INDICATOR STUDIES OF ACIDS AND BASES IN BENZENE

VICTOR K. LA MER AND HAROLD C. DOWNES

Department of Chemistry, Columbia University, New York

In the days before the electrolytic dissociation theory was developed, the term "acid" implied a corrosive substance with a sour taste which would turn blue litmus red when tested in dilute aqueous solution. The term "base" meant the residual substance remaining after the volatilization of the acid constituent, which was bitter, would turn red litmus blue, and was capable of neutralizing the properties of acids.

The ionization theory as developed by Arrhenius and Ostwald introduced the principle that these properties were dependent upon dissociable hydrogen and hydroxyl radicals. The remarkable success which the theory achieved in explaining the behavior of weak acids and bases in particular by correlating their conductance ratios with their catalytic effects, for example, on the inversion of cane sugar by acids or the saponification of esters by bases, convinced most chemists that their older empirical statements of the strength of acids and bases could be simply yet adequately replaced by statements of the concentration of hydrogen ion. Thus, an acid became a substance that gives on dissociation hydrogen ion and an anion; a base, one that gives hydroxyl ion and a cation.

As long as attention was restricted to dilute aqueous solution, these concepts sufficed. However, when we enter the realm of non-aqueous solvents, we are immediately confronted with two questions: What is meant by acidity in a solvent in which the acid or base does not ionize perceptibly, as is the case in solvents like benzene? What do we mean by the term "base" when the substance and its solvent lack hydroxyl radicals?

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In 1923 Brönsted (1b) and Lowry (2) proposed, independently of each other, a scheme which greatly simplifies the answers. They define any substance as an acid which is capable of dissociating a proton, and correspondingly, define as a base any substance which will associate a proton.   Thus:

$$\text{Acid} \rightleftharpoons \text{Base} + \text{Proton} \tag{1}$$
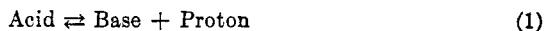
The scheme has the following advantages:

(1) Acid properties are ascribed to one factor—the ability to give up protons; basic properties, to the ability to accept protons. Unless the recently discovered neutron and positron should prove to be important in ordinary chemical changes, the unique properties of minute size and extraordinary mobility possessed by the proton are paralleled only by that of the electron in oxidation-reduction equilibria, where the corresponding scheme is

$$\text{Reductant} \rightleftharpoons \text{Oxidant} + \text{Electron} \tag{2}$$
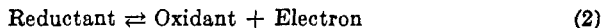
These definitions thus embrace the most fundamental processes in ordinary chemical changes and do so by employing only fundamental concepts of the structure of matter.

(2) The definition is independent of the solvent, so that it is unnecessary to redefine the term "base" on passing to new solvents, as is customary in many existing systems.

(3) Hydroxyl ion loses its exalted position as the unique carrier of basic properties, which position it acquired only because of the frequency with which aqueous solutions are encountered.

(4) Acids and bases are not restricted to electrically neutral molecules.   The only restriction is that the base possesses one less positive charge than its conjugate acid.
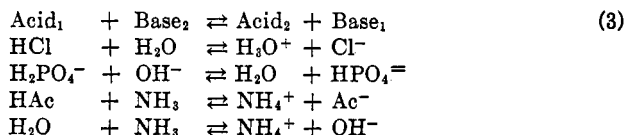
Properties like freezing point depression, hydrogen electrode potentials, and indicator colors involve equilibrium states and are, therefore, closely correlated for thermodynamic reasons.   On the other hand, properties like the conductance ratio, and hydrogen and hydroxyl ion catalysis are not determined by reversible processes.   Consequently when it was demonstrated in dilute aqueous solution that there was a close correlation between such thermodynamic and non-thermodynamic properties, it was tacitly

assumed that a similar correlation would hold without change when the acids or bases were dissolved in other solvents (7).

Thus, the classical theory held that a solution like that of hydrogen chloride in benzene should not have the properties of an acid, since it failed to conduct electricity and at best reacted very slowly with metals and carbonates.   The experimental work of Hantzsch (3), of Brönsted (1), and of Hall and Conant (5) has been primarily responsible for demonstrating that this assumed parallelism between thermodynamic and non-thermodynamic properties does not hold on changing the solvent.   The lines of evidence which demonstrate that the classical consideration of acids and bases must be profoundly modified if they are to be applied to non-aqueous solvents and even to certain properties of aqueous solutions (see (2) below), are as follows: (1) properly chosen indicators respond promptly to additions of acids and bases when dissolved in solvents like glacial acetic acid (5) or benzene (1e, 6), whereas the conductivity indicates extremely low ionization; (2) acid (or basic) catalysis is produced by undissociated acids (or bases) (1d), the catalysis being dependent primarily upon the facility with which protons can be transferred from catalyst to substrate (or vice versa); (3) the degree of dissociation as indicated by the conductance ratio in any given solvent depends not only upon the dielectric constant but also upon the extent to which the proton of the acid is transferred to basic molecules in the system (1c).

