CLXII.—*Acid and Salt Effects in Catalysed Reactions. Part XX. The Ionisation of Acids in Salt Solutions.*

By HARRY MEDFORTH DAWSON and WILLIAM LOWSON.

THE methods which have been used for the determination of the degree of ionisation of acids in accordance with the classical ionic theory depend on measurements of electrical conductivity, freezing-point change, potential difference and reaction velocity. Such observations continue to provide the necessary data, although the method of interpretation has been modified in all cases by recent theoretical developments.

The most widely used method is, of course, the conductivity method and it is probable that this yields substantially correct results if its application is restricted to dilute solutions of the weaker acids. When salt solutions are substituted for water as the solvent medium, the conductivity method fails for obvious reasons, and in these circumstances it is necessary to look for other methods which may permit of the determination of the degree of ionisation of acids. The present paper gives an account of an attempt to derive the required hydrogen-ion concentration (as distinguished from the hydrogen-ion activity) from reaction velocity data and to ascertain the influence of the concentration of the salt solution on the ionisation constants of acids.

In general, the application of this method must take account of the fact that catalytic effects may be produced by both positive and negative ions and by neutral molecules and that the magnitudes of the coefficients which characterise the various catalytic entities vary with the nature of the reaction medium. If the catalysed reaction and the salt solution in question are such that the only measurable catalytic effects are those due to the acid under investigation, the equation for the specific reaction velocity may be written

$$v = v_h + v_a + v_m = k_h[\mathrm{H}^+] + k_a[\mathrm{A}^-] + k_m[\mathrm{HA}] \quad . \quad (1)$$

in which the coefficients k_h, k_a, and k_m depend on the nature and concentration of the salt solution. Since $[\mathrm{H}^+] = [\mathrm{A}^-]$ and $[\mathrm{HA}] = c - [\mathrm{H}^+]$, where c is the concentration of the acid, the above equation may be written

$$[\mathrm{H}^+] = (v - k_m c)/(k_h + k_a - k_m) \quad . \quad . \quad . \quad (1\text{A})$$

The experimental data to which this equation is now applied have reference to the rate of hydrolysis of ethyl acetate in sodium chloride solutions (0—4 moles per litre) with acetic, glycollic, chloroacetic and dichloroacetic acids as catalyst. One of the advantages attaching to the study of this particular reaction is that the coefficients k_a and k_m have for the most part such small values that they can be neglected in comparison with k_h. In other words we are mainly concerned with hydrogen-ion catalysis.

In the application of equation (1A) it is assumed that hydrochloric acid is completely ionised in the sodium chloride solutions and that observations made with this acid (0·01N) afford therefore a measure of k_h. If this assumption is valid, it follows that the reaction velocity data for the other acids will not be disturbed to any measurable extent by the interaction of hydrogen ion with chlorine ion even when the ratio $[Cl^-]/[H^+]$ is of the order 10^3—10^4. The absence of such interference is obviously dependent on the ionisation constant of hydrochloric acid and the order of magnitude of this would appear to be very uncertain. The value $K = 10^6$ is given by Schreiner (*Z. physikal. Chem.*, 1924, **111**, 419) and $K = 10^7$ by Ebert (*Naturwiss.*, 1925, **13**, 393). On the other hand, the electrical conductivities of very dilute solutions of hydrochloric acid might suggest that it is much smaller. In these circumstances, it is necessary to consider the possibility that the reaction velocity data, more particularly in the case of concentrated sodium chloride solutions, may be measurably affected by the formation of undissociated hydrochloric acid, for this may be confidently expected to be an extremely active catalytic agent.

