CLXII.—*Acid and Salt Effects in Catalysed Reactions. Part XIV. The Influence of Inert Salts on the Catalytic Catenary for Acetic Acid–Acetate Mixtures.*

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In the preceding paper experiments were described which show that the catalytic effects produced by acetic acid in the acetone–iodine reaction are appreciably modified by the addition of sodium chloride or other catalytically inert salts to the pure acid solution. Small quantities of inert salt increase the reaction velocity, but as the concentration is further augmented the velocity attains a maximum and then decreases. In explanation of these results, it has been suggested that there are two distinct effects which are involved in the action of the inert salt. The first is represented by an increase in the catalytic activity of the hydrogen ion, and the second by a change in the ionisation constant of the acid. The former increases continuously with the salt concentration, whilst the ionisation constant increases to a maximum value and then decreases.

The object of the present paper is to show that the inert-salt effects referred to above do not modify to any marked extent the character of the relations which are exhibited by the reaction velocities for the acid–salt mixtures which have been investigated in previous experiments. For mixtures of the type $c\mathrm{HA} + x\mathrm{MA}$, where HA is a weak acid, c is constant, and x is variable, it has been shown that the reaction velocity in aqueous solution is a function of the hydrogen-ion concentration such that the plot of v against $\log [\mathrm{H}^+]$ is represented by a catenary curve. The experiments now described show that the relations are unaltered when inert-salt solutions are substituted for water as the medium in which the catalysed reaction takes place.

The salt solutions used were 0·1, 0·5, 2·0, and 4·0*M*-solutions of sodium chloride, and the active catalytic mixtures were those represented by the formula $0{\cdot}1\mathrm{CH_3{\cdot}CO_2H} + x\mathrm{CH_3{\cdot}CO_2Na}$. In all the solvents the reaction velocity falls rapidly to a minimum and subsequently increases in a linear manner as the concentration of the acetate is continuously increased. So far as the empirical relations between v and x are concerned, there is no essential difference between the results obtained with water and those with the various sodium chloride solutions. In all cases, the catalytic properties of the group of acetic acid–acetate mixtures can be expressed in terms of an equation of the form *

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

and such differences as are found are, for the most part, to be attributed to changes produced by the inert salt in the magnitudes of the catalytic coefficients k_h, k_a, and k_m, and of the ionisation constant of the acetic acid. These changes modify to some extent the hydrogen-ion concentration and the minimum reaction velocity which characterise the isocatalytic point, but the general relations which find expression in the catalytic catenary are not affected.

The calculation of reaction velocities from equation (1) presumes a knowledge of the values of k_h, k_a, and k_m and of the ionisation constant K. It will be assumed that k_h for the various solvents is given by the reaction velocities obtained with hydrochloric acid as catalyst (compare Dawson and Key, *loc. cit.*). The values of k_a and k_m may be obtained by the method described by Dawson and Carter (J., 1926, 2282), according to which k_a is given by the slope of the v–x line, and k_m by extrapolation of this line to $x = 0$. In this procedure, an error in the determination of k_a will, however, affect the value obtained for k_m. For this reason, a method has been adopted for the evaluation of k_m in which k_a plays no essential part. This consists in determining the reaction velocities for varying concentrations of acetic acid in acetate-free solutions. If c denotes the concentration of the acid, equation (1) may be written

$$v = (k_h + k_a - k_m)[\mathrm{H}^+] + k_m c \quad . \quad . \quad . \quad (2)$$

and since $k_a - k_m$ can be neglected by comparison with k_h, and $[\mathrm{H}^+]$ is given approximately by $\sqrt{Kc}$ when c is not too small, this equation may be put in the form

$$v/\sqrt{c} = k_h\sqrt{K} + k_m\sqrt{c} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

According to equation (3), the plot of $v/\sqrt{c}$ against $\sqrt{c}$ should yield a straight line of slope k_m intersecting the ordinate ($c = 0$) at a point which affords a measure of $k_h\sqrt{K}$. In actual fact, the experimental data for 0·02, 0·1, and 0·5M-solutions of acetic acid