These results emphasize the distinction that must be drawn between extent of dissociation and acidity when comparison is made in different solvents.   To say that a solution is highly acid does not necessarily imply that the concentration of hydrogen ions, behaving as particles osmotically independent of the other constituents of the solution, is large.   Instead, the term "acidity" requires only a knowledge of the reversible work of transferring hydrogen ions from the given medium to some standard of reference.   The hydrogen electrode potential is thus the logical (1b, 1c) measure of acidity when this quantity can be freed from the perplexing complications of liquid junction potentials and individual ion activities (1f).

The extent of dissociation, on the other hand, is conditioned by all the factors which regulate the separation of ions, the dielectric constant being particularly important in this connection. The reciprocal rôles of the solvent and solute in the ionization process can be interpreted most clearly by recognizing their interaction as an equilibrium between two conjugate acid–base systems with the elimination of the proton as an independent entity.

$$\text{Acid}_1 \quad + \quad \text{Base}_2 \quad \rightleftarrows \text{Acid}_2 + \text{Base}_1 \qquad (3)$$
$$\text{HCl} \quad + \quad H_2O \quad \rightleftarrows H_3O^+ + Cl^-$$
$$H_2PO_4^- + \quad OH^- \quad \rightleftarrows H_2O \quad + HPO_4^=$$
$$\text{HAc} \quad + \quad NH_3 \quad \rightleftarrows NH_4^+ + Ac^-$$
$$H_2O \quad + \quad NH_3 \quad \rightleftarrows NH_4^+ + OH^-$$

BENZENE AS A SOLVENT

Ordinarily the solvent, by virtue of its own acid or basic properties, operates as the second acid–base system and thus facilitates ionization, a property most highly developed in water because of its amphoteric character. Benzene, on the other hand, presents an extreme contrast to water. Owing to the absence of acid and basic properties, benzene can act only as an inert diluent; consequently a second acid–base system must always be added to produce and define the equilibrium. By the same token, the range of acidity possible in benzene should be greater and depend only upon the intrinsic character of the acids and bases added, i.e., not be limited as in the case of water by the acid strength of H_3O^+ and the basic strength of OH^-. The low dielectric constant ($D = 2.28$) introduces complications which are not encountered in water, one of the most important being the greatly increased association of ions as a result of the electric forces (8b). The significant problem in such a solvent may be stated as follows: How constant will the relative acidities of a series of acids of the same electric charge type remain on transferring from water to benzene?

Were it possible to refer hydrogen electrode potentials measured in different media to a common scale, new definitions of acidity would be unnecessary. In the present state of knowledge regarding individual ionic activities and junction potentials, the

strength of any acid, HA, can be measured most satisfactorily by the extent to which it reacts with any one base, B, chosen as standard for the solvent in question by employing the relation

$$\left[\frac{HB}{B}\right]\left[\frac{A}{HA}\right] = \frac{K_{HA}}{K_{HB}} = K \tag{4}$$

valid for a constant environment. The brackets designate the *concentrations* of the components. K is then one measure of the acidity and depends mutually on the strength of HA as an acid (K_{HA}) and on the strength of HB as an acid (K_{HB}).

$$a_{H^+} \equiv K_{HA}\left[\frac{HA}{A}\right] = K_{HB}\left[\frac{HB}{B}\right] \tag{5}$$

The proton activity a_{H^+} of the solution may be defined by equation 5 and measured in terms of whichever acid–base system (HA:A) or (HB:B) is most convenient.