If the solvent for the acids under investigation is a concentrated solution containing x mols. of sodium chloride per litre, and if such solutions contain undissociated hydrochloric acid, the relation between [HCl] and $[H^+]$ is given by $[HCl] = x[H^+]/K$ and the specific reaction velocity for a solution of hydrochloric acid by

$$v = k_h[H^+] + k_m[HCl] = k_h[H^+](1 + k_m x/k_h K) \quad . \quad (2)$$

For the corresponding solution of any other acid HA, account must be taken of the equilibria $HA \rightleftharpoons H^+ + A^-$ and $H^+ + Cl^- \rightleftharpoons HCl$, and it is evident that the formation of undissociated hydrochloric acid will lead to a hydrogen-ion concentration smaller than that which would have been obtained in the absence of interaction between the hydrogen and chlorine ions. The specific reaction velocity for this solution is given by

$$v = k_h[H^+](1 + k_m x/k_h K) + k_a[A^-] + k_m[HA] \quad . \quad (3)$$

in which $[H^+]$ is less than $[A^-]$. If the second and third terms in equation (3) can be neglected, or alternatively evaluated, it is apparent that the combination of equations (2) and (3) would permit us to derive the relative hydrogen-ion concentrations of the two solutions, but does not enable us to determine the ionisation constant of the acid HA. This, indeed, cannot be obtained from the reaction velocity data unless the formation of undissociated hydrochloric acid is stoicheiometrically and catalytically negligible. Since $[\mathrm{HCl}] = x[\mathrm{H}^+]/K$ and the maximum value of x is about 5, it follows that the stoicheiometric effect will be negligible if K is greater than about 10^3 and that the catalytic effect will be negligible if k_m/k_hK is less than about 10^{-3}. In this connexion it is important to recognise that k_m/k_h is a function of K. According to Brönsted (*Trans. Faraday Soc.*, 1928, **24**, 630) these quantities are connected by an equation of the form $k_m/k_h = aK^n$, where a and n are constants which depend on the nature of the catalysed reaction and $n > 0 < 1$. Since this relation is used by us in an attempt to show that k_m/k_hK is negligibly small, attention may be directed to the values of k_m and K which have been derived for a series of acids from catalytic observations on the acetone–iodine reaction (Dawson, Hall, and Key, J., 1928, 2844). By plotting $\log k_m$ against $\log K$, a straight line is obtained, and from this constants are derived which lead to the equation $k_m = 0{\cdot}0014K^{0{\cdot}64}$, or since $k_h = 4{\cdot}65 \times 10^{-4}$, to $k_m/k_h = 3{\cdot}00\ K^{0{\cdot}64}$. The values of k_m calculated from this equation are in close agreement with the values derived from the experimental data, as may be seen from Table I, in which the first row of figures gives the values of K, the second gives the observed values of k_m, and the third the calculated values.

TABLE I.

Acid ……	Propionic	Acetic	β-Chloro-propionic	Glycollic	Chloro-acetic	Dichloro-acetic
K ………	$1{\cdot}38 \times 10^{-5}$	$1{\cdot}85 \times 10^{-5}$	$1{\cdot}01 \times 10^{-4}$	$1{\cdot}50 \times 10^{-4}$	$1{\cdot}51 \times 10^{-3}$	$5{\cdot}0 \times 10^{-2}$
$k_m . 10^6$ obs. …	1·1	1·35	3·7	5·7	22·2	200
$k_m . 10^6$ calc. …	1·09	1·31	3·88	5·0	22·0	206

Within limits which are represented by a variation of the ionisation constant in the ratio 1 : 4000, it is evident from the above table that the relation between k_m/k_h and K can be accurately represented by an equation of the type $k_m/k_h = aK^n$. An equation of this type, namely, $k_m/k_h = K^{0{\cdot}5}$, was first suggested by Taylor (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, **2**, No. 37) as the result of observations on the hydrolysis of ethyl acetate. In view of the limited scope of those experiments it is probable that the value assigned to the exponent n is not very exact. Brönsted's observations on the mutarotation of glucose (*loc. cit.*) may be expressed by the equation $k_m/k_h = 0{\cdot}4\ K^{0{\cdot}2}$ and are of particular importance for our purpose in that they show that this type of equation is valid over an extremely wide range of K values. Further confirmation of its validity has been provided by observations on the hydrolysis of ethyl orthoacetate, orthopropionate and orthocarbonate (Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, 1929, **25**, 59). There is thus very substantial evidence for the general applicability of the relation $k_m/k_h = aK^n$.