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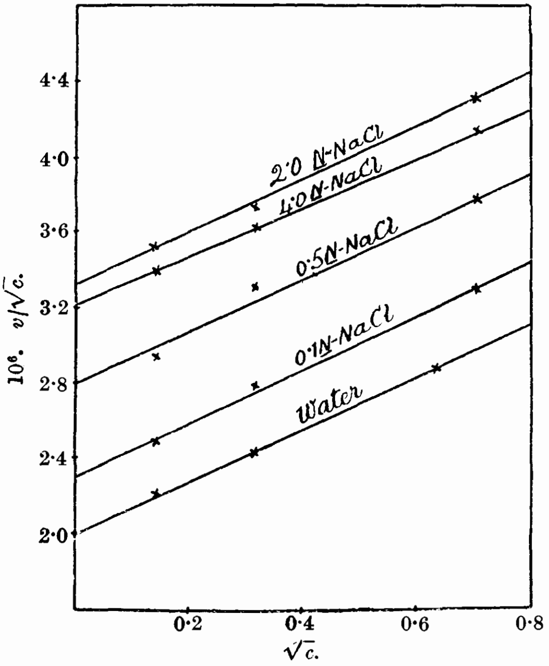
* It has been shown that the water molecule has a measurable activity (Dawson and Key, this vol., p. 543). The effect in question is very small and in this paper it is not specifically taken into account, but may be supposed to be included in the term which corresponds with the undissociated acetic acid.

are in close agreement with the requirements of equation (3), and as Fig. 1 shows, the lines for water and for the 0·1, 0·5 and 2·0*M*-sodium chloride solutions are very nearly parallel, with the common value $k_m = 1{\cdot}4 \times 10^{-6}$. The slope of the line for the 4·0*M*-chloride solutions is somewhat less and corresponds with $k_m = 1{\cdot}3 \times 10^{-6}$. These observations show clearly that the catalytic activity of the acetic acid molecule is scarcely affected by the inert salt, even when this is present in large quantity.

Fig. 1.

Graph of $v/\sqrt{c}$ against $\sqrt{c}$ for acetic acid as catalyst in water and sodium chloride solutions.



Since the linear portion of the v–x curves for the mixtures of the series $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$ can be expressed by the equation $v = 0{\cdot}1k_m + k_a x$, it is obvious that this may be used to determine the values of k_a. In the actual experiments with such mixtures, it was found expedient to limit the concentration of the acetate to values not greater than 0·4 mol. per litre. This limitation is necessitated by the circumstance that the iodoacetone which is formed in the first stage of the reaction begins to react at an appreciable rate with a further quantity of iodine, and thus tends to disturb the measurement of the velocity of the primary change.

The k_a values derived in this way are shown in col. 3 of Table I, and it is apparent that the influence of the inert salt on the magnitude of the coefficient which measures the catalytic activity of the acetic ion is also comparatively slight.

Col. 4 of Table I shows the values of $k_h\sqrt{K}$ which are given by the intercepts of the $v/\sqrt{c}$–$\sqrt{c}$ lines in Fig. 1 on the zero ordinate. If these are divided by the corresponding values of k_h (col. 5) given by the reaction-velocity data with hydrochloric acid as catalyst, we obtain $\sqrt{K}$. The squares of these are tabulated under K in col. 6, and these numbers represent the values of the ionisation constant of the acid in the various solutions.

TABLE I.

Catalytic Constants for Acetic Acid in Sodium Chloride Solutions.

Reaction Medium.	$k_m \cdot 10^6$.	$k_a \cdot 10^6$.	$k_h \cdot \sqrt{K} \cdot 10^6$.	$k_h \cdot 10^6$.	$K \cdot 10^5$.
Water	1·4	4·0	2·00	465	1·85
0·1N-NaCl	1·4	4·0	2·30	478	2·31
0·5N-NaCl	1·4	3·7	2·80	530	2·79
2·0N-NaCl	1·4	3·4	3·32	726	2·09
4·0N-NaCl	1·3	3·4	3·22	1110	0·84

It may be noted that the values of k_m are but slightly different from the value $1·5 \times 10^{-6}$ assigned to the acetic acid molecule in 1913 by Dawson and Powis (J., **103**, 2135). The k_a value for the pure aqueous solution is definitely smaller than that recorded by Dawson and Carter (*loc. cit.*), namely, $k_a = 4·5 \times 10^{-6}$, but the higher value is in all probability due to the less complete elimination of the disturbing effect of subsequent reactions in the case of the solutions which contain relatively large amounts of acetate.