By the aid of equation 4, Brönsted (1e) arranged a series of twenty-four acid–base systems in accordance with their decreasing acid strengths in benzene (see reference 5c). No numerical data were presented and he emphasized that his results were entirely provisional.
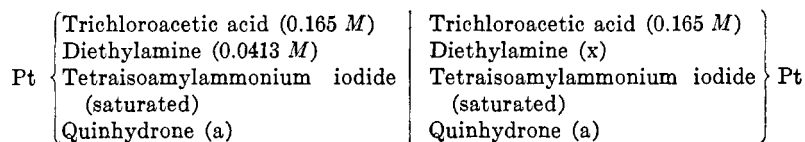
EXPERIMENTAL

To explore to what extent salt formation may proceed in benzene, we (7) determined the changes in conductivity produced by alternate additions of trichloroacetic acid and the soluble base, diethylamine. A special low resistance cell was used and the conductance measured by noting the deflections on a Leeds and Northrup type 2500 galvanometer when the cell and galvanometer were placed in series in the 110-volt direct current line, a method since established by Kraus and Fuoss (8a) as being entirely reliable when the conductivity is extremely minute.

The equivalent conductance is of the very low order of 10^{-11} to 10^{-9} reciprocal ohms, and depends upon concentration in a peculiar manner (8a, 8b). The minimum conductance, however, occurred at points corresponding to equal additions of acid and base and clearly indicates that a prompt reaction occurs.

Electrometric titrations

We next investigated the change in hydrogen electrode potential by the use of a quinhydrone electrode cell of the type

Pt $\left\{\begin{array}{l}\text{Trichloroacetic acid (0.165 } M) \\ \text{Diethylamine (0.0413 } M) \\ \text{Tetraisoamylammonium iodide} \\ \quad \text{(saturated)} \\ \text{Quinhydrone (a)}\end{array}\right.$ $\left|\begin{array}{l}\text{Trichloroacetic acid (0.165 } M) \\ \text{Diethylamine (x)} \\ \text{Tetraisoamylammonium iodide} \\ \quad \text{(saturated)} \\ \text{Quinhydrone (a)}\end{array}\right\}$ Pt

For the standard half-cell on the left we used trichloroacetic acid partly neutralized by diethylamine, and on the right side diethylamine was added progressively to the trichloroacetic acid. To improve the conductivity, the benzene was first saturated with tetraisoamylammonium iodide, a salt which is moderately soluble in this solvent.

The E.M.F. was measured by charging a 10-microfarad condenser and discharging it through a ballistic galvanometer. In dry weather the E.M.F. can be determined to less than one millivolt. Typical titration curves were obtained which showed that the trichloroacetic acid system is 0.43 volt more acid than the diethylammonium system, while the monochloroacetic acid system is 0.35 volt more acid, relative to the same standard.

FORMULATION OF INDICATOR RESULTS (9)

(a) Ideal case

Consider an acid, HA, a very much weaker acid, HB, and an indicator, HI, dissociating to their conjugate bases, A, B, and I. Starting with a solution of the acid HA with a small but constant amount of indicator present, the reaction which occurs as the base B is added is HA + B = HB + A. The indicator must also adjust its dissociation with the change in hydrogen ion activity, thus: HA + I = HI + A. From equation 5

$$\log\left[\frac{A}{HA}\right] = \log\left[\frac{I}{HI}\right] - pK_{HA} + pK_{HI} \tag{6}$$

Experimentally $\left[\dfrac{I}{HI}\right]$ is measured with a colorimeter. For

the ratio $\left[\dfrac{A}{HA}\right]$, we assume that the neutralization reaction goes practically to completion, as indicated by the conductivity and electrometric titrations; i.e., the added base B must be strong enough to produce a quantitative conversion, so that the ratio is given by the amount of base added, divided by the amount of un-neutralized acid remaining.
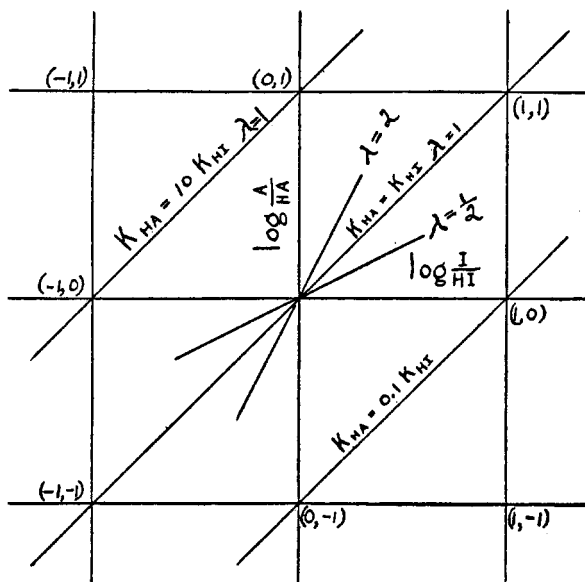

FIG. 1

By plotting $\log\left[\dfrac{A}{HA}\right]$ against $\log\left[\dfrac{I}{HI}\right]$ as in figure 1, a family of parallel lines with unit slopes results, three members of which have been selected to cut the $\log\left[\dfrac{I}{HI}\right]$ axis at the points $+1$, 0, and -1, corresponding to the condition that the strength of the acid HA is respectively less than, equal to, or greater than the strength of the indicator acid HI by one logarithmic unit (or to a factor of tenfold in the acid strength constants K_{HA}). Consequently for ideal solutes where the slope λ is unity, the intercept on either

axis is a measure of the strength of the acid relative to the indicator.