When this value for k_m/k_h is introduced into the expression $k_m x/k_h K$ which affords a measure of the relative catalytic effect produced by undissociated hydrochloric acid (compare equation 2), this becomes ax/K^{1-n}, in which x and K are determined by the strength of the sodium chloride solution, whilst a and $(1—n)$ depend on the nature of the catalysed reaction. The available evidence indicates that a does not differ greatly from unity and that $(1—n)$ is a positive quantity less than unity. From this it follows that, if a solution of hydrochloric acid in sodium chloride (*e.g.*, $0{\cdot}01N$-HCl + $1{\cdot}0N$-NaCl) contains a catalytically effective quantity of undissociated acid, the effect of the latter may be expected to vary with the catalysed reaction. Experiment shows, however, that the change in the reaction velocity produced by the addition of sodium chloride is within narrow limits the same for different reactions ; for example, sucrose inversion, ester hydrolysis, and the keto-enol change of acetone. This constancy of the salt effect would seem to show conclusively that undissociated hydrochloric acid is not responsible for any appreciable catalytic effect. Since the relative magnitude of this effect is represented by a/K^{1-n}, it may be inferred that the ionisation constant of hydrochloric acid is very large, possibly not less than the values suggested by Schreiner and Ebert (*loc. cit.*). It follows further that the reaction velocity data obtained for the various acids in solutions of sodium chloride may be applied to the derivation of the required hydrogen-ion concentrations by the use of equation (1A).

A further point to which attention may be directed is that the interpretation of the reaction velocity data does not involve any assumption which necessarily distinguishes between the activities and the concentrations of the reacting substances. If for the sake of simplicity we confine our attention to the action of one of the catalytic entities, namely, the hydrogen ion, and suppose that the rate of hydrolysis is determined by the respective activities, we may write

$$v = k_h a_H a_e a_w = k_h f_h[H^+]f_e[\text{ester}]f_w[H_2O]$$

and since the ester concentration is constant and the values of k_h, f_h, f_e, f_w and $[H_2O]$ are determined by the concentration of the sodium chloride, it follows that the above equation reduces in general to the form represented by the term for the action of the hydrogen ion in equation (1). Rigid adherence to the concept of ionic strength might suggest that this is not strictly true in the case of the more dilute salt solutions containing the stronger acids, but the behaviour of such solutions does not suggest any need for differentiation.

Before proceeding to the description of the results obtained with the different acids, it should be mentioned that the actual procedure varies somewhat with the strength of the catalysing acid. With acetic acid, the auto-catalytic effect must be taken into account, and with dichloroacetic acid the catalytic influence of the undissociated acid is very appreciable.

If, in the case of acetic acid, the original concentrations of the ester and of the acid are denoted by a and b respectively, that of the acetic acid formed by y, then, since $[H^+] = \sqrt{K(b + y)}$, we may write

$$dy/dt = k_h[H^+][\text{ester}][H_2O] = k'_h\sqrt{K}(a - y)(b + y)^{\frac{1}{2}}$$

which on integration gives

$$k'_h\sqrt{K} = \frac{1}{t\sqrt{a + b}}\left\{\log\frac{\sqrt{a + b} + \sqrt{b + y}}{\sqrt{a + b} - \sqrt{b + y}} - \log\frac{\sqrt{a + b} + \sqrt{b}}{\sqrt{a + b} - \sqrt{b}}\right\} \quad (4)$$

where $k'_h\sqrt{K}$ represents the specific catalytic effect of the acetic acid. For a given salt solution, k'_h is given by the data for hydrochloric acid (Dawson and Lowson, this vol., p. 393), whence K is derived from $K = (k'_h\sqrt{K}/k'_h)^2$.

In the experiments with glycollic, chloroacetic and dichloroacetic acids the auto-catalytic effect of the acetic acid produced may be neglected, and in these circumstances the reaction velocity for unit ester concentration is given by $v = 1/t\,.\log_e a/a - y$. This velocity is entirely due to the hydrogen ion when glycollic acid is used. With chloroacetic acid, a slight effect is attributable to the undissociated acid, and this is quite appreciable in the case of dichloroacetic acid. In order to determine the value of k_m for dichloroacetic acid, the procedure described by Dawson, Hall, and Key (*loc. cit.*) has been followed. To what extent the value of k_m obtained in this way is affected by the salt concentration is uncertain, but it may readily be shown that such variations in k_m are not of much importance in the present connexion.

