in practice is to eliminate it or make it constant as far as possible. The cell used in the present work was designed to give a reproducible junction and is essentially as shown in the diagram.



The glass electrodes were made of Corning 015 glass and had a resistance of less than 20 Megohms. The bulb was filled with $^{N}/5$ HCl and the internal electrode was a Ag-AgCl electrode as used in the emf work. A saturated calomel electrode was used as the reference half cell. The cell was immersed in an oil thermostat kept at 25°C. ±0.5°C. The glass electrode compartment was rinsed several times with solution at 25°C., filled with solution and left for half an hour. This portion of solution was then drained off and the compartment again filled. A was rinsed several times with saturated aqueous KCl solution from the reservoir, without allowing the KCl solution to touch the tip of the capillary tube E. The KCl solution was then allowed to rise in A until it just failed to touch the tip of E and the junction was finally made by opening tap C to allow the test solution to flow slowly down the capillary tube and gently make contact with the KCl solution in A. Readings were taken during 20 - 30 minutes on a Tinsley Type 3378 B Potentiometer using a triode valve circuit with a Pye Scalamp galvanometer as null-point indicator. When the reading was constant the electrode compartment and A were emptied by opening tap B, the electrode compartment filled with a fresh sample of the test solution and another liquid junction made as before. In aqueous solution a steady, reproducible reading was obtained almost at once but as the percentage dioxan was increased the glass electrode took longer to settle, though even in 50% dioxan half an hour was found to be sufficient.

The pH scale was standardised using aqueous 0.01 M Borax, 0.05 M KH phthalate and 0.025 M phosphate buffers (D2) and not more than three solutions in mixed solvent were measured consecutively without the reading of a standard buffer being rechecked. The chemicals were all as described in the previous sections. Solutions were made up, by weight just before use, by dissolving a suitable weight of potassium hydrogen benzoate in the appropriate solvent.

The thermodynamic dissociation constant, K, of an acid is given by

$$K = \frac{\{H^+\}\{A^-\}}{\{HA\}}$$

therefore $\log K = \log \{H^+\} + \log \frac{\{A^-\}}{\{HA\}}$

and, substituting as previously,

$$pK = pH - \log \frac{[A^-]}{[HA]} - \log \frac{fA'}{fHA}$$

It is interesting to consider critically the different ways of obtaining pK from the measured pH.

In the usual titration procedure $\log \frac{[A^-]}{[HA]}$ is taken as the logarithm of the concentration of the base added, divided by the difference between the initial concentration of acid and the concentrated of base added. At exactly half neutralisation, this term is zero. The activity coefficient of the undissociated acid, γ_0 is assumed to be 1 and the activity coefficient of the ions is calculated from the simplest form of the Debye-Hückel equation for very dilute solutions

$$- \log \gamma = A'\sqrt{I} \quad . \; . \; . \; . \; . \; (1)$$

pKs for benzoic acid in water and in 40% dioxan have been calculated in this way and are given in column 3 of table D1 as pK_1. The average of these values would normally be taken as pK.

The simplest form of the Debye-Hückel equation is only valid for very dilute solutions ($m < 0.003$), whereas in practice solutions are usually more concentrated. It is therefore more correct to use the Güntelburg form of the Debye-Hückel equation

$$-\log \gamma = \frac{A'\sqrt{I}}{1+\sqrt{I}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

It is obvious that the larger the value of m, the greater will be the difference between the two activity coefficients and so the effect of using equation (2) is more noticeable in 40% dioxan than in water. Comparison of the averages for column 3 and for column 4 of table D1 illustrates this point.

The pKs in 40% dioxan still show a steadily increasing value with increasing concentration (i.e., normal salting out effect). As in the emf results it may be due to the inaccuracy of taking γ_0 as unity and can be counteracted by plotting apparent pK against ionic strength (R & F)[C13]. This has been done in graph D1.

The graph for aqueous solution shows marked curvature towards the lower values of ionic strength. In this region the dissociation of the benzoic acid is sufficient to make an appreciable effect on **pK** through the term $\log \frac{[A^-]}{[HA]}$. The hydrogen ion concentration can easily be calculated from the measured pH of the solution and $[A^-]$ and $[HA]$ adjusted accordingly. pKs including this correction are given as pK_3 in table D1. The plot against ionic strength now gives a straight line. In 40% dioxan the smaller dissociation and higher concentrations used made such a correction unnecessary.

Lastly, the still more accurate form of the Debye-Hückel equation

$$- \log \gamma = \frac{A' \sqrt{I}}{1 + \beta' a_i \sqrt{I}} \quad \ldots\ldots\ldots \quad (3)$$

was used. Frequently it is not possible to use equation (3) owing to lack of knowledge of a_i, the distance of closest approach of the ions. For the calculation to give the pK_4s of table D1, the values for a_i estimated from the slopes of the lines in the Brown-McInnes plots of the emf data were used. These values are not very accurate since the slope of the line varies considerably according to the points used in drawing it, although the intercept giving E^o remains almost constant. In water the difference between pK_3 and pK_4 is extremely small but in 40% dioxan the pKs at the higher concentrations are noticeably reduced.

It is therefore concluded that 1) when the ionic strength is less than 0.025 and the dissociation constant greater than 10^{-5} it is necessary to correct $\log \frac{[A^-]}{[HA]}$ for the dissociation of the acid: 2) when the ionic strength is greater than 0.015 it is not correct to take the average of the pKs for the individual points, since apparent pK increases with increasing ionic strength, and an extrapolation

of apparent pK against ionic strength should be used:
3) when the correct pK can be taken as the average of the apparent pKs, e.g., in water, it is worth while applying the most exact equation for the activity coefficient (equation (3) above) but when an extrapolation is being used it is not necessary to go beyond equation (2) above, since the further refinement only alters the slope of the line without affecting the intercept. If the simplest equation is used the result will tend to be high.

It must be remembered, however, that in achieving these results great care was given to details of technique and as high an accuracy as possible was aimed at. In many of the measurements made in the normal way the refinements of calculation are meaningless on account of the experimental error.

The results for 20, 30 and 50% dioxan are given in tables D2, D3 and D4 respectively.

Part 4.

Discussion.

A summary of the results obtained by the different methods is given below

% dioxan	$E^o_{H_2/Pt}$	$E^o_{Quin.}$	$pK_{Cond.}$	$pK_{Emf./H_2}$	$pK_{Emf./Quin.}$	pK_{pH}
0	.2222	.4770	4.205	4.203	4.189	4.203
20	.2031	.5055	4.863	4.864	4.876	4.831
30	.1900	.5223	5.272	5.296	5.26	5.230
40	.1738	.5388	5.784	5.789	5.72	5.690
50	.1510	.5625	6.385	6.342	6.12	6.208

There is good agreement between the results obtained by conductivity and emf using a hydrogen electrode, but the results by the pH method show an increasing deviation from those of the other two methods as the percentage dioxan in the solvent increases.

Though there have been many determinations of E^o and of pK for benzoic acid in water, very little has been done in dioxan-water mixtures, so not many values are available for comparison. Interpolation, where necessary, of Harned and Morrison's (E1) values of E^o for a Ag-AgCl electrode at 25°C. gives for water, 20, 30, 40 and 50% dioxan 0.2224, 0.2030, 0.1900, 0.1735 and 0.1526 respectively and agreement is good especially in the lower concentrations of dioxan. No values were found in literature for E^o for a cell consisting of a quinhydrone and a Ag-AgCl electrode in dioxan-water mixtures but in water Hovorka and Dearing (E2) obtained 0.6994 for the quinhydrone electrode and the recommended value, due to Harned and Ehlers (13), for the Ag-AgCl electrode in water is 0.2224, from which we would expect 0.4770 for E^o in the present work. Again agreement is good. Values given for the pK for benzoic acid in water at 25°C. include 4.201 (E3), 4.199 (B23), 4.212, 4.200 (45), 4.21 (54) and at 20°C., 4.22, 4.24 (59). The present one, 4.203 lies well within this range. In dioxan-water solution, Lynch and La Mer (B5) give the pK in 50% dioxan as 6.115 and Cavill, Gibson and Nyholm (54) 6.07 in the same solvent and also 4.78 in 20% and 5.14 in 30% dioxan. All these mixed solvents, however, are on a volume basis. Speakman (59) obtained 5.35 and 5.2 in 30% ($^w/_w$) dioxan at 20°C. As a check, a full titration in 30% dioxan was carried out in place of the single measurement on a half neutralised solution as previously and the result confirmed the value reported in this paper.

The discrepancy between the results obtained by the pH method and the other two methods calls for some comment and in this connection the question of correcting the pH results for the solvent effect on the glass electrode arises. Recent workers (23, 65, 70, 73, E4) have applied no correction to readings in mixed solvents, particularly alcohol-water mixtures. According to Dole (111) the error is due to the reduced activity of the water in the solvent and can be calculated from $\Delta E = \frac{RT}{F} \ln \{H_2O\}$. This was substantiated by further work done by Dole (14) in alcohol-water and strongly acid solutions. In the present case, however, application of Dole's correction increases rather than decreases the discrepancy.

In order to see if some arbitrary correction could be found experimentally, it was decided to measure the pH of approximately $^M/_{100}$ HCl in each of the solvent mixtures used and to compare it with the theoretical pH calculated from the $\{H^+\}$ of the solution, assuming the HCl to be completely dissociated in every case and using mean activity coefficients for HCl obtained by interpolation of the data of Harned and Morrison (E5). For interest, acetone-water and alcohol-water mixtures were also used as solvent and the results are given in table E1 and plotted in figure E1. The deviation from the calculated pH was greatest in the case of dioxan-water mixtures and least with acetone-water mixtures while that of the alcohol-water mixtures was in the opposite sense from the other two, the measured pH being higher than expected in alcohol-water and lower in dioxan-water and acetone-water mixtures. This would seem to indicate that the nature of the solvent mixture is more important than the reduced activity of the water present. If a correction based on these measurements is applied to the pK values obtained by the pH method, it brings them much closer to those obtained by the other two methods.

% dioxan	pK	Correction	Corrected pK	pK by emf
0	4.203	-	4.203	4.203
20	4.831	.023	4.854	4.864
30	5.230	.037	5.267	5.296
40	5.690	.060	5.750	5.789
50	6.208	.121	6.329	6.342

In this case, at any rate, the correction seems justified but further work, including other solvents, is required before any definite conclusion can be reached. It would also be interesting to measure the pH of such solutions using a glass electrode and apparatus not involving a liquid junction so that the effect due to the glass electrode could be separated from that due to the liquid junction.

In considering the difference between the dissociation constant of a substance in water and in some other solvent there is the difficulty that the activities of any species are referred to infinite dilution in each particular solvent and therefore are not mutually comparable. To get over this difficulty, the hypothetical situation of the dissociation taking place in the gas phase may be postulated. This is quite impracticable but is a useful expedient since it removes solvent effects from the equilibrium

$$\begin{tikzcd}
\mathrm{HAaq} \arrow[dd] & + & \mathrm{H_2Oaq} \arrow[dd] \arrow[r] & \mathrm{H_3O^+aq} & + & \mathrm{A'aq} \\
 & \mathrm{I} & & & \mathrm{III} & \\
\mathrm{HAg} & + & \mathrm{H_2Og} \arrow[r, "\mathrm{II}"] & \mathrm{H_3O^+g} \arrow[uu] & + & \mathrm{A'g} \arrow[uu]
\end{tikzcd}$$

(The hydrogen ion is still shown as the hydrated proton, H_3O^+, since it is usually presumed that in partially aqueous solvents the water only hydrates the proton.) The total change in free energy during any process is not dependent on the intermediate stages so that the change in free energy in going from the initial to the final stage will be the same either by the direct route or stages I, II and III as shown in the diagram. Stage I is the evaporation of a solution of unit activity to give a gas with partial vapour pressures p^o_{HAaq} and $p^o_{H_2Oaq}$. As this is an equilibrium step, there is no change in free energy. If the gas is then compressed to unit pressure there is a gain in free energy

$$\Delta G_I = RT \ln \frac{1}{p^o_{HAaq}} + RT \ln \frac{1}{p^o_{H_2Oaq}}$$

In stage II, the reaction takes place, giving H_3O^+ and A' gas also at unit pressure

$$- \Delta G_{II} = RT \ln Kg$$

where Kg is the dissociation constant for the gas. Next the ionic gas is allowed to expand to give a gas of such a vapour pressure that, when it is finally condensed, the solution has unit activity

$$-\Delta G_{III} = RT \ln \frac{1}{p^{o}_{H_3O^+aq}} + RT \ln \frac{1}{p^{o}_{A^-aq}} \; .$$

Adding all three together

$$-\Delta Gaq = -\Delta G_{I} - \Delta G_{II} - \Delta G_{III} = RT\ln Kg + RT\ln \frac{p^{o}_{HAaq} \cdot p^{o}_{H_2Oaq}}{p^{o}_{H_3O^+aq} \cdot p^{o}_{A^-aq}}$$

$$\text{or } \log Kaq = RT\log Kg + \log \frac{p^{o}_{HAaq} \cdot p^{o}_{H_2Oaq}}{p^{o}_{H_3O^+aq} \cdot p^{o}_{A^-aq}}$$

By an exactly analogous argument but starting from a mixed solvent, S,

$$\log K_s = RT\log Kg + \log \frac{p^{o}_{HA_s} \cdot p^{o}_{H_2O_s}}{p^{o}_{H_3O^+{}_s} \cdot p^{o}_{A^-{}_s}}$$

Subtracting the one from the other and rearranging,

$$pK_s - pKaq = \log \frac{p^{o}_{HAaq}}{p^{o}_{HA_s}} - \log \frac{(p^{o}_{H_3O} + \cdot p^{o}_{A} -)aq}{(p^{o}_{H_3O} + \cdot p^{o}_{A} -)s} - \log \frac{p^{o}_{H2O_s}}{p^{o}_{H_2Oaq}}$$

A solution of HA of unit activity in water will not be in equilibrium with a solution of HA of unit activity in solvent S (each activity being referred to infinite dilution in its own solvent), therefore the partial pressures of HA in the two cases will be different and, usually, will be greater over water. If the concentration of HA in water is reduced until the two partial pressures are equal, the two solutions will be in equilibrium and the ratio of their activities $\frac{a_{HAs}}{a_{HAaq}}$ will be equal to the distribution ratio of HA between S and water (ℓ_{HA}). To be more precise, it is the limiting value of the actual concentration distribution ratio as $C \rightarrow 0$ (ℓ^{o}_{HA}) and can be found experimentally. Similar treatment of the ratio $\frac{(p^{o}_{H_3O^+} \cdot p^{o}_{A^-})_{aq}}{(p^{o}_{H_3O^+} \cdot p^{o}_{A^-})_{s}}$ shows it to be equal to $\ell^{o}_{H_3O^+A^-}$ but this is not so easily estimated. The above equation can now be written

$$pK_s - pK_{aq} = \log \ell^{o}_{HA} - \log \ell^{o}_{H_3O^+A^-} - \log a_{H_2O_s} \quad . \; . \; . \quad (A)$$

where $\log a_{H_2O_s}$ represents the activity of water in S relative to that in pure water. This equation is similar to the one given by Kolthoff (E6) except that, since in the present work the solvent is partially aqueous, a term for the change of activity of the water present is included.