(b) Indicator or acid associated

If either the indicator or the acid or both are associated, the simple relationship just developed will not hold. The deviations from the ideal mechanism could, of course, be taken care of by introducing activity coefficients, but it seems preferable to reformulate the mechanism in a way which will recognize the possibility of association, and thus diminish the burden which the activity coefficient must bear.

The stoichiometric concentration will be represented by brackets, and the activity by parentheses. The activity coefficient, f, will refer to any deviation from the behavior of an ideal solute, when the solute is considered as associated m-fold in the case of the acids, or n-fold in the case of the indicator.

The generalized mass law relations are:

$$a_{H^+}^m = K'_{(HA)_m} \left[\frac{(HA)_m}{(A)_m} \right] \left(\frac{f_{(HA)_m}}{f_{(A)_m}} \right) \tag{7}$$

$$= K_{(HA)_m} \left[\frac{(HA)_m}{(A)_m} \right] \tag{8}$$

$$a_{H^+}^n = K_{(HI)_n} \left[\frac{(HI)_n}{(I)_n} \right] \tag{9}$$

It is important to note that K'_{HA} is an activity constant and consequently does not vary with change of solvent. The constant $K_{(HA)_m}$ in equation 8 is an acidity constant, i.e., equal to the activity constant times the activity coefficient ratio. The acidity constants will vary with changes in the medium and are the quantities which are actually employed. By extracting the mth and n^{th} root, equating 8 and 9, and casting into logarithmic form, the general equation becomes:

$$\frac{1}{m} \log \left[\frac{(A)_m}{(HA)_m} \right] = \frac{1}{n} \log \left[\frac{(I)_n}{(HI)_n} \right] - \frac{1}{m} pK_{(HA)_m} + \frac{1}{n} pK_{(HI)_n} \tag{10}$$

Since m and n cannot be determined independently, multiply through by m and get the ratio $m/n = \lambda$. If, during the process

of titrating an acid with a base B, no appreciable change in environment is produced, i.e., no change in activity coefficient ratio, then a plot of the color ratio log $\left[\dfrac{I}{HI}\right]$ against log $\left[\dfrac{A}{HA}\right]$ will yield a straight line, but with a slope λ. This actually proves to be the case. Interpreted physically, these equations mean that if λ is less than unity, one molecule of the associated indicator base can combine with more protons than can one molecule of the associated base A. In other words, a slope less than unity means that the indicator is associated relatively more than is the acid.

Figure 2 shows the results of titrating dichloroacetic, monochloroacetic, formic, benzoic, and acetic acids with diethylamine, using brom phenol blue as indicator. This figure is typical of the results obtained with other indicators. The slopes of the curves of these acids lie between one-third and one-half, depending upon the total concentration and the particular acid and indicator used. Most of the curves approximate most closely to a slope of 1/2, so that in general the degree of association of the indicator system is about twice that of the acid system.

Figure 3 gives the results for brom cresol purple, an indicator which in water changes in the acid range of pH 5.2 to 6.3 and thus is one logarithmic unit weaker than acetic acid. A similar relationship holds in benzene, except that acetic acid is only 0.3 logarithmic unit instead of one logarithmic unit more acid (i.e., higher) than brom cresol purple. In order to develop the basic color of brom cresol purple it is necessary to employ the strongest base which is soluble in benzene, namely, piperidine. In benzene, the piperidine–piperidinium system is only 1.4 pK units more basic or less acid than brom cresol purple, whereas in water the difference is 4.8 units. Saturation with water did not produce changes in relative acidity greater than 0.1 pK unit for monochloroacetic acid when compared with solutions which were especially dried and protected from moisture. This result is gratifying but the conclusion may have to be modified when very strong acids like hydrochloric acid are considered.