On the assumption that K for salt-free solutions of dichloroacetic acid is equal to $5{\cdot}0 \times 10^{-2}$, the value obtained by the method referred to is $k_m = 0{\cdot}8 \times 10^{-3}$. The following table shows that the observed reaction velocities for acid concentrations over the range $c = 0{\cdot}01$

to $c = 0{\cdot}2$ are in close agreement with the values calculated from the equation

$$v = v_h + v_m = 6{\cdot}5 \times 10^{-3}[\mathrm{H}^+] + 0{\cdot}8 \times 10^{-3}[\mathrm{HA}] \quad . \quad (5)$$

The first and second rows give the concentration of the acid and of the hydrogen ion, the third and fourth the values of v_h and v_m, and the fifth and sixth show the calculated and observed velocities.

TABLE II.

Catalytic activity of dichloroacetic acid.

c	0·01	0·02	0·05	0·1	0·2
$[\mathrm{H}^+]$	0·00854	0·0153	0·0309	0·0500	0·0780
$v_h \,.\, 10^4$	0·555	0·995	2·01	3·25	5·07
$v_m \,.\, 10^4$	0·012	0·037	0·15	0·40	0·98
$v \,.\, 10^4$ cal.	0·567	1·03	2·16	3·65	6·05
$v \,.\, 10^4$ obs.	0·564	1·04	2·16	3·78	5·93

The observed velocities are obviously closely reproduced by taking into account the catalytic activity of the undissociated acid, which, since $k_m/k_h = 0{\cdot}8/6{\cdot}5$, is about one-eighth as active as the hydrogen ion.

For the most part, reaction velocities were measured with an ester concentration of 20·0 c.c. per litre, but on account of salting-out effects this was reduced to 8·0 c.c. in the experiments with $3M$- and $4M$-salt solutions. This reduction in the ester concentration does not appreciably affect the velocity when hydrochloric acid is the catalyst, but a slight increase is observed in the case of the weaker acids. The increase does not, however, materially affect the relations shown by the numbers in the following tables. In the case of acetic acid (Table III) the data recorded are the sodium chloride concentration (x), the value of $k'_h\sqrt{K}$ given by equation (4), and the value of K. For glycollic acid (Table IV) and dichloroacetic acid (Table V) the data given are x, the velocity $v = 1/t\,.\log_e a/a - y$, the hydrogen-ion concentration $[\mathrm{H}^+]$, and the ionisation constant K. The corresponding data for chloroacetic acid were recorded in the preceding paper (*loc. cit.*), which also gives the values of k'_h derived from the experiments with hydrochloric acid.

TABLE III.

Ionisation of acetic acid (0·1N) *in sodium chloride solutions.*

x.	$k'_h\sqrt{K}\,.\,10^4$.	$K\,.\,10^5$.	x.	$k'_h\sqrt{K}\,.\,10^4$.	$K\,.\,10^5$.
0	0·269	1·71	0·50	0·397	2·94
0·01	0·285	1·91	1·0	0·423	2·70
0·04	0·308	2·20	2·0	0·439	1·96
0·10	0·331	2·46	3·0	0·444	1·41
0·30	0·367	2·77	4·0	0·400	0·81

TABLE IV.

Ionisation of glycollic acid (0·1N) *in sodium chloride solutions.*

x.	$v \cdot 10^4$.	$[H^+] \cdot 10^3$.	$K \cdot 10^4$.	x.	$v \cdot 10^4$.	$[H^+] \cdot 10^3$.	$K \cdot 10^4$.
0	0·255	3·92	1·60	0·3	0·350	5·01	2·64
0·01	0·262	4·02	1·68	0·5	0·372	5·08	2·71
0·02	0·271	4·15	1·80	1·0	0·410	5·04	2·67
0·03	0·278	4·24	1·88	2·0	0·450	4·55	2·17
0·04	0·285	4·34	1·97	3·0	0·492	4·17	1·81
0·10	0·307	4·61	2·23	4·0	0·480	3·40	1·20

TABLE V.