The effect due to the anion in $\log \ell^{o}_{H_3O^+A^-}$ will be small compared with that of the cation and Braude and Stern (116) consider the difference in pKs to be due mainly to the difference in proton affinity of the solvents, which can be measured by the change in free energy on going from one to the other. Butler and Robertson (E7) also held this view but stated that some other effect was also present. It is therefore expected that $\log \ell^{o}_{H_3O^+A^-}$ will account for most of the difference between pK_s and pK_{aq}, but, according to the calculation shown in the table below, this appears not to be the case when dioxan-water mixtures are the solvents.

Benzoic Acid.

Solvent %age dioxan	Solubility g.mol/ 1000 g.	pK	log ℓ^o_{HA}	-log $a_{H_2O_s}$	log ℓ^o_{HA} -log a_{H_2O}	$pK_s - pK_{aq}$
0	*.0276	4.205	0	0	0	0
20	*.1304	4.863	.674	.011	.685	.658
30	.407	5.272	1.169	.019	1.188	1.067
40	1.068	5.784	1.588	.026	1.614	1.579
50	2.018	6.385	1.864	.038	1.902	2.180

The solubility of the benzoic acid was determined by stirring an excess of solid acid in the required solvent for several days at 25°C. and then estimating the amount of acid in solution by titration, under nitrogen, with standard barium hydroxide, using phenolphthalein as indicator.

From the Born equation applied to the dissociation of an acid in two different solvents of dielectric constants D^o and D ,

$$\log \ell^o_{H^+A^-} = \frac{Nz^2e^2}{2.3x2RT}\left(\frac{1}{r_{H^+}} + \frac{1}{r_{A^-}}\right)\left(\frac{1}{D} - \frac{1}{D^o}\right)$$

it is possible to get an estimate of $\log \ell^o_{H_3O^+A^-}$. The main difficulty lies in knowing what value to use for $r_{H_3O^+}$ and

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* Data of Bockris and Egan (E8).

r_{A^-}. For two spherical, uniformly charged ions, the distance of closest approach of the ions in solution gives, very approximately, the sum of their radii, but the benzoate ion is neither spherical nor uniformly charged and the distance of closest approach of the ions of benzoic acid, about 5Å, is very much less than is to be expected as the sum of their radii. In any case, between 0 and 40% dioxan more than the difference in pK has been accounted for by the other two terms in equation (A). The negative value of log $\ell^o_{H3O^+A^-}$ (which is inadmissible) need not be taken too seriously since the error in taking log $\ell^o_{H_3O^+A^-}$ as log S/S_0 at concentrations of 0.1M and above will be appreciable, but it is safe to say that log $\ell^o_{H_3O^+A^-}$ will be small.

Kolthoff (E6) showed by his work with benzoic acid that in pure ethanol and pure methanol log $\ell^o_{H_A}$ does not account for most of the difference between pK_S and pKaq. This may be attributed to the fact that the solvation of the ions must be entirely different in each solvent so the ionic radius will change appreciably and log $\ell^o_{H^+A^-}$ will be large.

Cavill, Gibson and Nyholm (54) have determined dissociation constants for benzoic acid in alcohol-water mixtures and Bockris and Egan (E8) give values for its solubility.

Interpolation of these results allowed the following table to be worked out:

%alc.	pK	S	log S/S_o	-log* a_{H_2O}	log S/S_o -log a_{H_2O}	pK_s-pK_{aq}
0	4.21	.0276	0	0	0	0
10	4.27	.0418	.181	.023	.20	.06
20	4.48	.0915	.521	.056	.58	.27
30	4.77	.322	1.068	.141	1.21	.56
50	5.49	1.721	1.795	.399	2.19	1.28

Again log ℓ^o_{HA}-log a_{H_2O} more than accounts for the difference between pK_s and pK_{aq} and the discrepancy is greater than in the case of dioxan-water mixtures, but Cavill, Gibson and Nyholm's value for pK in dioxan-water is lower by up to 0.3 pK unit than the results obtained in the present work. If a similar uncertainty existed in their values in alcohol-water it would increase the difference betwen pK_s and pK_{aq} and make the discrepancy much less.

In graph E2, pK, log ℓ^o_{HA} and log a_{H_2O} have been plotted against mol fraction of organic solvent. This is just a visual method of expressing the figures in the tables but shows very clearly how large a contribution is made by log ℓ^o_{HA}.

Thus it appears that, in solvents composed of water and up to 30 or 40% of an organic substance such as dioxan

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* From interpolation of data given by Martin and Brown (E9).

or ethanol, by far the largest part of the decrease in dissociation constant of an acid, such as benzoic acid, can be accounted for by the increased solubility of the acid, but further work covering more acids and solvents and a greater range of solvent mixtures is required before a general statement can be made.

Section 3.

Electrolytic Dissociation of Magnesium Sulphate and Lanthanum Ferricyanide in Mixed Solvents.

The work reported in this section was done in collaboration with the late Dr. J.C. James and the discussion given in the reprint written entirely by him.

Following work on polyvalent electrolytes previously done by Dr. James (F1,35) the electrolytic dissociation of magnesium sulphate in water, 10 and 20% dioxan, and 0.1, 0.25, 0.5M aqueous glycine solutions and of lanthanum ferricyanide in 0.1, 0.25 and 0.5M aqueous glycine solutions was measured by the conductivity method. Urea-water solutions were also tried but found to be unsatisfactory solvents owing to a drift in solvent resistance which made accurate readings impossible. The aqueous glycine solutions were used to give solvents of dielectric constant higher than that of water in contrast with the lower dielectric constants usually obtained, e.g., in alcohol-water and dioxan-water mixtures.

The apparatus and experimental technique have already been described in Section 2, Part 1 of this thesis. The purification of materials, details of calculation and experimental results are all given in the reprint at the end of the appendix.

It has been shown that the dissociation constant of both salts varies linearly with the reciprocal of the dielectric constant of the solution (which is taken as the dielectric constant of the solvent since the solutions are all very dilute) and that the increase in extent of dissociation with increase in dielectric constant can be accounted for by simple electrostatic considerations. The radii of the ion pairs have also been calculated and it is suggested that, in glycine solutions, glycine molecules as well as water molecules are present in the solvation sheaths while in dioxan-water mixtures only water takes part in solvation.

APPENDIX.

Table A1.

Titration of p-chloroaniline

Burette Readings	Volume Added	Potentiometer Readings	Δ E	Δ pH	pH
1.861	0	0.0659			
2.735	0.874	0.1196	-0.0609	-1.07	3.57
2.869	1.008	0.1323	-0.0482	-0.85	3.79
3.040	1.179	0.1469	-0.0336	-0.59	4.05
3.170	1.309	0.1614	-0.0191	-0.34	4.30

b	$[H^+]$	$b + [H^+]$	$h - b - [H^+]$	$a - (h - b - [H^+])$	$K_a \times 10^{-4}$	pK_a
0.003175	0.000270	0.003445	0.002730	0.001320	1.42	3.85
0.003650	0.000162	0.003812	0.002363	0.001687	1.25	3.90
0.004275	0.0000892	0.004364	0.001811	0.002239	1.20	3.92
0.004750	0.0000504	0.004800	0.001375	0.002675	1.17	3.93

$\frac{\Delta E}{\Delta pH} = 0.0570$

$a = 0.004050$

$h = 0.006175$

E.P. = 1.70 cc. caustic soda added

$f_1 = 0.92$

Average $pK_a = 3.90$

$pK_b = 10.27$

Table A2.

Titration of p-bromoaniline.

Burette Readings	Volume Added	Potentiometer Readings	Δ E	Δ pH	pH
1.920	0	0.0616			
2.969	1.049	0.1215	-0.0588	-1.03	3.61
3.037	1.117	0.1276	-0.0527	-0.92	3.72
3.068	1.148	0.1299	-0.0504	-0.88	3.76
3.201	1.281	0.1450	-0.0353	-0.62	4.02

b	$[H^+]$	b + $[H^+]$	h- (b+ $[H^+]$)	a - h + (b+ $[H^+]$)	K_a x 10^{-4}	pK_a
0.003815	0.000246	0.004061	0.002109	0.000821	1.04	3.96
0.004060	0.000190	0.004250	0.001920	0.001010	1.09	3.95
0.004170	0.000174	0.004344	0.001826	0.001104	1.14	3.94
0.004665	0.000096	0.004761	0.001409	0.001521	1.13	3.95

$$\frac{\Delta E}{\Delta pH} = 0.0570$$

a = 0.002930

h = 0.006170

f_1 = 0.92

E.P. = 1.693 cc. caustic soda added.

Average pK_a = 3.95 $\therefore$ pK_b = 10.22.

Table A3.

Titration of benzidine.

Volume Added	Potentiometer Readings	Δ E	Δ pH	pH	b	$[H^+]$
1.010	0.1619	-0.0173	-0.302	4.338	0.003670	0.0000460
1.075	0.1690	-0.0102	-0.178	4.462	0.00391	0.0000345
1.140	0.1768	-0.0024	-0.042	4.598	0.00415	0.00002521
1.205	0.1862	+0.0070	+0.122	4.762	0.00438	0.00001689
1.305	0.1960	+0.0168	+0.293	4.933	0.00475	0.00001167
1.373	0.2049	+0.0257	+0.448	5.088	0.00500	0.00000817

$b + [H^+]$	N $= h-(b+[H^+])$	M $= N-a$	L $= 2a-N$	X $\times 10^{-9}$	Y $\times 10^{-6}$
0.003716	0.002459	0.000081	0.002297	2.82	1.67
0.003945	0.002230	-0.000148	0.002526	1.93	-2.52
0.004175	0.002000	-0.000378	0.002756	1.25	-5.23
0.004397	0.001778	-0.000600	0.002978	0.89	-6.25
0.004762	0.001413	-0.000965	0.003343	0.46	-8.76
0.005008	0.001167	-0.001211	0.003589	0.29	-9.31

$h = 0.006175$ $a = 0.002378$ E.P. = 1.69 cc. caustic soda added.

Points taken are all in second half of neutralisation

$\therefore$ I is constant and = h $f_1 = 0.91$ $f_2 = 0.70$

$$\frac{\Delta E}{\Delta pH} = 0.05725$$

Table B1.

% dioxan (w/w)	$\eta \times 10^2$ poises	D	d_4^{25} g/cc.
0	0.8949	78.54	0.9971
20	1.292	60.79	1.0141
30	1.532	51.90	1.0210
40	1.743	42.98	1.0270
50	1.904	34.26	1.0334

Table B2.

% dioxan (w/w)	Δ_oHCl	Δ_oKCl	Δ_oPot.Benz.	Δ_oBenz.Acid
0	426.16	149.86	105.88	382.1
20	302.7	105.40	73.62	270.92
30	247.2	88.05	61.50	220.65
40	201.0	73.90	53.04	180.14
50	161.0	62.40	45.61	144.21

Table B3

POTASSIUM BENZOATE.

20% dioxan

$c \times 10^4$	Λ
4.0000	72.45
5.0000	72.31
7.0000	72.05
10.0000	71.72
15.0000	71.29
20.0000	70.93
25.0000	70.62

b = 72.096 Λ_o = 73.62

30% dioxan

$c \times 10^4$	Λ
4.0000	60.17
5.0000	60.03
7.0000	59.77
10.0000	59.45
15.0000	59.01
20.0000	58.64
25.0000	58.32

b = 69.423 Λ_o = 61.50

40% dioxan

$c \times 10^4$	Λ
3.0000	51.79
4.0000	51.60
5.0000	51.42
7.0000	51.12
10.0000	50.75
15.0000	50.30
20.0000	49.97

b = 71.772 Λ_o= 53.04

50% dioxan

$c \times 10^4$	Λ
4.0000	43.83
5.0000	43.62
7.0000	43.25
10.0000	42.79
15.0000	42.16
20.0000	41.63
25.0000	41.18
30.0000	40.78
35.0000	40.41

b = 79.04 Λ_o= 45.61

Table B4

POTASSIUM CHLORIDE.

20% dioxan

$c \times 10^4$	Δ
3.0000	103.61
4.0000	103.35
5.0000	103.11
7.0000	102.71
10.0000	102.20
15.0000	101.50
20.0000	100.90
25.0000	100.36
30.0000	99.88

$b = 82.780$ $\Delta_o = 105.40$

30% dioxan

$c \times 10^4$	Δ
3.0000	86.67
4.0000	86.42
5.0000	86.21
7.0000	85.84
10.0000	85.38
15.0000	84.74
20.0000	84.22
25.0000	83.74

$b = 80.736$ $\Delta_o = 88.05$

40% dioxan

$c \times 10^4$	Δ
3.0000	72.39
4.0000	72.13
5.0000	71.92
7.0000	71.54
10.0000	71.08
15.0000	70.43
20.0000	69.88
25.0000	69.40

$b = 83.527$ $\Delta_o = 73.90$

50% dioxan

$c \times 10^4$	Δ
3.0000	60.64
4.0000	60.28
5.0000	59.97
7.0000	59.42
10.0000	58.74
15.0000	57.80
20.0000	57.00
25.0000	56.28
30.0000	55.62

$b = 92.38$ $\Delta_o = 62.40$

Table B5.

BENZOIC ACID

Water.

$\Lambda_o = 382.1$ $b = 147.606$

	$c \times 10^4$	$\sqrt{c}$	Λ	Λ_x	pK'	pK_c
b	0.8078	0.00898	216.79	381.10	4.2173	(4.2240)
a	1.4558	0.01207	179.60	380.88	4.2129	(4.2213)
b	1.9953	0.01413	161.80	380.74	4.2030	4.2124
a	2.9607	0.01721	139.40	380.56	4.2028	4.2134
b	2.9895	0.01729	139.32	380.56	4.1993	4.2099
a	4.4063	0.02099	119.36	380.36	4.1990	4.2110
b	4.5531	0.02134	118.05	380.35	4.1965	4.2087
a	5.6942	0.02362	107.55	380.23	4.1964	4.2094
b	5.9500	0.02439	105.83	380.20	4.1946	4.2077
a	7.1715	0.02678	97.71	380.10	4.1953	4.2091
b	7.5900	0.02755	95.56	380.06	4.1931	4.2072
b	9.4095	0.03068	87.16	379.93	4.1920	4.2070

Average value, pK = 4.210±0.002.

$c \times 10^4$	$\sqrt{c}$	Λ	Λ_x	C_u	pK'	pK_c
0.006287	0.07929	36.711	378.46	0.005677	4.1837	4.2088
0.009722	0.09860	29.777	378.02	0.008956	4.1839	4.2121
0.01198	0.1095	26.936	377.79	0.01113	4.1831	4.2129
0.01434	0.1198	24.679	377.58	0.01340	4.1834	4.2146

Extrapolation of pK_c vs. C_u, pK = 4.205±0.001

Table B6.