To determine the relative strengths of acids in respect to a given indicator, one has only to compare the intercepts on the log

$\left[\dfrac{A}{HA}\right]$ axes, i.e., at the point of half change of the indicator, for a numerical result. However, when the acid studied is more than one pK unit stronger or weaker than the indicator it becomes difficult to establish the intercept, since the equilibrium between
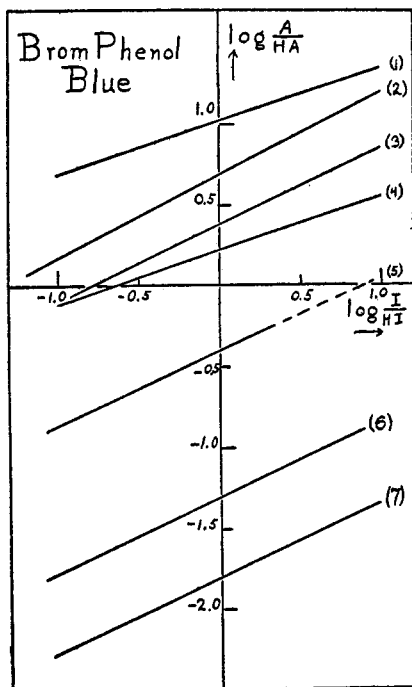

FIG. 2. BROM PHENOL BLUE
1. Dichloroacetic acid......... 0.10 M
2. Salicylic acid............... 0.01 M
3. Monochloroacetic acid...... 0.01 M
4. Monochloroacetic acid...... 0.10 M
5. Formic acid................ 0.01 M
6. Benzoic acid............... 0.01 M
7. Acetic acid................ 0.10 M
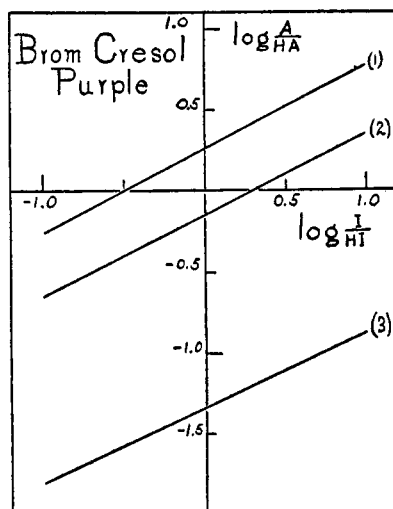
FIG. 3. BROM CRESOL PURPLE
1. Acetic acid................. 0.1 M
2. Diethylammonium ion...... 0.1 M
3. Piperidinium ion........... 0.1 M

acid and indicator systems is established so far from the point of half neutralization of the acid that a small experimental error becomes considerably magnified. This difficulty seriously restricts the number of acids that can be studied with a given indicator. However, if the relative acidity of two indicator systems

can be established, the acid systems studied with these two indicators can then be compared.

For example, dichloroacetic acid is weaker than dimethyl yellow but stronger than brom phenol blue. The experimental curves for these two indicators are then displaced along the $\log\left[\dfrac{I}{HI}\right]$ axis until they become continuous. Dimethyl yellow is several units more acid than is brom phenol blue. By a progressive step-wise
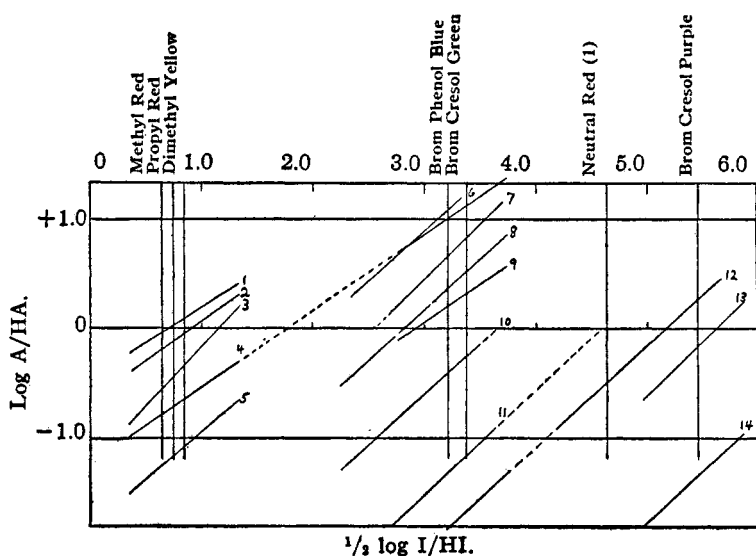