Ionisation of dichloroacetic acid (0·05N) *in sodium chloride solutions.*

x.	$v \cdot 10^4$.	$[H^+] \cdot 10^2$.	$K \cdot 10^2$.	x	$v \cdot 10^4$.	$[H^+] \cdot 10^2$.	$K \cdot 10^2$.
0	2·16	3·09	5·0	1·0	2·96	3·49	8·05
0·04	2·24	3·19	5·6	2·0	3·43	3·33	6·65
0·1	2·36	3·34	6·7	3·0	3·94	3·22	5·8
0·3	2·48	3·37	7·0	4·0	4·33	2·95	4·25
0·5	2·64	3·44	7·6				

From the above data and the corresponding numbers for chloroacetic acid it is apparent that the ionising tendency of the different acids is affected in the same manner by the added salt. As the salt concentration increases, the ionisation constant increases to a maximum and then decreases. There is indeed a close approximation in the behaviour of the different acids, as may be readily seen by comparing the values of $R_x = K_x/K_0$, where K_x is the ionisation constant in the x molar salt solution and K_0 the constant for the salt-free solution. The values of R_x are shown in Table VI.

TABLE VI.

Values of $R_x = K_x/K_0$ *in sodium chloride solutions.*

x.	$R_x(CH_3{\cdot}CO_2H)$.	$R_x(OH{\cdot}CH_2{\cdot}CO_2H)$.	$R_x(CH_2Cl{\cdot}CO_2H)$.*	$R_x(CHCl_2{\cdot}CO_2H)$.	R_x cal.
0	1	1	1	1	1
0·01	1·12	1·05	1·09	—	1·12
0·02	—	1·12	1·15	—	1·17
0·03	—	1·17	1·21	—	1·21
0·04	1·29	1·23	1·23	1·12	1·24
0·05	—	—	1·29	—	1·27
0·10	1·44	1·39	1·42	1·34	1·38
0·20	—	—	1·51	—	1·50
0·30	1·62	1·65	1·56	1·40	1·58
0·50	1·72	1·69	1·66	1·52	1·67
1·0	1·58	1·67	1·57	1·61	1·66
2·0	1·15	1·35	1·28	1·33	1·33
3·0	0·83	1·13	0·98	1·16	0·94
4·0	0·47	0·75	0·64	0·85	0·63

* The K_x values for chloroacetic acid recorded in the preceding paper have been slightly modified as the result of supplementary reaction velocity measurements; the resulting changes are not of any importance.

From this table it is apparent that the addition of sodium chloride raises the ionisation constant of the acid in all cases to a maximum which is 60 to 70% greater than the constant for the salt-free solution and that this maximum is reached at a sodium chloride concentration which lies between 0·5 and 1·0 mol. per litre. In this connexion it may be noted that previous observations on the acetone–iodine reaction with acetic acid as catalyst in solutions of lithium, sodium and potassium chloride (Dawson and Key, J., 1928, 1239) have shown that the curves which represent the connexion between K_x and x are of the same type. The quantitative differences would seem to depend only on the nature of the ions of the inert salt.

Analysis of the R_x–x curve shows that it corresponds with an equation of the form $R_x = 10^{a\sqrt{x}-bx}$. Characteristic points on this curve are the maximum point ($R_x = R_m$, $x = x_m$) and the point ($R_x = 1$, $x = x_1$) at which the ionisation constant of the acid has the same value as in the salt-free solution.

The equation may be written

$$\log R_x = a\sqrt{x} - bx \quad . \quad . \quad . \quad . \quad . \quad (6)$$

whence

$$d \log R_x = (\tfrac{1}{2}ax^{-\frac{1}{2}} - b)dx$$

and therefore

$$R_x = R_m \text{ when } x = x_m = a^2/4b^2 \quad . \quad . \quad . \quad (7)$$

and

$$\log R_m = a\sqrt{x_m} - bx_m = a^2/4b \quad . \quad . \quad . \quad . \quad (8)$$

Furthermore, it is evident that $R_x = 1$ when $a\sqrt{x} - bx = 0$, that is to say, when

$$x = 0 \text{ and } x = x_1 = a^2/b^2 \quad . \quad . \quad . \quad . \quad (9)$$

and by comparing equations (7) and (9) we obtain

$$x_1 = 4x_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

According to the last equation, the salt concentration at which the degree of ionisation of the acid is the same as in the salt-free solution is four times the concentration for which the ionisation is a maximum. Since the specific effects of the ions find expression in the constants a and b, it follows that this relation is independent of the nature of the inert salt.