BENZOIC ACID

20% dioxan

Λ_o = 270.92

b = 138.42

	c$\times10^4$	$\sqrt{c}$	Λ	Λ_x	pK'	pK_c
a	0.7681	0.00876	91.53	270.21	4.8753	4.8829
b	1.0907	0.01044	81.32	270.12	4.8429	4.8515
a	1.8126	0.01346	64.71	270.01	4.8635	4.8734
b	2.3003	0.01517	59.32	269.94	4.8466	4.8572
a	2.8644	0.01692	53.15	269.88	4.8591	4.8704
b	3.8373	0.01959	47.180	269.79	4.8470	4.8593
a	4.3887	0.02095	43.988	269.75	4.8556	4.8683
b	5.6718	0.02381	39.455	269.66	4.8470	4.8606
a	6.0648	0.02463	37.991	269.64	4.8534	4.8673
a	8.2288	0.02867	33.026	269.53	4.8517	4.8667
b	10.247	0.03201	29.976	269.44	4.8456	4.8615
a	11.031	0.03321	28.799	269.42	4.8504	4.8666
b	12.905	0.03592	26.887	269.35	4.8451	4.8621

Average value, pK = 4.865±0.004

c$\times10^4$	$\sqrt{c}$	Λ	Λ_x	C_u	pK'	pK_c
0.01568	0.1252	7.992	267.93	0.01522	4.8421	4.8745
0.03876	0.1969	5.052	267.17	0.03803	4.8501	4.8905
0.04839	0.2198	4.495	266.97	0.04758	4.8553	4.8979
0.07661	0.2768	3.511	266.52	0.07560	4.8706	4.9181

Extrapolation of pK_c vs. C_u, pK = 4.863±0.001.

Table B7.

BENZOIC ACID

30% dioxan

$\Lambda_o = 220.65$ $b = 137.24$

	$c \times 10^4$	$\sqrt{c}$	Λ	Λ_x	pK'	pK_c
a	3.1526	0.01776	27.443	219.79	5.2506	5.2625
b	3.8723	0.01968	26.118	219.72	5.2069	5.2198
a	5.2391	0.02289	21.549	219.67	5.2526	5.2662
b	6.2071	0.02491	20.155	219.61	5.2398	5.2542
a	7.5487	0.02748	18.086	219.57	5.2533	5.2682
b	8.1654	0.02857	17.638	219.54	5.2418	5.2571
a	9.5028	0.03083	16.189	219.50	5.2533	5.2692
b	10.657	0.03265	15.489	219.46	5.2433	5.2597
a	11.370	0.03372	14.846	219.45	5.2533	5.2699
b	13.729	0.03705	13.682	219.38	5.2445	5.2620
a	14.767	0.03843	13.080	219.36	5.2531	5.2709
b	22.417	0.04735	10.632	219.22	5.2564	5.2761

Average value, pK = 5.265±0.005.

$c \times 10^4$	$\sqrt{c}$	Λ	Λ_x	C_u	pK'	pK_c
0.01327	0.1152	4.4496	218.39	0.01300	5.2495	5.2807
0.03092	0.1758	2.9053	217.86	0.03051	5.2539	5.2924
0.04495	0.2120	2.3803	217.61	0.04447	5.2645	5.3065
0.05715	0.2391	2.1115	217.42	0.05660	5.2641	5.3088
0.06251	0.2500	2.0123	217.35	0.06193	5.2670	5.3126
0.06859	0.2619	1.9112	217.28	0.06799	5.2713	5.3179

Extrapolation of pK_c vs. C_u, pK = 5.272±0.001.

Table B8

BENZOIC ACID

40% dioxan

Λ_o = 180.14 b = 143.64

	$c \times 10^4$	$\sqrt{c}$	Λ	Λ_x	pK'	pK_c
b	3.0414	0.01744	12.480	179.48	5.8012	(5.8128)
b	5.8878	0.02427	9.189	179.35	5.7880	5.8019
a	5.9754	0.02444	9.215	179.34	5.7791	5.7930
a	10.256	0.03203	7.136	179.22	5.7713	5.7874
b	12.151	0.03486	6.523	179.18	5.7780	5.7947
b	18.395	0.04289	5.341	179.08	5.7716	5.7903
a	19.247	0.04387	5.271	179.06	5.7648	5.7837
a	23.611	0.04860	4.7714	179.00	5.7634	5.7836
a	25.785	0.05078	4.5465	178.96	5.7676	5.7880
a	30.009	0.05478	4.2482	178.93	5.7613	5.7846
b	34.612	0.05883	3.9409	178.89	5.7651	5.7870
a	37.240	0.06103	3.8236	178.86	5.7597	5.7821
b	41.148	0.06415	3.6224	178.83	5.7637	5.7866
a	46.099	0.06790	3.4433	178.79	5.7586	5.7823
b	50.599	0.07113	3.2739	178.76	5.7623	5.7865

Average value, pK = 5.788±0.004

$c \times 10^4$	$\sqrt{c}$	Λ	Λ_x	C_u	pK'	pK_c
0.01323	0.1150	2.0347	178.38	0.01308	5.7591	5.7900
0.04455	0.2111	1.1010	177.75	0.04427	5.7646	5.8063
0.06770	0.2602	0.8845	177.50	0.06736	5.7722	5.8184
0.09178	0.3030	0.7517	177.31	0.09139	5.7808	5.8305

Extrapolation of pK_c vs. C_u, pK = 5.784±0.001.

Table B9

BENZOIC ACID

50% dioxan.

$\Lambda_0 = 144.21$ $b = 157.38$

	$c \times 10^4$	$\sqrt{c}$	Λ	Λ_x	pK'	pK_c
a	3.0162	0.01737	5.794	143.66	6.2914	(6.3038)
a	5.8008	0.02409	3.8329	143.59	6.3730	6.3869
b	6.2340	0.02497	3.7483	143.58	6.3603	6.3745
a	9.4589	0.03076	3.0221	143.51	6.3681	6.3838
b	12.344	0.03513	2.6846	143.45	6.3570	6.3740
a	13.118	0.03622	2.5755	143.45	6.3670	6.3840
a	20.185	0.04493	2.0815	143.36	6.3647	6.3839
b	22.149	0.04706	2.0165	143.33	6.3530	6.3727
b	27.908	0.05283	1.7984	143.28	6.3514	6.3723
a	29.4175	0.05424	1.7315	143.27	6.3616	6.3826
b	32.762	0.05724	1.6630	143.24	6.3499	6.3717
b	41.175	0.06417	1.4853	143.18	6.3490	6.3721

Average value, pK = 6.378 ± 0.006.

$c \times 10^4$	$\sqrt{c}$	Λ	Λ_x	C_u	pK'	pK_c
0.01968	0.1403	0.6706	142.70	0.01958	6.3599	6.3939
0.02561	0.1600	0.5893	142.59	0.02551	6.3573	6.3937
0.03869	0.1967	0.47604	142.42	0.03856	6.3628	6.4030
0.04985	0.2233	0.41839	142.30	0.04971	6.3643	6.4070
0.06064	0.2463	0.37905	142.21	0.06048	6.3646	6.4095
0.07022	0.2650	0.35194	142.13	0.07004	6.3649	6.4115
0.08636	0.2939	0.31559	142.03	0.08616	6.3693	6.4182

Extrapolation of pK_c vs. C_u, pK = 6.385 ± 0.002.

Table B10

$\Lambda_0\eta$

% dioxan $(^w/_w)$	KCl	KBz	HBz
0	1.3416	0.94752	3.4194
20	1.3618	0.95117	3.5003
30	1.3489	0.94218	3.3804
40	1.2281	0.92449	3.1398
50	1.1881	0.86841	2.7458

Table B11

pK

% dioxan $(^w/_w)$	Method 1	Method 2
0	4.210±0.002	4.205±0.001
20	4.865±0.004	4.863±0.001
30	5.265±0.005	5.272±0.001
40	5.788±0.004	5.784±0.001
50	6.378±0.006	6.385±0.002

Throughout the tables for Section 2, Part 2

$$X = E + 2k \log m - 2kA'\sqrt{\mu}$$

$$Y = (E - E^{o} + 2k \log m)\sqrt{\mu}$$

$$k = \frac{2.303RT}{F} = .05916$$

Debye-Hückel Constants, A'

% dioxan	A'
0	.5084
20	.7529
30	.9579
40	1.2746
50	1.7955

Table C1

Water

Quinhydrone electrode

C	E	X	Y x 10^3
.004992	.2016	.4782	.245
.009985	.2355	.4782	.519
.01997	.2693	.4789	.989
.03994	.3033	.4808	1.722
.04976	.3137	.4813	2.124
.04993	.3140	.4815	2.098
.09985	.3477	.4851	3.574
.09985	.3472	.4846	3.732
.1997	.3812	.4909	5.997

Extrapolated value of E^o = .4771.

m	E	X	Y x 10^3
.03083	.2904	.4797	1.374
.05846	.3212	.4817	2.394
.11561	.3539	.4852	4.158

Extrapolated value of E^o = .4770

m_{KHBz_2}	m_{KCl}	E	pK'
.002111	.005007	.0920	4.182
.006567	.006966	.1011	4.189
.009993	.02370	.1330	4.184
.01087	.01153	.1144	4.185
.01984	.04706	.1498	4.201
.02107	.02235	.1311	4.194

Average pK = 4.189.

Table C3

30% dioxan.

Quinhydrone electrode

m	E	X	$Y \times 10^2$
.02107	.3087	.5230	.228
.03406	.3350	.5296	.251
.03690	.3377	.5286	.296
.04677	.3495	.5310	.342
.05976	.3601	.5322	.434
.06473	.3650	.5345	.423
.09159	.3800	.5369	.597
.1015	.3843	.5380	.650
.1305	.3958	.5411	.798

Extrapolation value E^o = .5223.

m_{KHBz_2}	m_{KCl}	E	pK'
.03282	.03125	.1235	5.236
.03707	.03453	.1244	5.264
.05595	.05328	.1345	5.282
.07685	.07160	.1432	5.263
.1134	.1057	.1556	5.222
.1139	.1076	.1520	5.291

Average value pK = 5.26.

Table C4

40% dioxan.

m	E	X	$Y \times 10^2$
.02963	.3426	.5490	.272
.03353	.3453	.5470	.355
.03954	.3566	.5518	.337
.05523	.3715	.5554	.442
.07824	.3879	.5607	.567
.1097	.4025	.5658	.761
.1204	.4055	.5664	.859
.1589	.4156	.5700	1.137

Extrapolation value E^o = .5388

m_{KHBz_2}	m_{KCl}	E	pK'
.02474	.01976	.1006	5.703
.03762	.03005	.1126	5.682
.05189	.05742	.1281	5.701
.07857	.08694	.1375	5.723
.08334	.06657	.1291	5.749

Average value pK = 5.72.

Table C5

50% dioxan.

Quinhydrone electrode

m	E	X	Y x 10^2
.04192	.3755	.5816	.499
.07465	.4029	.5940	.725
.08524	.4048	.5931	.919
.1385	.4288	.6093	1.208
.1644	.4357	.6145	1.388

Extrapolation value E^o = .5625.

m_{KHBz_2}	m_{KCl}	E	pK'
.05612	.04977	.1174	6.221
.05754	.05675	.1216	6.207
.08271	.08158	.1427	6.008
.1087	.09643	.1402	6.123
.1422	.1402	.1547	6.040

Average value pK = 6.12.

Table C6

Water

Hydrogen Electrode

m	E	X	$Y \times 10^3$
.002170	.5399	.2220	.110
.005261	.4957	.2217	.265
.006059	.4887	.2216	.305
.008558	.4716	.2214	.422
.01055	.4613	.2212	.515
.02732	.4145	.2196	1.174

Extrapolation value E^o = .2222

m_{KHBz_2}	m_{KCl}	I	E	pK'
.006351	.006451	.01289	.6002	4.191
.008224	.008353	.01664	.5947	4.212
.01446	.01468	.02920	.5794	4.201
.01790	.01809	.03605	.5741	4.203
.02330	.02367	.04703	.5674	4.207

Average pK = 4.203.

Table C7

20% dioxan

Hydrogen electrode

m	E	X	Y x 10^3
.003032	.5056	.2027	.250
.003798	.4945	.2026	.309
.006545	.4679	.2023	.516
.008429	.4556	.2020	.650
.01012	.4468	.2018	.772

Extrapolation value E^o = .2032.

m_{KHBz_2}	m_{KCl}	I	E	pK'
.006090	.005991	.01209	.6229	4.870
.01003	.01002	.02007	.6100	4.876
.01605	.01745	.03351	.5958	4.877
.02240	.02204	.04445	.5901	4.883
.02765	.02762	.05529	.5847	4.890

Extrapolation value pK = 4.864.

Table C8

30% dioxan.

Hydrogen electrode

m	E	X	Y x 10^3
.005209	.4675	.1892	.531
.008542	.4438	.1886	.837
.009297	.4397	.1884	.899
.01384	.4211	.1878	1.312

Extrapolation value E^o = .1900

Platinum electrode

m_{KHBz_2}	m_{KCl}	I	E	pK'
.01731	.01767	.03499	.6071	5.298
.02280	.02412	.04692	.5996	5.306
.03986	.03743	.07729	.5884	5.308
.05080	.05186	.1026	.5796	5.291
.05347	.05657	.1100	.5788	5.325
.06315	.06299	.1261	.5768	5.337
.07782	.08081	.1586	.5705	5.339

Extrapolation value pk $\approx$ 5.288.

Palladium electrode

m_{KHBz_2}	m_{KCl}	I	E	pK'
.01152	.01144	.02296	.6189	5.308
.01440	.01427	.02867	.6133	5.310
.02927	.02908	.05835	.5960	5.326
.04036	.03999	.08035	.5884	5.336

Extrapolation value pK = 5.296.

Table C9

40% dioxan.

Hydrogen electrode

m	E	X	$Y \times 10^3$
.003695	.4700	.1729	.523
.006141	.4458	.1721	.824
.01043	.4213	.1713	1.350
.01288	.4117	.1708	1.640

Extrapolation value E^0 = .1738.

Platinum electrode

m_{KHBz_2}	m_{KCl}	I	E	pK'
.02433	.01760	.04193	.6202	5.791
.04874	.04757	.09631	.5958	5.811
.06271	.04538	.1081	.5971	5.812
.09496	.07676	.1717	.5838	5.816

Extrapolation value pK $\approx$ 5.802.

Palladium electrode

m_{KHBz_2}	m_{KCl}	I	E	pK'
.009852	.009718	.01957	.6354	5.790
.01607	.01585	.03192	.6238	5.807
.02147	.02090	.04237	.6164	5.802
.02401	.02336	.04737	.6136	5.803
.03230	.03186	.06416	.6060	5.809

Extrapolation value pK = 5.789.

Table C10

50% dioxan.

Hydrogen electrode

m	E	X	$Y \times 10^3$
.002151	.4756	.1502	.422
.003234	.4564	.1497	.617
.005029	.4356	.1486	.903
.007897	.4152	.1476	1.380
.009294	.4083	.1474	1.638
.009305	.4079	.1471	1.607
.01416	.3899	.1459	2.409
.01433	.3893	.1457	2.426
.02004	.3749	.1439	3.267
.02143	.3723	.1437	3.501
.02250	.3700	.1432	3.620

Extrapolation value $E^0 = .1508$.

Platinum electrode

m_{KHBz_2}	m_{KCl}	I	E	pK'
.03875	.03492	.07367	.6138	6.369
.04253	.03843	.08096	.6115	6.372
.07419	.06893	.1431	.5980	6.398
.08572	.07747	.1632	.5951	6.399
.1153	.1039	.2192	.5892	6.427

Extrapolation value pK = 6.342.