FIG. 4

1. Trichloroacetic acid......... 0.10 M	8. Monochloroacetic acid.... 0.01 M
2. Trichloroacetic acid......... 0.05 M	9. Monochloroacetic acid.... 0.10 M
3. Trichloroacetic acid......... 0.01 M	10. Formic acid............. 0.01 M
4. Dichloroacetic acid......... 0.10 M	11. Benzoic acid............. 0.01 M
5. Dichloroacetic acid......... 0.05 M	12. Acetic acid.............. 0.10 M
6. Dichloroacetic acid......... 0.01 M	13. Diethylammonium ion.... 0.10 M
7. Salicylic acid.............. 0.01 M	14. Piperidinium ion......... 0.10 M

correlation of the indicators in this manner, it is possible to establish a numerical scale for all the acid and indicator systems studied.

Figure 4 gives a summary of the results obtained by this procedure when plotted against $1/2 \log \dfrac{I}{HI}$ to compress the results

into a reasonable space and also to make the results more comparable with the ideal case of unit slopes. The heavy lines represent the range over which experimental measurements can be made and the dotted lines the extrapolations employed in correlating the various indicator systems.

This figure provides a scale of acidity which is correct, within limits of experimental error, for those acids which are represented
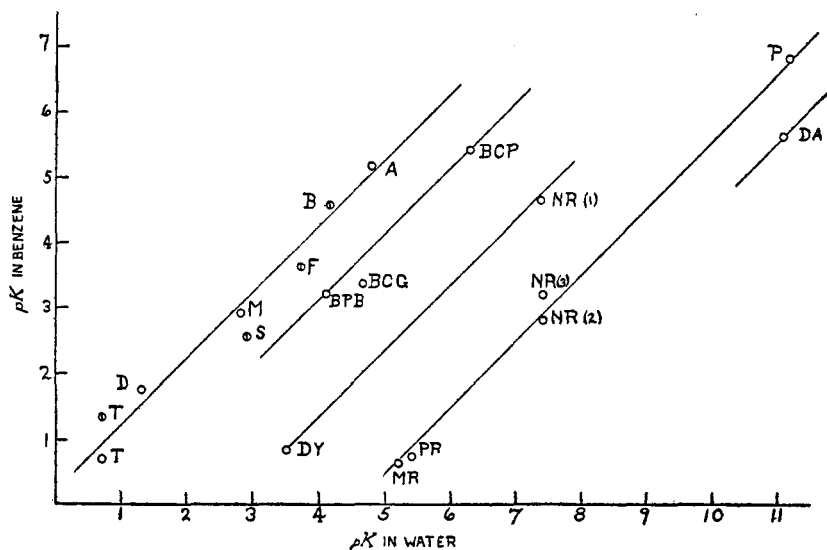

FIG. 5

T, Trichloroacetic acid..... 0.10 M	BCP, Brom cresol purple
D, Dichloroacetic acid..... 0.10 M	DY, Dimethyl yellow
M, Monochloroacetic acid.. 0.01 M	NR (1), Neutral red (1)
S, Salicylic acid........... 0.10 M	MR, Methyl red
F, Formic acid............. 0.01 M	PR, Propyl red
B, Benzoic acid............ 0.01 M	NR (2), Neutral red (2)
A, Acetic acid............. 0.10 M	NR (3), Neutral red (3)
BPB, Brom phenol blue	DA, Diethylamine
BCG, Brom cresol green	P, Piperidine

by lines having a unit slope and is approximately correct for those having slopes but slightly different from unity. This form of presentation has the advantage of representing the experimental results directly. Our knowledge of benzene solutions, however, is too incomplete at present to allow of a more exact interpretation of the effects of dilution.

In figure 5, the acid strengths in water are compared with those in benzene by plotting the values of pK benzene obtained from the intercepts on $1/2 \log \dfrac{I}{HI}$ axis in the preceding figure.   It is interesting and important to note that the uncharged acids retain practically the same differences in strength that exist in water. This means that their activity coefficient ratios undergo almost parallel changes when the acids are transferred from water to benzene.   On the other hand, the strengths of the cationic acids represented by the indicators and substituted ammonium ions have increased to a very considerable amount over their strengths in water relative to the uncharged acids.   It remains an interesting problem to determine whether these changes can be accounted for quantitatively on the basis of the electrical work of transfer, or whether it will be necessary to invoke further hypotheses dependent upon the molecular structure (10, 11).   The answer to this question must await an independent determination of the charge type before definite conclusions can be drawn.

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