On account of the flatness of the R_x–x curve in the neighbourhood of the maximum, it is not possible to determine x_m from the graph with any exactitude, but it may readily be shown that the data recorded in the present paper, as well as the results obtained for acetic acid in solutions of other alkali-metal chlorides (*loc. cit.*), are in approximate agreement with equation (10).

Since R_m and x_1 can be readily derived from the experimental curves, the values of these quantities may be utilised in the calculation of the constants a and b, which are given by the equations

$$a = 4 \log R_m/\sqrt{x_1} \text{ and } b = 4 \log R_m/x_1.$$

In accordance with the data of Table VI, the values assigned to these constants are $a = 0{\cdot}54$ and $b = 0{\cdot}32$. These correspond with $x_m = 0{\cdot}71$, $R_m = 1{\cdot}68$ and $x_1 = 2{\cdot}85$. The values of R_x calculated from $\log R_x = 0{\cdot}54\sqrt{x} - 0{\cdot}32x$ are shown in the last column, and when due consideration is given to the magnitude of the error * which may attach to the individual figures, it is apparent that this equation affords for the most part a satisfactory account of the experimental results. The most concentrated solutions must, however, be excepted and the differences shown by the various acids in the 4-molar salt solutions are such as to suggest that new specific effects, which vary with the nature of the acid, come into play at these large salt concentrations. In spite of this divergence, the important fact remains that the logarithmic formula reproduces fairly closely the observed relations for a series of acids with ionisation constants which vary in the ratio 1 : 3000 over a wide range of salt solutions. It is indeed possible that the applicability of this formula is not restricted by the magnitude of the ionisation constant.

The constant *a* affords a measure of the inert salt effect which is responsible for the initial increase in the ionisation constant, whilst *b* measures the effect responsible for the subsequent decrease. Since the observations relate to solutions of one and the same salt, the further consideration of the logarithmic formula will be limited to a comparison of the experimental results with the relation indicated by the Debye–Hückel theory.

Assuming that the ions concerned are univalent and adopting the usual symbols for activities, activity coefficients and ionic strengths, then, since

$$R_x = K_x/K_0 = K_x/K_a \,.\, K_a/K_0$$

or

$$\log R_x = \log K_x/K_a - \log K_0/K_a$$

it follows that a theoretical expression for $\log R_x$ may be obtained by evaluating K_x/K_a and K_0/K_a in terms of the interionic force theory.

We may write $K_a = a_+a_-/a = f_+f_-/f \,.\, c_+c_-/c = K_x \,.\, f_\pm^2/f$

or $\log K_x/K_a = \log f - 2\log f_\pm$

and since $-\log f_\pm = \alpha\sqrt{\mu} - \beta\mu$

and $\log f = \gamma \,.\, \mu$

we obtain $\log K_x/K_a = 2\alpha\sqrt{\mu} - \beta'\mu$ (11), where $\beta' = 2\beta - \gamma$.

The corresponding expression for $\log K_0/K_a$ may be written

$$\log K_0/K_a = 2\alpha\sqrt{\mu_0} - \beta''\mu_0$$

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* In the case of dichloroacetic acid, which is 60—70% ionised, the probable error in K is increased by the circumstance that [H$^+$] and [HA] are both affected by an error in the measured reaction velocity.

where μ_0 is the ionic strength of the salt-free solution and β'' is in general different from β', and therefore