Palladium electrode

m_{KHBz_2}	m_{KCl}	I	E	pK'
.01068	.01057	.02125	.6426	6.337
.02385	.02367	.04751	.6246	6.383
.02872	.02841	.05713	.6191	6.369
.05186	.05147	.1033	.6051	6.391

Extrapolation value pK $\approx$ 6.342.

Table D1

Benzoic Acid

In Water.

m	pH	pK_1	pK_2	pK_3	pK_4
.003560	4.192	4.222	4.220	4.204	4.204
.003929	4.188	4.220	4.217	4.203	4.203
.006006	4.181	4.220	4.218	4.208	4.207
.008759	4.165	4.213	4.209	4.202	4.200
.01084	4.165	4.218	4.213	4.208	4.206
.01336	4.150	4.209	4.203	4.198	4.196
.01679	4.147	4.211	4.204	4.200	4.198
.01910	4.150	4.220	4.212	4.209	4.206
Average		4.217	4.212	4.204	4.203

In 40% dioxan

m	pH	pK_1	pK_2	pK_4
.009196	5.603	5.725	5.715	5.712
.01186	5.578	5.717	5.703	5.699
.02241	5.554	5.745	5.720	5.713
.03385	5.527	5.761	5.725	5.715
.04019	5.529	5.785	5.742	5.730
.04432	5.515	5.783	5.738	5.725
.06314	5.512	5.832	5.768	5.753
.06668	5.497	5.826	5.759	5.742
Average		5.772	5.734	5.724
Extrapolated value		5.694	5.690	5.690

Table D2

Benzoic Acid in 20% dioxan.

m	pH	pK_3
.004966	4.791	4.838
.007678	4.776	4.835
.008592	4.780	4.842
.01016	4.773	4.841
.01188	4.762	4.835
.01224	4.771	4.845
.01609	4.764	4.848
.01612	4.758	4.842
.01704	4.767	4.853
.02010	4.761	4.854
.02280	4.749	4.847
.02490	4.753	4.853
.02589	4.747	4.853

Extrapolated pK = 4.831.

Table D3

Benzoic Acid in 30% dioxan.

m	pH	pK_3
.003967	5.199	5.254
.004163	5.204	5.261
.008436	5.169	5.249
.008728	5.164	5.245
.009929	5.166	5.252
.01004	5.157	5.244
.01933	5.156	5.273
.02218	5.136	5.260
.02465	5.138	5.268
.02565	5.137	5.269
.03067	5.126	5.269
.03264	5.129	5.276
.03517	5.125	5.276
.04053	5.131	5.292
.04269	5.124	5.288
.04780	5.112	5.284

Extrapolated pK = 5.230.

Table D4.

Benzoic Acid in 50% dioxan.

m	pH	pK
.008073	6.057	6.205
.01522	6.032	6.229
.02513	5.988	6.234
.03162	5.961	5.232
.03944	5.954	6.252
.04752	5.935	6.256
.05498	5.917	6.258
.06906	5.905	6.279

Extrapolated pK = 6.208.

Table E1

Solvent	pH meas.	pH calc.	Difference
0% dioxan	1.967	1.997	.030
10% "	1.956	2.013	.057
20% "	2.019	2.072	.053
30% "	2.038	2.095	.057
40% "	2.025	2.115	.090
50% "	1.927	2.098	.171
60% "	1.651	1.999	.348
80% "	1.309	2.495	1.186
0% alcohol	2.095	2.059	.036
10% "	2.056	2.060	.004
20% "	2.100	2.074	.026
30% "	2.179	2.086	.093
40% "	2.349	2.177	.172
50% "	2.311	2.052	.259
60% "	2.469	2.155	.314
0% acetone	1.993	2.007	.014
10% "	1.979	2.028	.049
20% "	1.972	2.019	.047
30% "	1.993	2.038	.045
40% "	1.989	2.043	.054
50% "	1.965	2.060	.095
60% "	1.963	2.167	.204.

Figure A1

Solubility of p-chloroaniline.

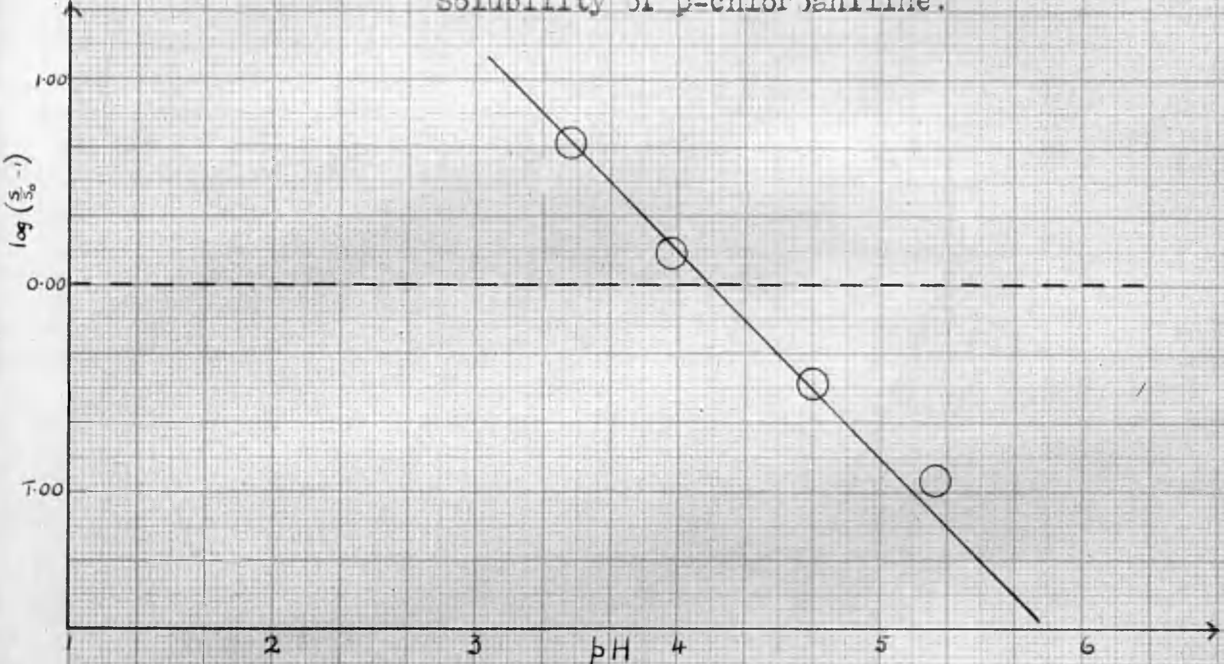


Figure A2

Solubility of p-bromoaniline.

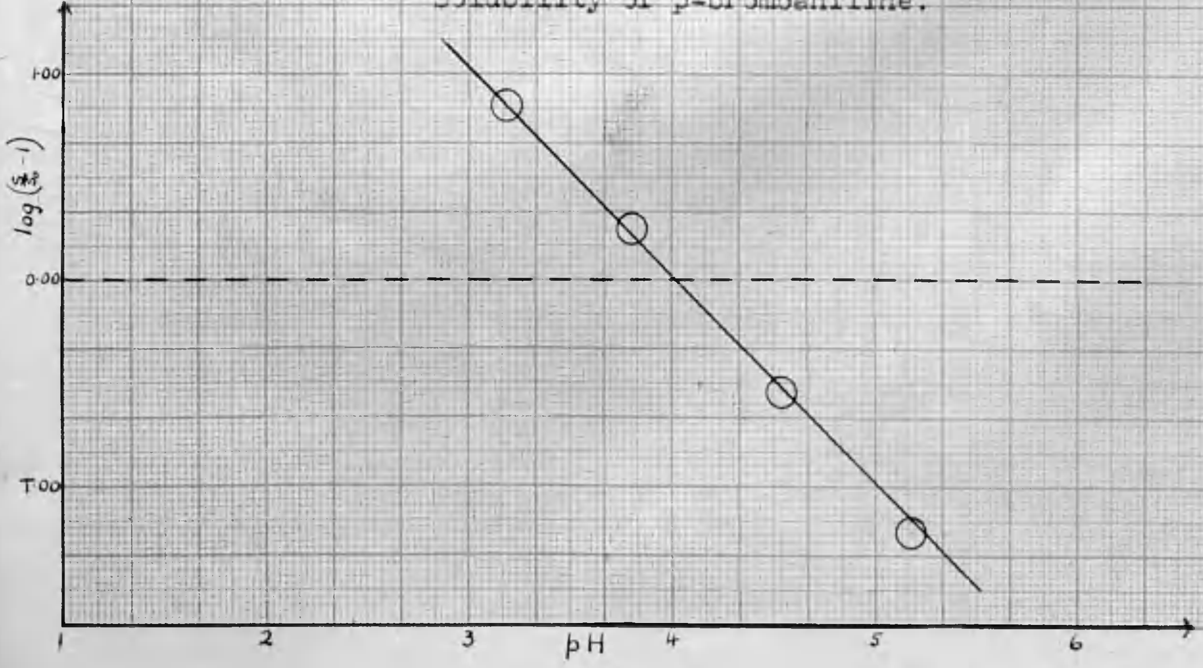


Figure A3.

Graph of X against Y in equation for titration of benzidine.

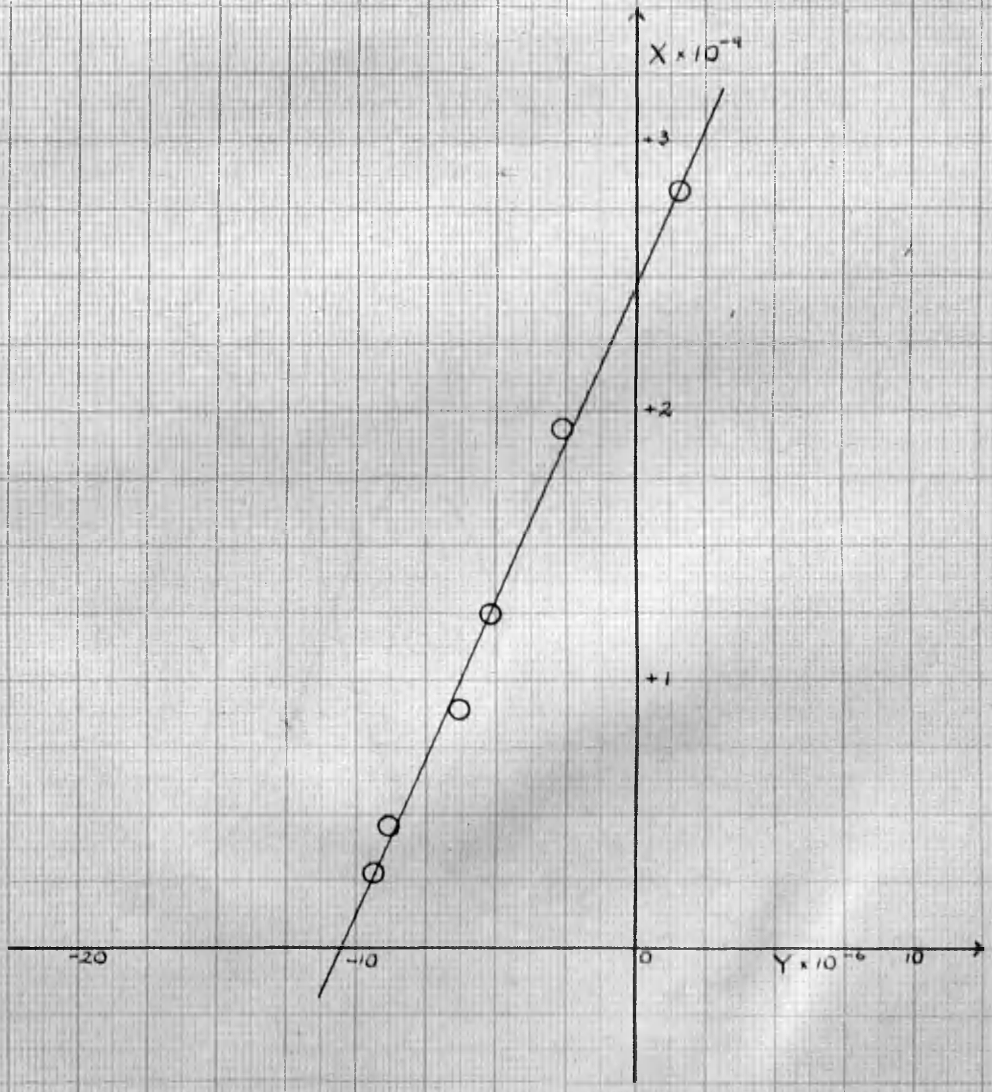


Figure A4.

Graph showing proportion of neutral molecules, mono- and divalent ions of benzidine present at different pHs.

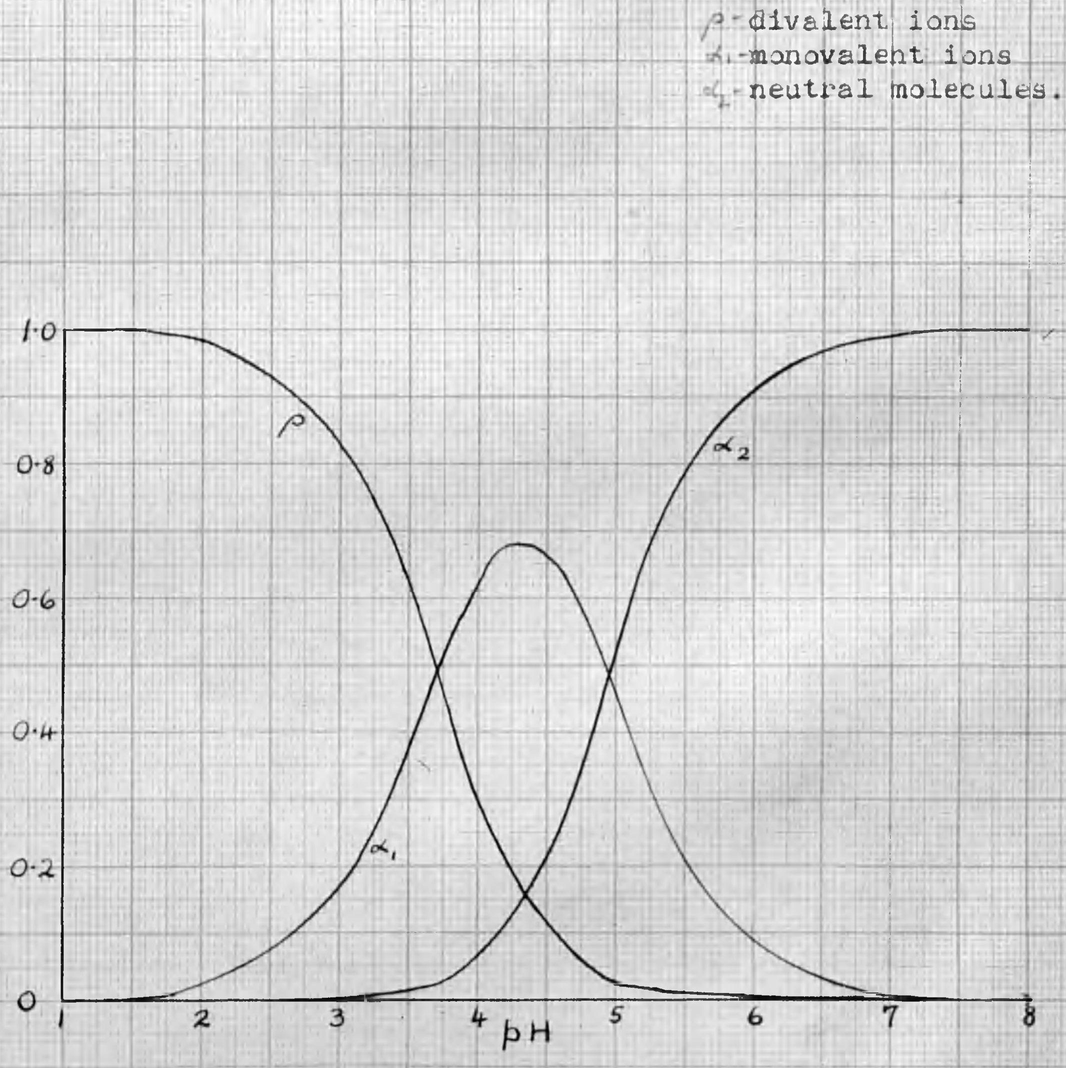


Figure A5

Solubility of benzidine.