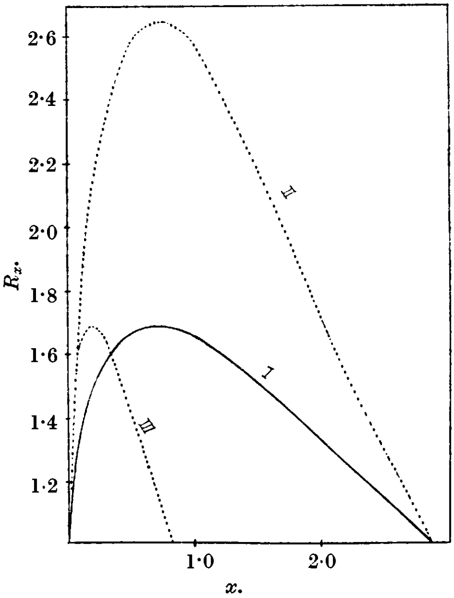
$$\log R_x = 2\alpha(\sqrt{\mu} - \sqrt{\mu_0}) - \beta'\mu + \beta''\mu_0 \quad . \quad . \quad (12)$$

Comparison of this theoretical relation with equation (6) shows the existence of a difference at small salt concentrations in that the ratio $(\sqrt{\mu} - \sqrt{\mu_0})/\sqrt{x}$ varies with the salt concentration for a given acid ($\sqrt{\mu_0}$ = constant) and with the nature of the acid for a given salt concentration. Effective comparison of the R_x values for such dilute salt solutions would, however, necessitate greatly increased accuracy in the measurement of the reaction velocities and for this reason we shall confine our attention to the consideration of differences which are entirely outside the range of experimental errors. In this connexion it may be noted that the theoretical relation reduces to the form

$$\log R_x = 2\alpha\sqrt{x} - \beta'x \quad . \quad . \quad . \quad . \quad (13)$$

if the ionisation constant of the acid is sufficiently small. This equation is identical in form with the empirical formula (equation 6), and since the applicability of the latter does not depend on the ionisation constant of the acid, it would seem permissible to compare the general Debye–Hückel coefficient $2\alpha = 1{\cdot}0$ with the empirical coefficient $a = 0{\cdot}54$. The difference between these two numbers is very large and by equating either the x or R_x values which correspond with the observed maximum value of the ionisation constant, it may readily be shown that the larger coefficient is incompatible with the experimental R_x–x curves. If, for example, we combine the assumption that $a = 2\alpha = 1{\cdot}0$ with the fact that $K_x = K_0$ when the salt concentration is about 3 mols. per litre, then from equation (10), $x_1 = 4x_m = 3{\cdot}0$, we obtain $b = a/\sqrt{x_1} = 0{\cdot}58$, and from equation (8) $\log R_m = a^2/4b = 0{\cdot}43$ or $R_m = 2{\cdot}70$. The observed mean value of R_m is 1·68 and it follows that the observed maximum increase in the ionisation constant is only 68/170 or 40% of what would be anticipated on the assumption that $a = 2\alpha = 1{\cdot}0$. On the other hand, if we combine this assumption with the observation that $R_m = 1{\cdot}68$, then from equation (8) we derive $b = 1{\cdot}11$, and this in accordance with equation (9) leads to $x_1 = 0{\cdot}8$, whereas the mean observed value of x_1 is 3·0 mols. per litre. Since the percentage errors involved in the determination of R_m and x_1 are quite small, there is obviously a very considerable discrepancy between the results of these experiments and the conclusions which follow from the application of the interionic attraction theory to the problem. The differences in question, which are illustrated in the diagram, suggest that the value of α which determines the magnitude of the mean activity coefficient $f_{\pm}$ of an acid in salt solutions is very much less than the value indicated by the Debye–Hückel theory.

A considerable amount of additional evidence might be cited in support of the view that the coefficient α is by no means independent of the nature of the ions concerned. The validity of the dilution law for the so-called transition acids, which is shown by the constancy of $K_0 = c_+c_-/c$ at moderate dilutions, suggests very forcibly that the magnitude of the interionic force effect in such solutions is very small compared with that in corresponding solutions of salts. In agreement with this, it has been found that the catalytic activity of acids of widely different ionising tendency varies with the concentration in a manner which can be satisfactorily interpreted in terms of a fixed value of the ionisation constant (K_0). This value, which is independently derived from the catalytic observations, is, moreover, identical with that afforded by measurements



Comparison of the R_x–x curves given by the experimental data with those derived from the application of the interionic attraction theory. Curve I corresponds with the experimental results given by $\log R_x = 0{\cdot}54\sqrt{x} - 0{\cdot}32x$; Curve II with the assumption that the maxima on the experimental and the theoretical curves coincide in respect of the salt concentration; Curve III with the assumption that the magnitudes of the observed and the theoretical maxima are identical.

of the electrical conductivity of the acids in dilute solution (compare Dawson, Hall, and Key, *loc. cit.*).

Attempts have recently been made to derive a value for α from the conductivity data for certain organic acids (Davies, *Phil. Mag.*, 1927, **4**, 244). The numbers obtained vary from 0·35 for *o*-chlorobenzoic acid to 0·44 for 3 : 5-dinitrobenzoic acid, the mean value for seven acids being 0·38. According to Nonhebel (*ibid.*, 1926, **2**, 1085), the most probable value for hydrochloric acid deduced from *E.M.F.* measurements is $\alpha = 0{\cdot}39$. The close agreement may be accidental, for there can be little doubt that the accurate determination of α for acids on the basis of such data is attended by considerable difficulties. In the light of all the evidence there is, however, much to be said in support of the view that the value of α for acids is much less than the normal Debye–Hückel value. From this it would follow that the ionic strength hypothesis as expressed by the equation $- \log f_{\pm} = 0{\cdot}5\sqrt{\mu}$ is not applicable when $f_{\pm}$ refers to an acid electrolyte. In this connexion it may be noted that the rigid application of the ionic strength hypothesis to acids has on occasion led to conclusions which are quite unacceptable. For example, Harned and Hawkins (*J. Amer. Chem. Soc.*, 1928, **50**, 85) have been led to express the opinion that the ionisation constant (K_a) of chloroacetic acid must be $4{\cdot}2 \times 10^{-3}$, which is nearly three times the usually accepted value furnished by conductivity data. There can be no doubt, however, that the conductivity value ($K_0 = 1{\cdot}5 \times 10^{-3}$) is substantially a correct measure of K_a. The conductivity value is, moreover, in close agreement with the entirely independent values afforded by catalytic data relating to the action of chloroacetic acid as catalyst in the acetone–iodine and ester hydrolysis reactions.

There are many other scattered data which are difficult to reconcile with the view that the activity coefficient of an electrolyte is uniquely determined by the ionic strength of the surrounding medium. Brönsted (*J. Amer. Chem. Soc.*, 1924, **46**, 558) has, for instance, called attention to differences of the order of 60% in the values which are afforded by 0·01 molar solutions of magnesium chloride and sodium sulphate respectively.

The observations cited above lend support to the conclusion which seems to follow from the experimental results described in this paper. These results show that the influence of salts on the ionisation of acids cannot be interpreted in terms of the interionic attraction theory unless it is assumed that the coefficient α, and therefore the mean ionic activity coefficient for acids, is much smaller than the value suggested by the Debye–Hückel theory.

Summary.

The influence of inert salts on the ionisation of a series of acids with widely different ionisation constants has been deduced from observations on the rate of hydrolysis of ethyl acetate in sodium chloride solutions.

It is shown that experiments with hydrochloric acid afford a measure of the catalytic activity of the hydrogen ion in the salt solutions and that the observations are not measurably influenced by the interaction of chlorine ions with hydrogen ions.

The method of determining the hydrogen-ion concentration is independent of any assumption which would distinguish between the concentrations and the activities of the entities which take part in the catalysed chemical change.

The influence of the inert salt on the ionisation of the various acids may be represented by the equation $\log R_x = \log K_x/K_0 = a\sqrt{x} - bx$, where K_x and K_0 represent the ionisation constants in an x-molar salt solution and in pure water respectively. The constants a and b are approximately independent of the nature of the acid. This relation is shown to be quantitatively incompatible with the expression for R_x which is derived by application of the Debye–Hückel theory.

In contradiction to the ionic strength hypothesis it would appear that the activity coefficient of an electrolyte varies with the nature of the electrolyte and of the ionic environment.

By reference to the data for the acetone–iodine reaction it is shown that the connexion between the catalytic coefficient k_m and the ionisation constant K is closely represented by the equation $k_m = 3{\cdot}0\ k_h K^{0{\cdot}64}$.

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