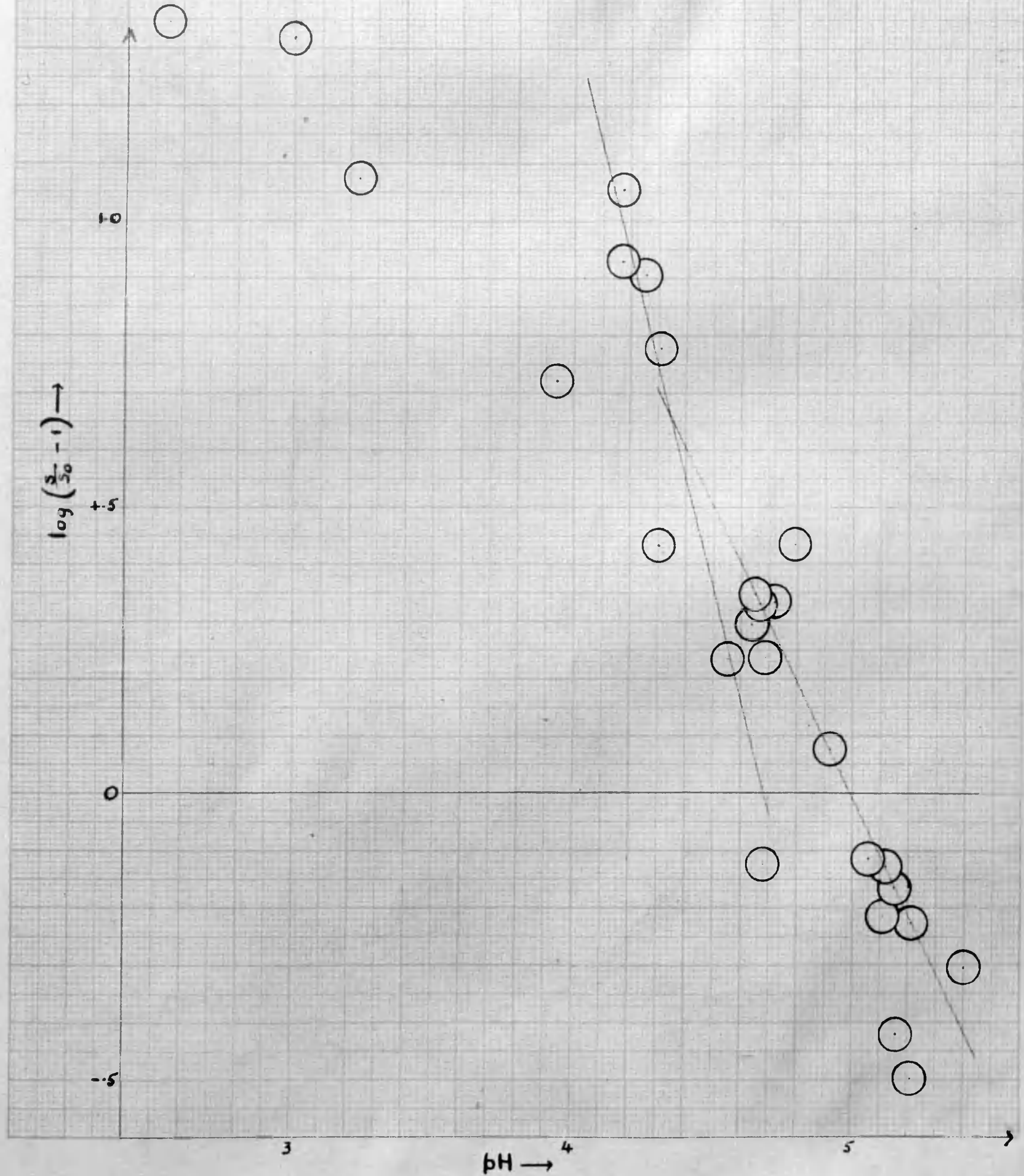
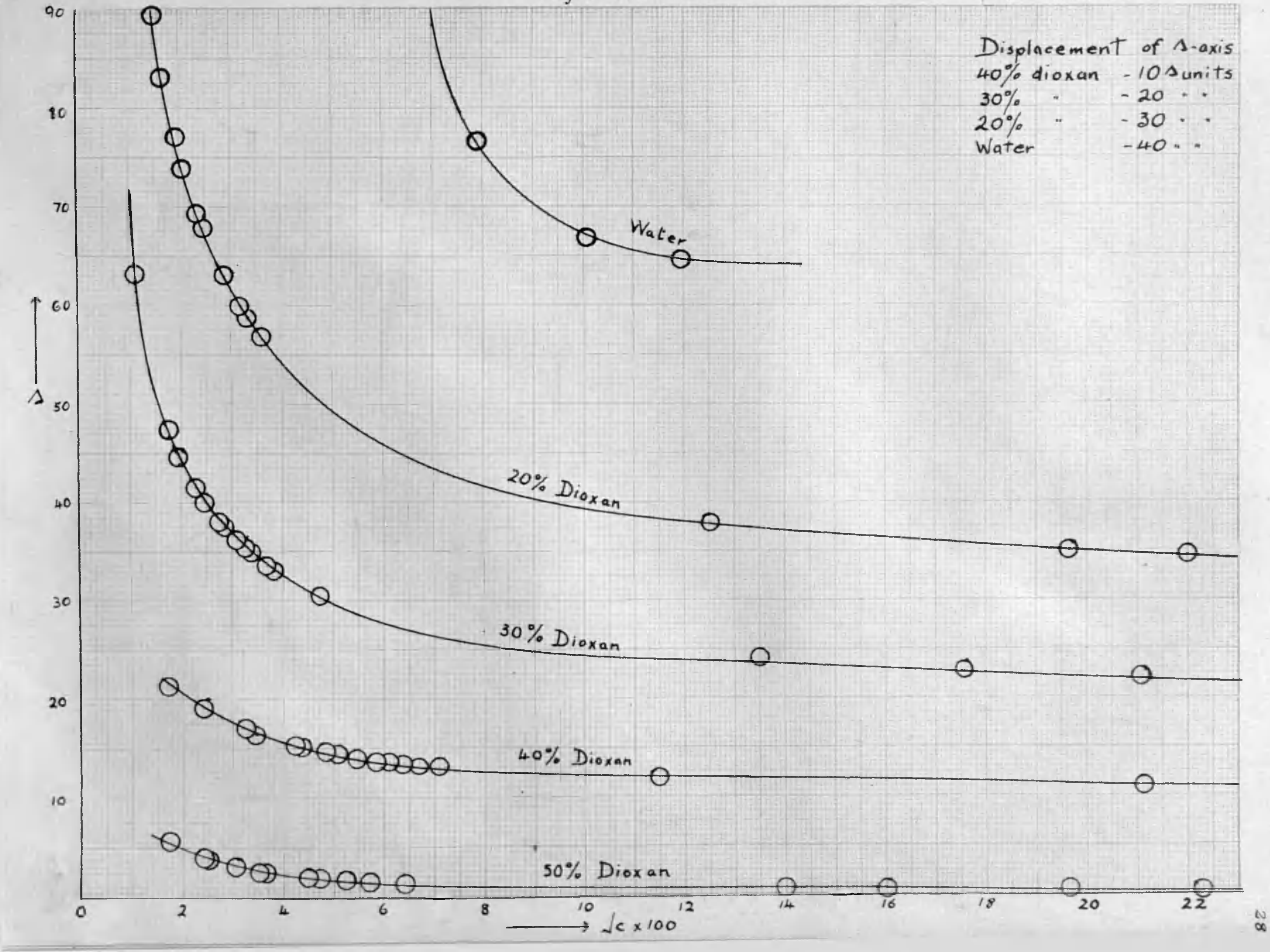


Figure B1.



Benzoic Acid

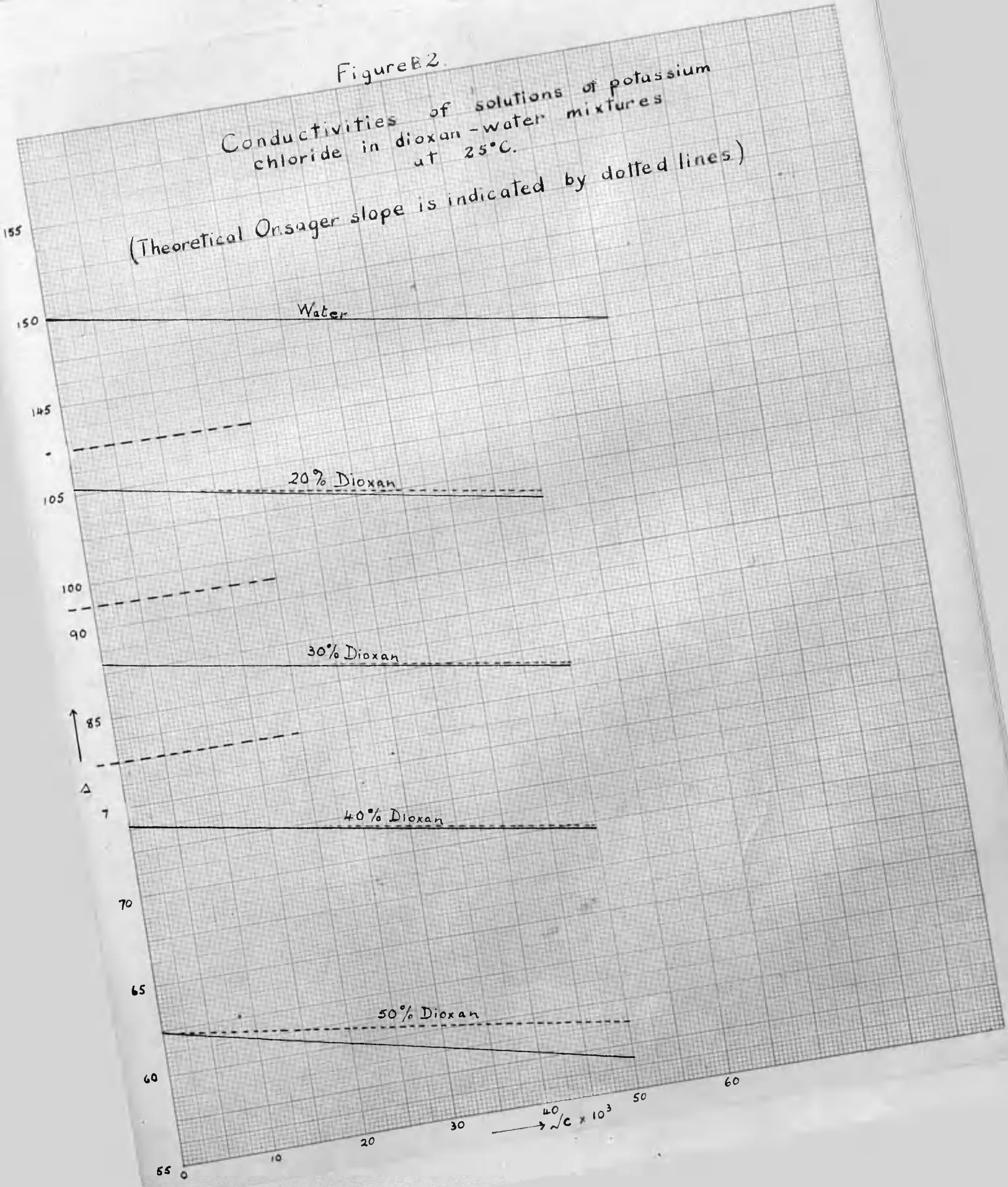
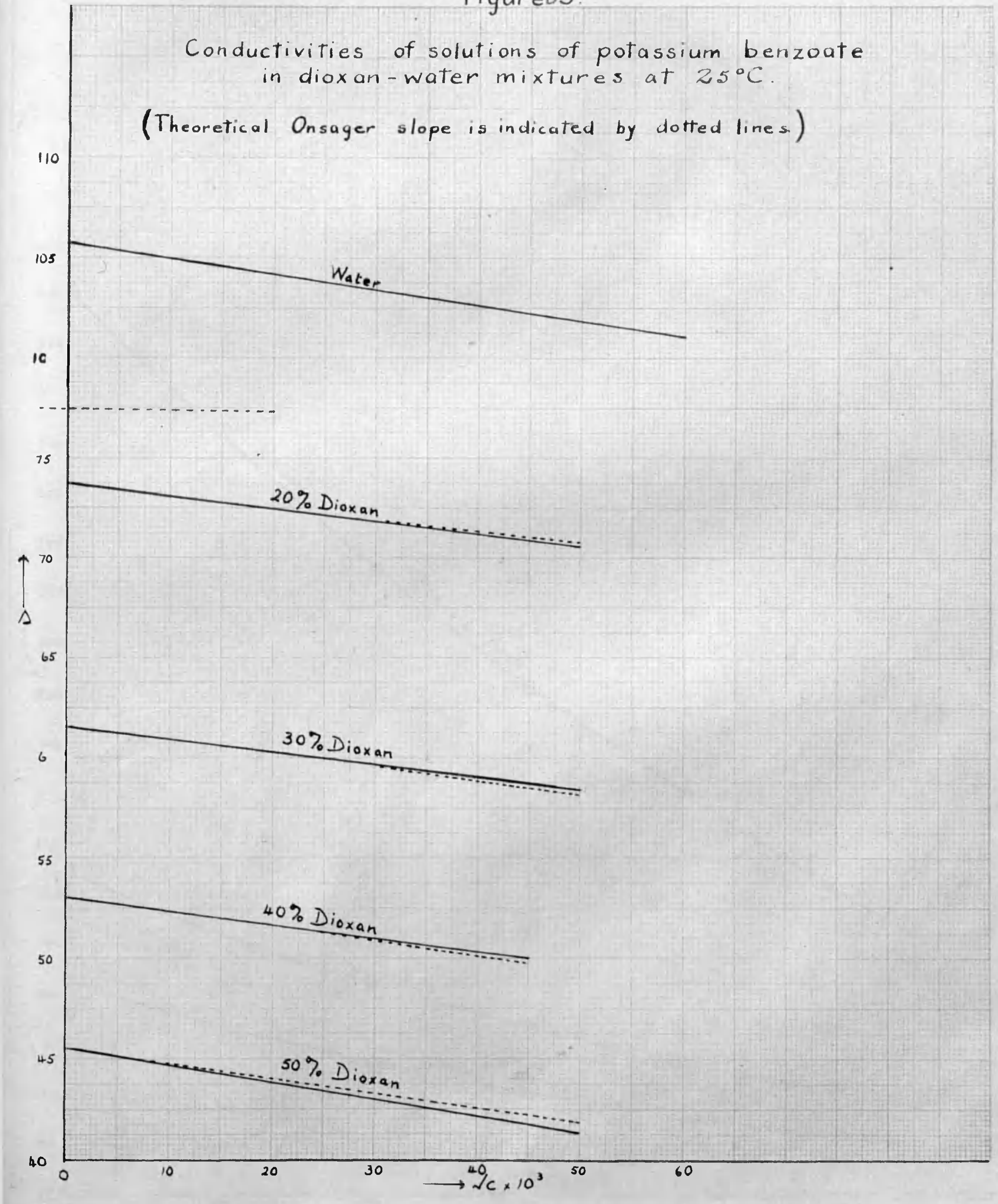


Figure B2.

Conductivities of solutions of potassium chloride in dioxan-water mixtures at 25°C.

(Theoretical Onsager slope is indicated by dotted lines)

Figure B3.



Conductivities of solutions of potassium benzoate in dioxan-water mixtures at 25°C.

(Theoretical Onsager slope is indicated by dotted lines.)

FigureB4.

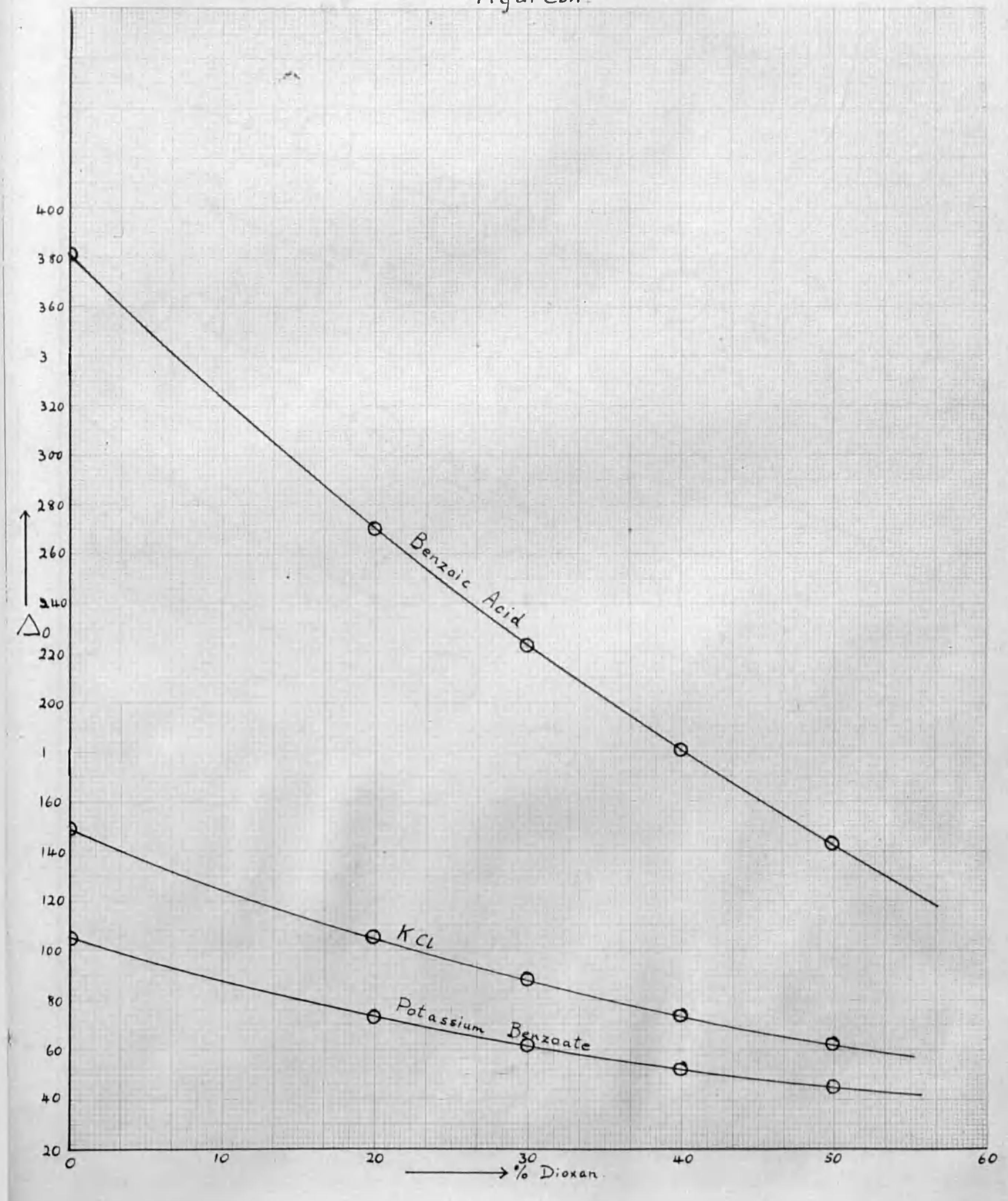
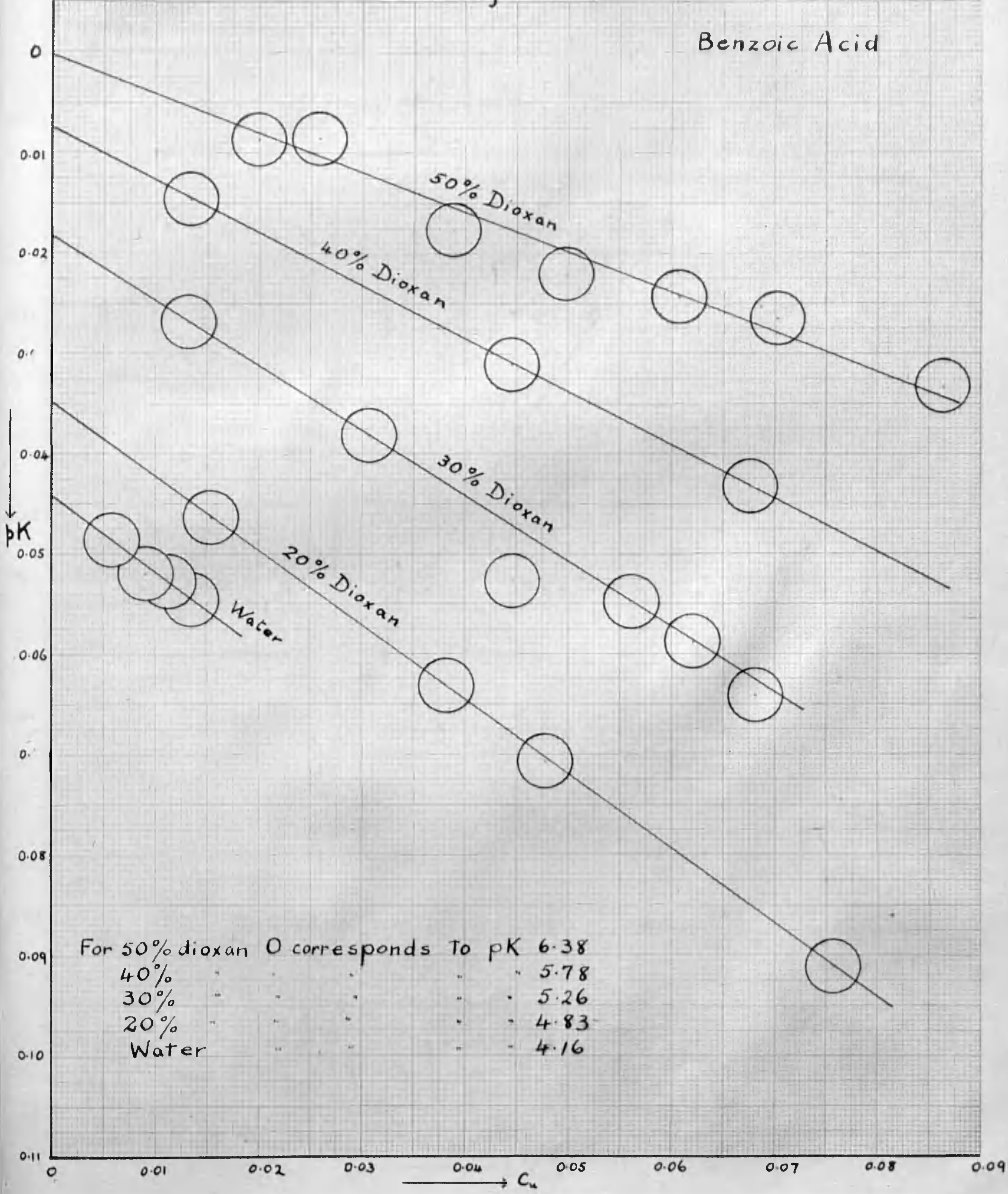

400
380
360
3
320
300
280
260
240
220
200
1
160
140
120
100
80
60
40
20
Δ0
0
10
20
30
40
50
60
% Dioxan
Benzoic Acid
KCl
Potassium Benzoate

Figure B5.



For 50% dioxan 0 corresponds to pK 6·38
40% " " " " 5·78
30% " " " " 5·26
20% " " " " 4·83
Water " " " " 4·16

Figure B6

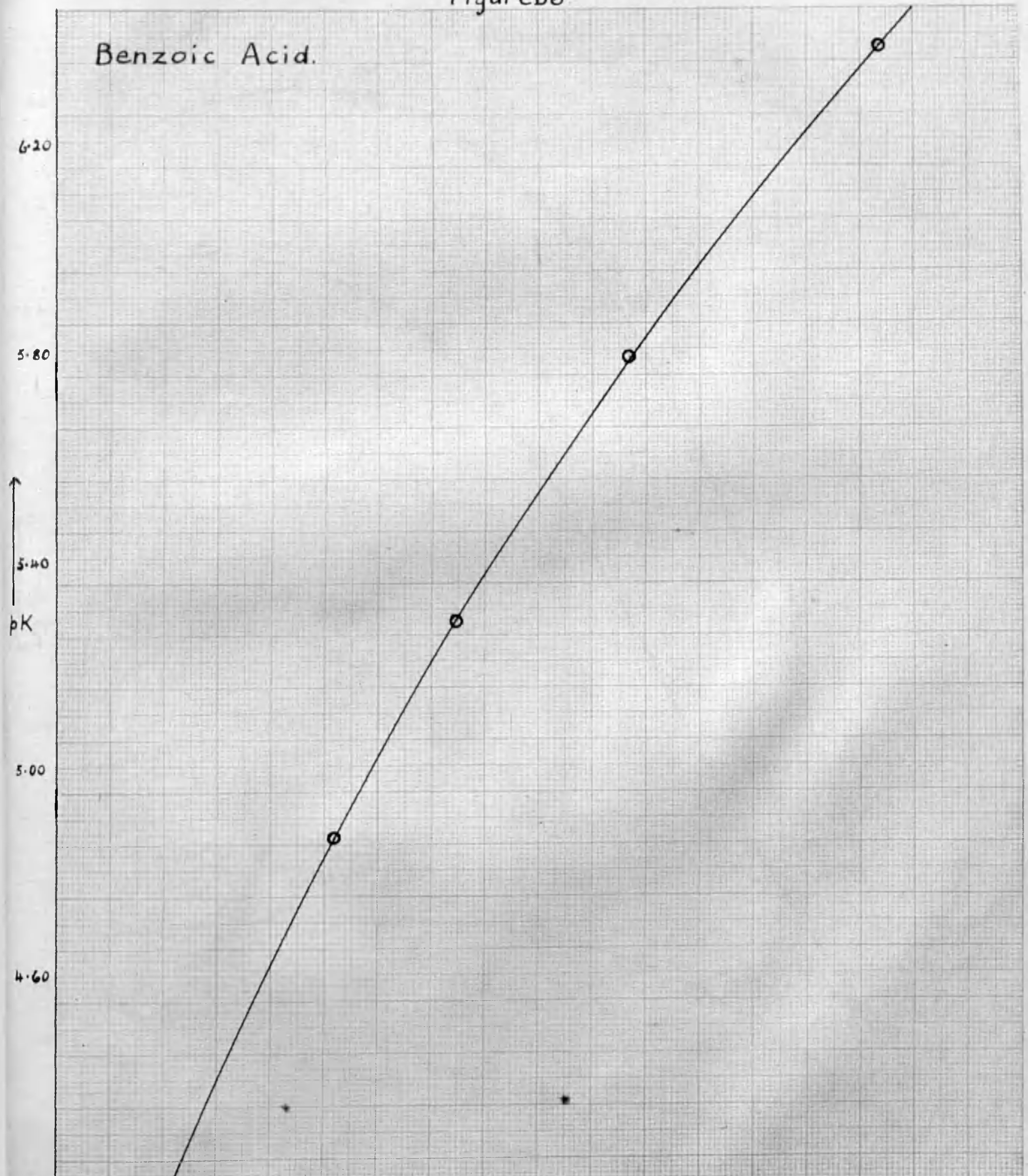
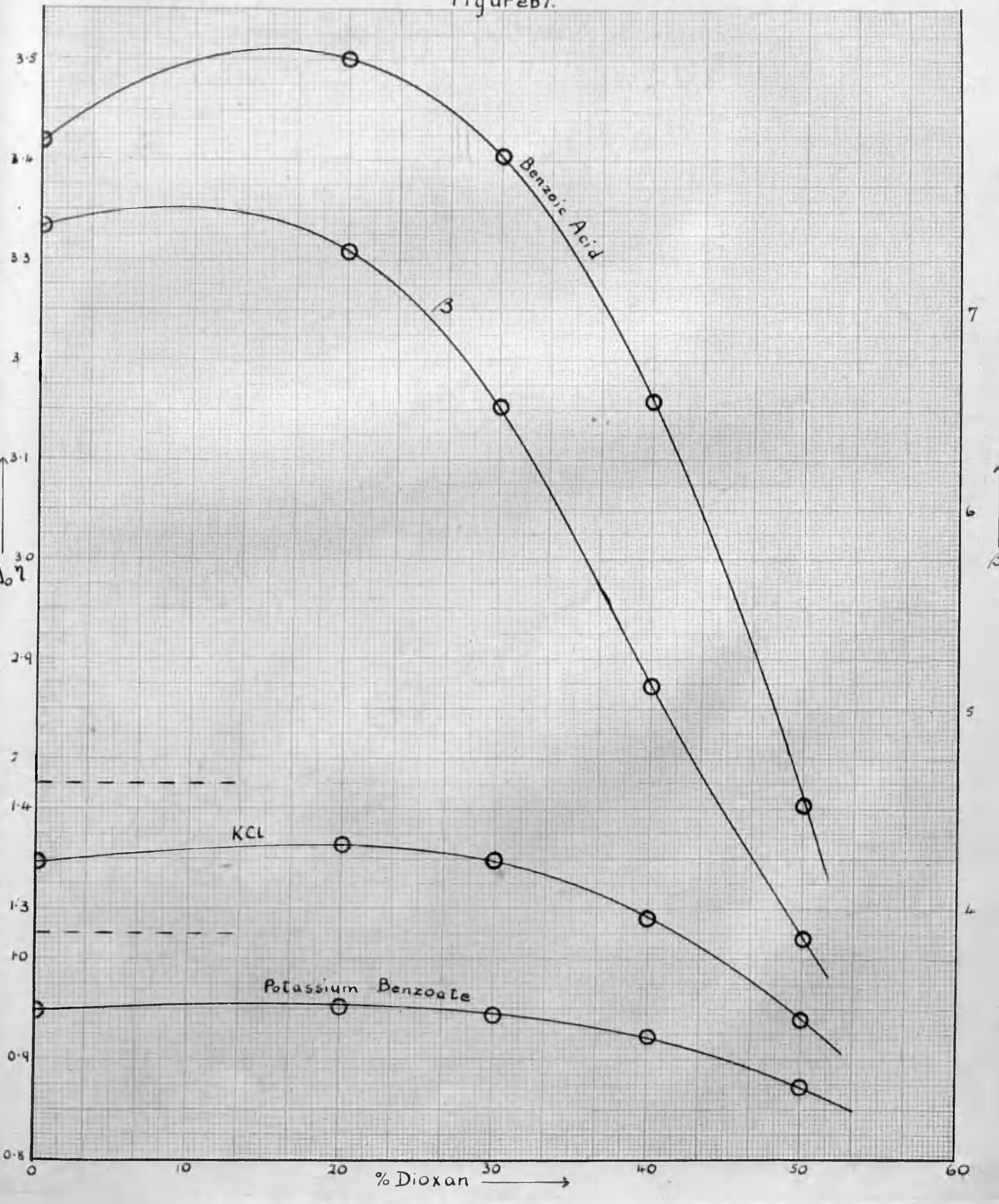
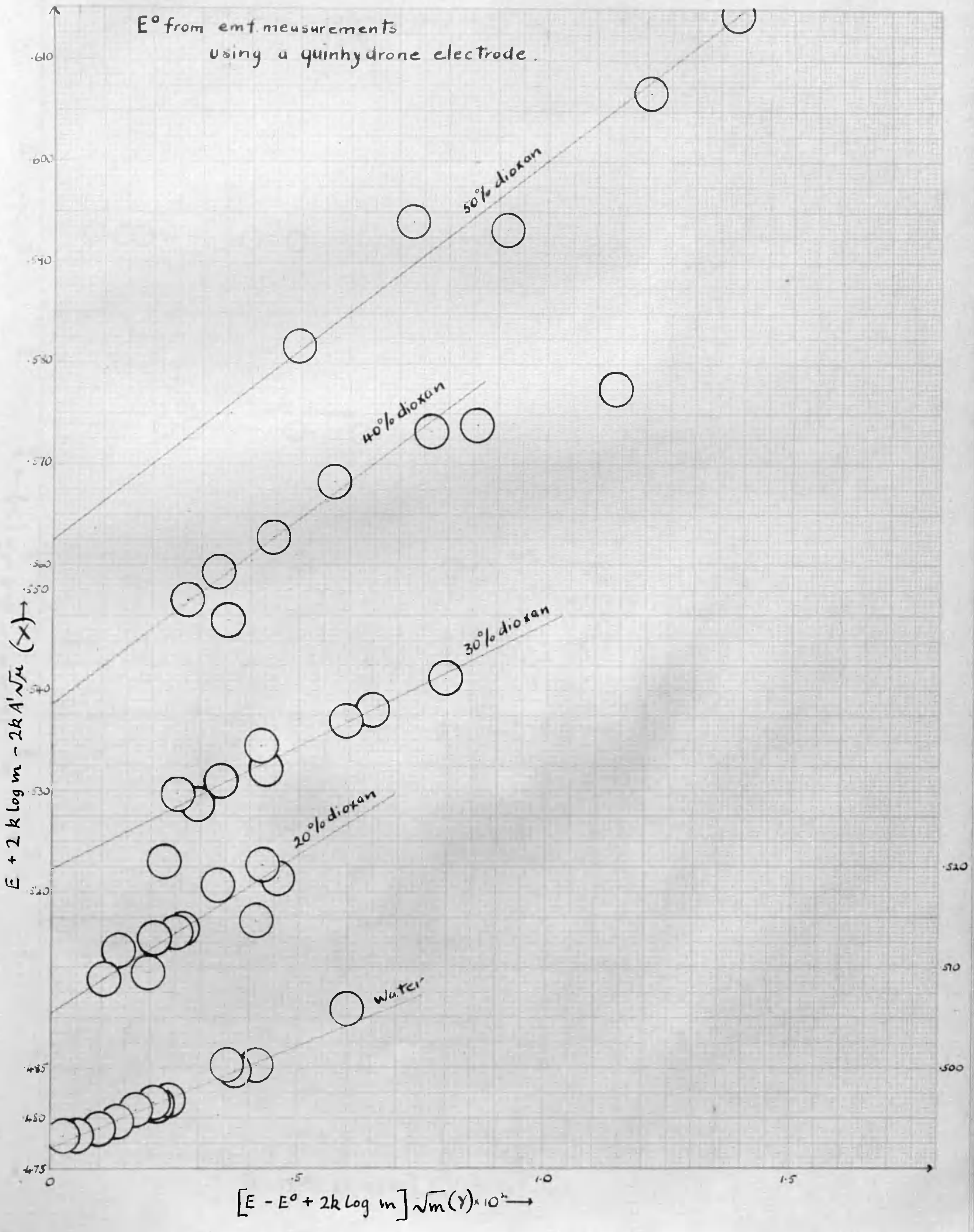
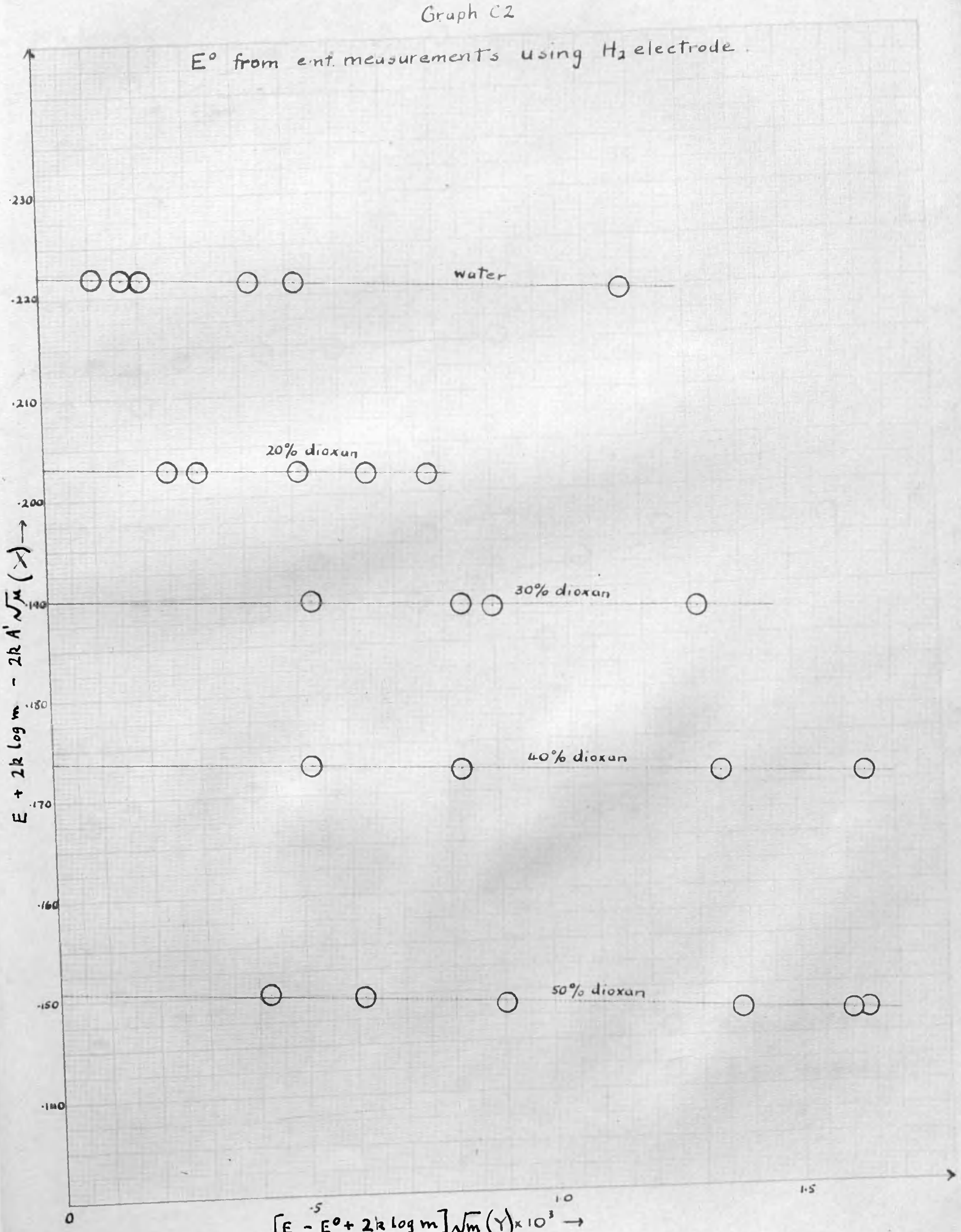

Benzoic Acid.
pK
6·20
5·80
5·40
5·00
4·60
4·20
10
20
30
$\frac{1}{D} \times 10^3$

Figure B7.


3·5
3·4
3·3
3
3·1
3·0
2·9
2
1·4
1·3
1·0
0·9
0·8
Δ₀η
7
6
5
4
β
0
10
20
30
40
50
60
% Dioxan
Benzoic Acid
β
KCL
Potassium Benzoate

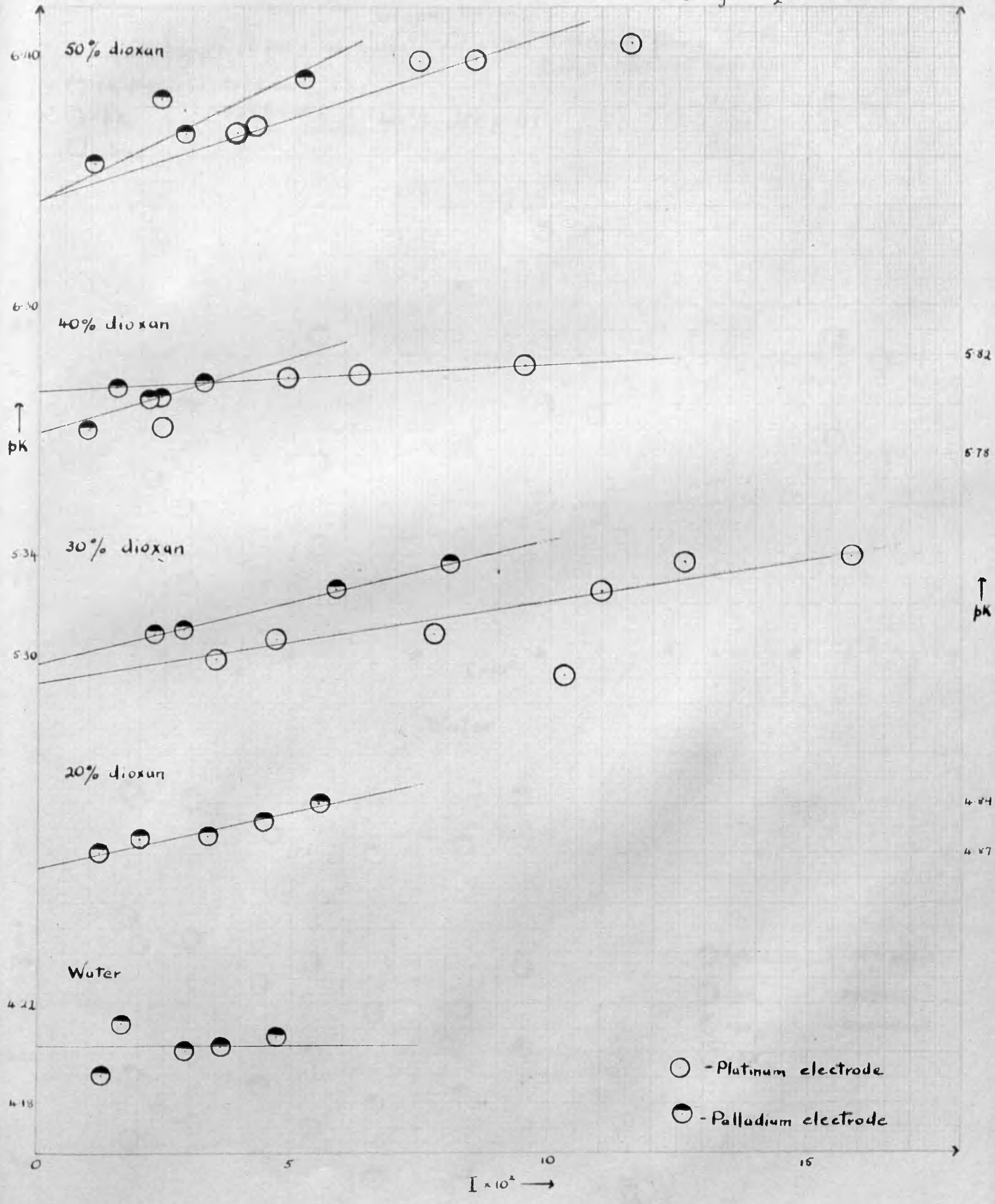
Graph C1


E° from emf measurements
using a quinhydrone electrode.
50% dioxan
40% dioxan
30% dioxan
20% dioxan
water
E + 2k log m − 2kA′√μ (X) →
[E − E° + 2k Log m] √m (Y) × 10² ⟶
·610
·600
·590
·580
·570
·560
·550
·540
·530
·520
·485
·480
·475
·520
·510
·500
0
·5
1·0
1·5


Graph C2
E° from e.m.f. measurements using H_2 electrode.
·230
·220
·210
·200
·190
·180
·170
·160
·150
·140
water
20% dioxan
30% dioxan
40% dioxan
50% dioxan
$E + 2k \log m - 2kA'\sqrt{\mu}$ (X) →
0
·5
1·0
1·5
$[E - E^0 + 2k \log m]\sqrt{m}$ (Y) × 10^3 →

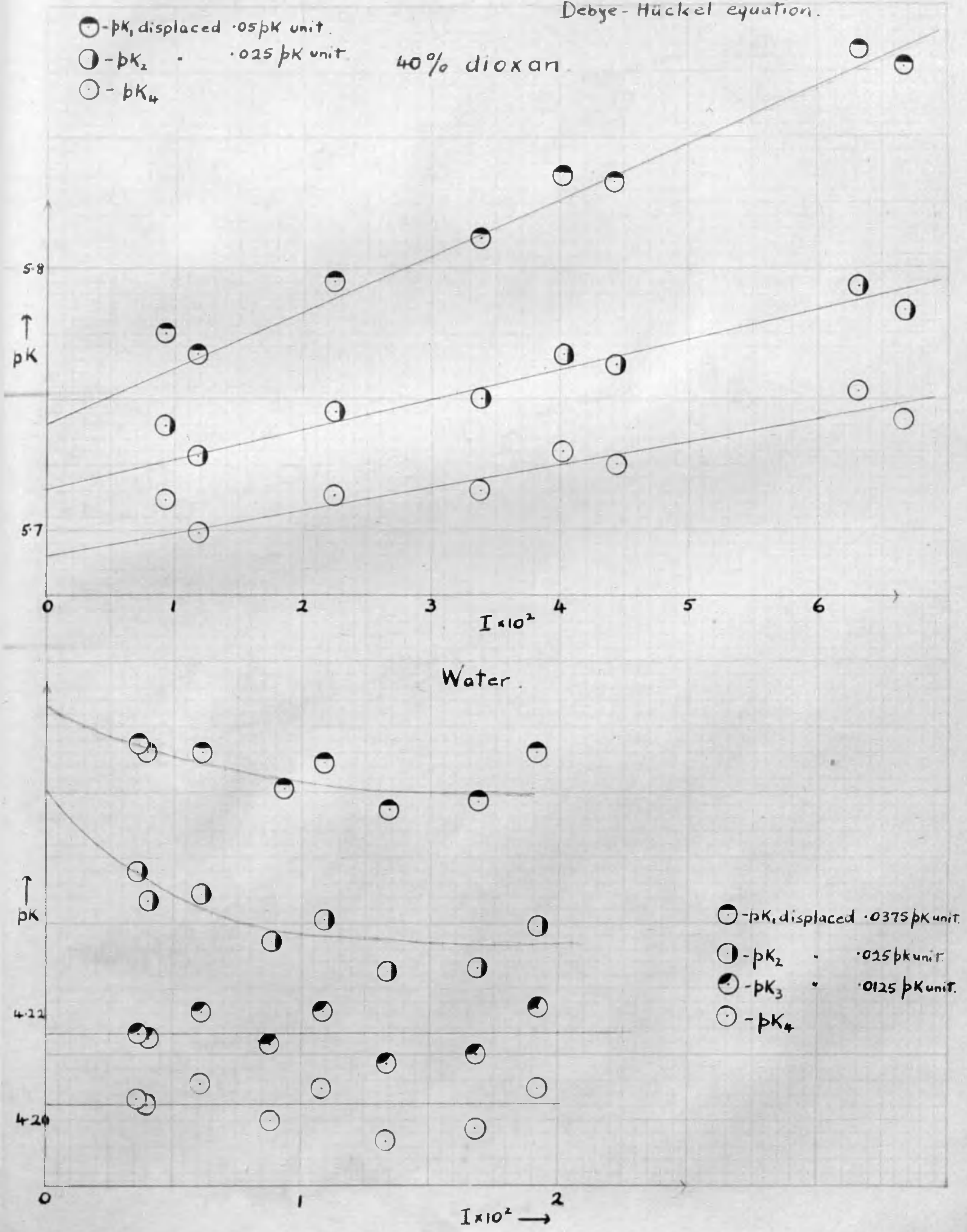
Graph C3.

Ionic strength against pK' from emf measurements using a H_2 electrode.

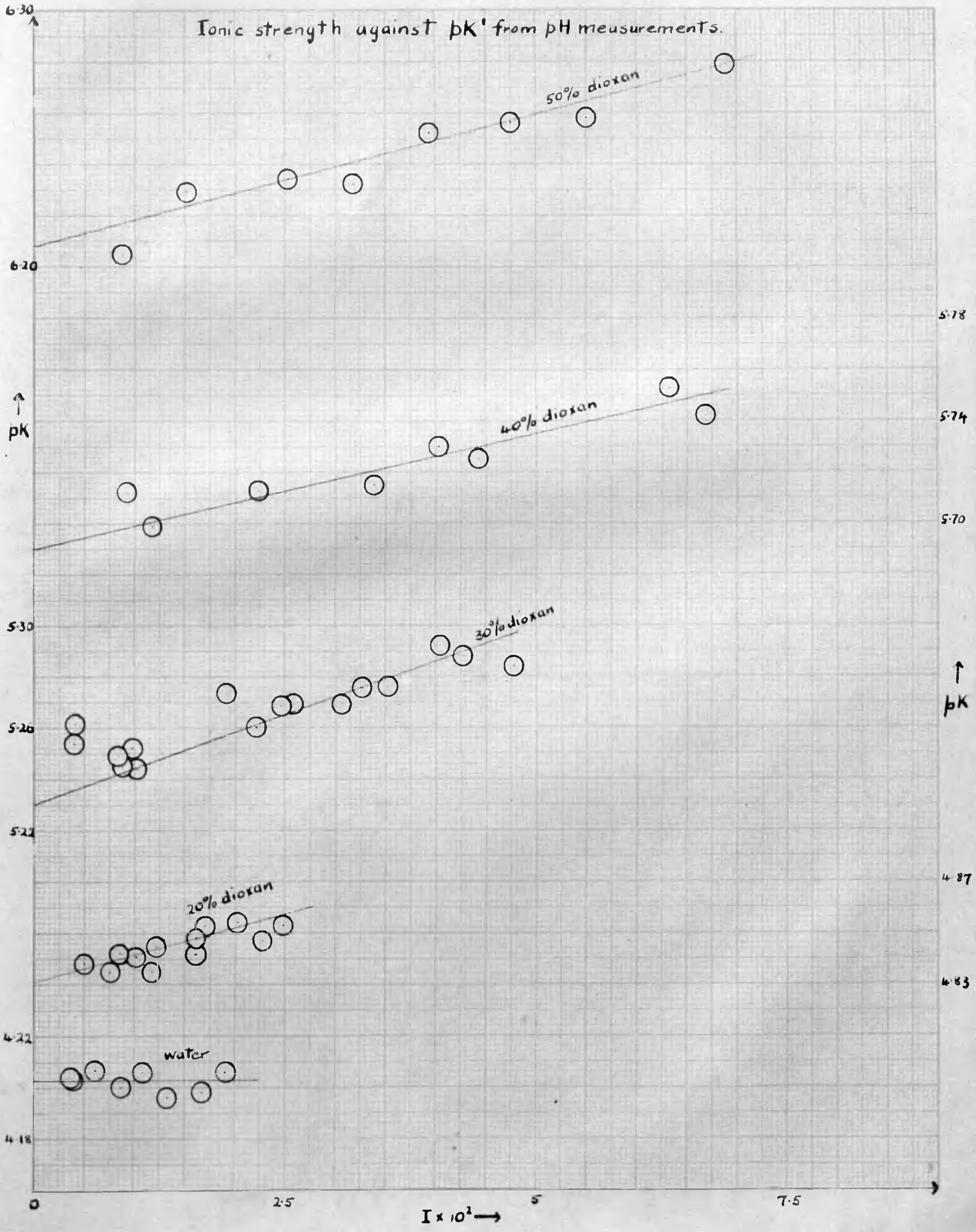


Graph D1.

Comparison of pK's as calculated using different forms of the Debye-Hückel equation.

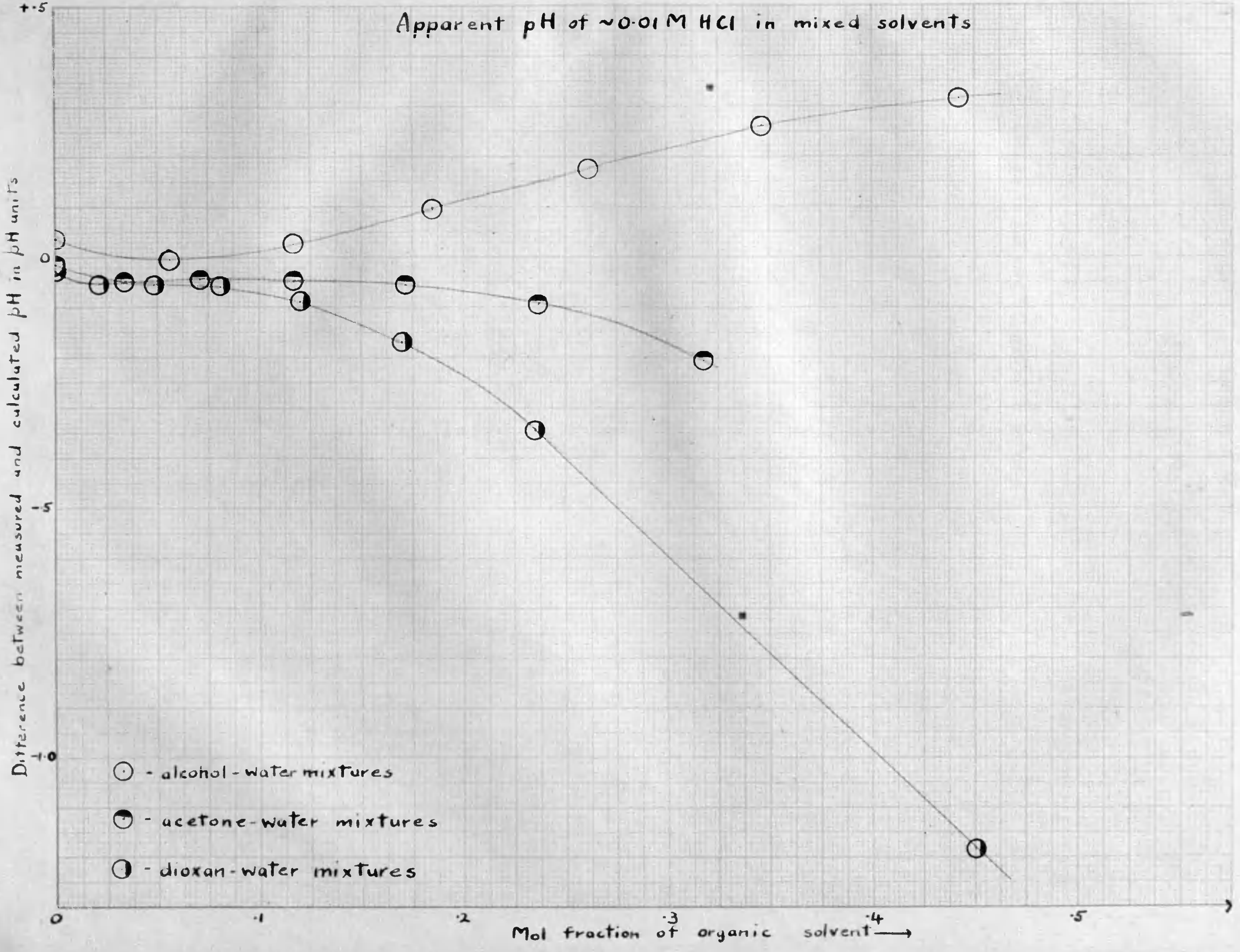


Graph D2



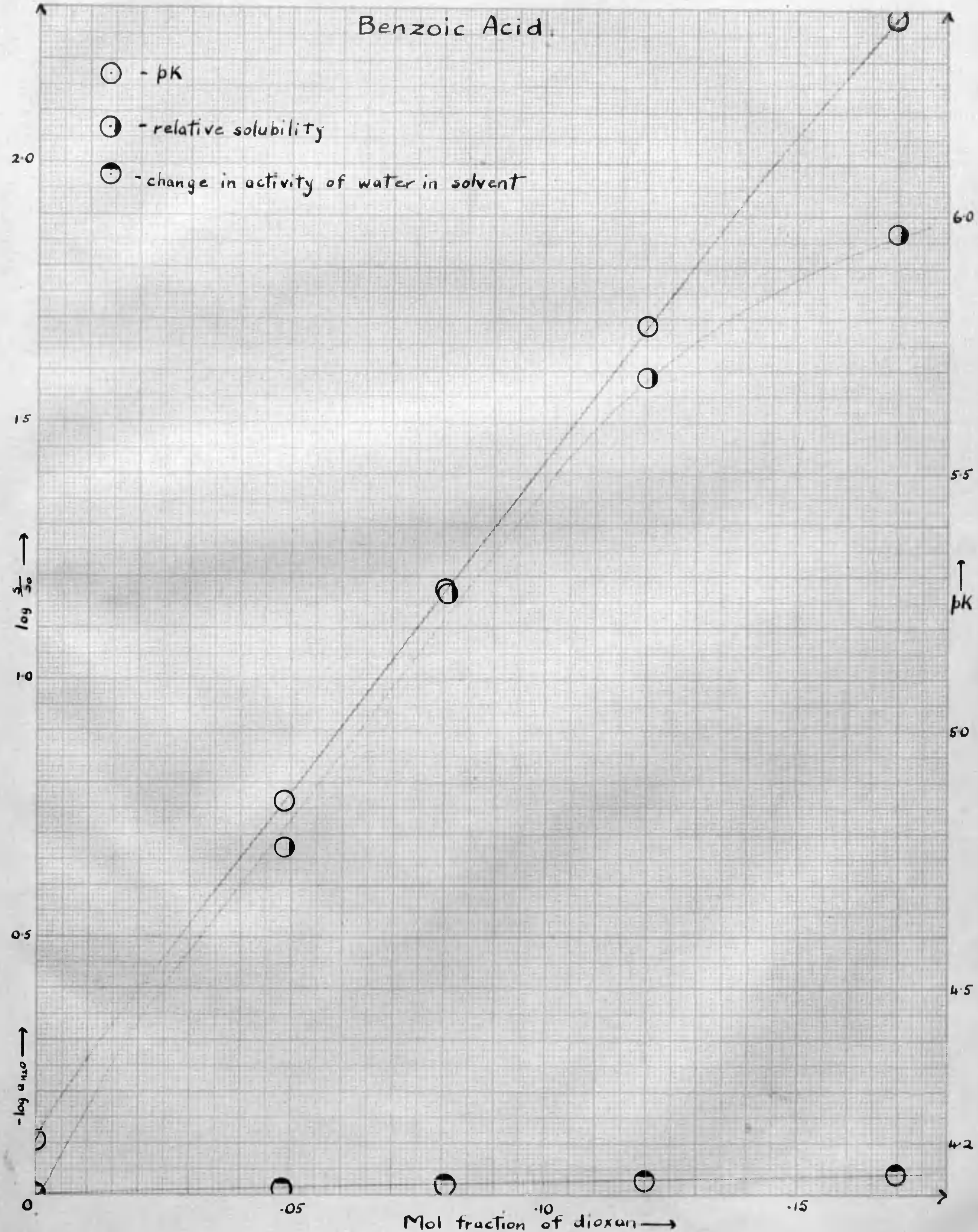
Ionic strength against pK' from pH measurements.

Graph E1



Apparent pH of ~0·01 M HCl in mixed solvents

Graph E2


Benzoic Acid.
⊙ - pK
◑ - relative solubility
◓ - change in activity of water in solvent
2·0
1·5
1·0
0·5
0
$\log \frac{S}{S_0}$ ⟶
$-\log a_{H_2O}$ ⟶
6·0
5·5
5·0
4·5
4·2
pK ⟶
·05
·10
·15
Mol fraction of dioxan ⟶

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