The slight variation of the k_m and k_a values with the solvent is in marked contrast to the relatively large changes in k_h and K. The variations of K correspond closely with those shown by the figures recorded in Table II of the previous paper. The latter were derived by a somewhat different procedure, but both methods involve the assumption that the reaction-velocity data for hydrochloric acid in the several sodium chloride solutions afford a measure of the catalytic activity of the hydrogen ion. The possibility that k_h determined in this way includes some factor other than that represented by the influence of the inert salt on the catalytic activity of the ion has already been discussed. It might be suggested that this view receives some support from the relations which are disclosed by the foregoing table, but it does not seem possible to carry the matter further at the present time.

Table II affords a comparison of the reaction velocities observed with free acetic acid in the various solvents and those calculated from equation (2) by means of the constants recorded in Table I. The required hydrogen-ion concentrations are those derived from $[H^+] = \sqrt{K(c - [H^+])}$. It is apparent that the differences between the observed and calculated reaction velocities for the pure acetic acid solutions are not greater than would be accounted for by experimental error.

TABLE II.

Catalyst : Acetic Acid. Temp. : 25°.

	$c = 0·02$.		$c = 0·1$.		$c = 0·5$.	
Solvent.	$v \cdot 10^6$ (obs.).	$v \cdot 10^6$ (calc.).	$v \cdot 10^6$ (obs.).	$v \cdot 10^6$ (calc.).	$v \cdot 10^6$ (obs.).	$v \cdot 10^6$ (calc.).
Water	0·312	0·308	0·770	0·772	1·82	1·83
0·1*N*-NaCl ...	0·350	0·349	0·883	0·866	2·33	2·33
0·5*N*-NaCl ...	0·412	0·418	1·055	1·025	2·67	2·68
2·0*N*-NaCl ...	0·500	0·491	1·175	1·185	3·05	3·04
4·0*N*-NaCl ...	0·480	0·477	1·150	1·145	2·92	2·92

The observed and calculated velocities for the constant-acid series of mixtures are compared in the same way in Table III. The calculated velocities are derived from equation (1) in which $[H^+]$, $[A^-]$, and $[HA]$ are given by $[H^+] = K(c - [H^+])/(x + [H^+])$, $[A^-] = x + [H^+]$, and $[HA] = c - [H^+]$, respectively. The results show that the reaction velocities in water and in the sodium chloride solutions are closely reproduced by an equation which takes account of the catalytic effects produced respectively by the hydrogen ion, the acetic ion, and the undissociated acetic acid molecule. By slight modifications of the values assigned to k_a

TABLE III.

Catalyst : $0·1CH_3·CO_2H + xCH_3·CO_2Na$. Temp. : 25°.

$x =$	0	0·005	0·01	0·02	0·03	0·05	0·1	0·2	0·4
Solvent : water.									
$v \cdot 10^6$ (obs.)	0·770	0·333	0·276	0·276	0·297	0·365	0·570	0·930	1·71
$v \cdot 10^6$ (calc.)	0·772	0·321	0·265	0·263	0·289	0·357	0·548	0·944	1·74
Solvent : 0·1*N*-NaCl.									
$v \cdot 10^6$ (obs.)	0·883	0·385	0·304	0·282	0·301	0·363	0·549	0·938	1·74
$v \cdot 10^6$ (calc.)	0·866	0·359	0·289	0·274	0·297	0·362	0·551	0·946	1·74
Solvent : 0·5*N*-NaCl.									
$v \cdot 10^6$ (obs.)	1·055	0·434	0·320	0·290	0·311	0·368	0·547	0·910	1·63
$v \cdot 10^6$ (calc.)	1·025	0·428	0·321	0·287	0·300	0·355	0·525	0·888	1·625
Solvent : 2·0*N*-NaCl.									
$v \cdot 10^6$ (obs.)	1·175	0·415	0·311	0·277	0·290	0·340	0·512	0·845	1·52
$v \cdot 10^6$ (calc.)	1·185	0·438	0·323	0·283	0·292	0·340	0·495	0·828	1·505
Solvent : 4·0*N*-NaCl.									
$v \cdot 10^6$ (obs.)	1·150	—	0·261	0·237	0·253	0·296	0·472	0·785	1·50
$v \cdot 10^6$ (calc.)	1·145	—	0·256	0·244	0·263	0·319	0·479	0·814	1·47

and k_m in Table I, it might be possible to bring the calculated numbers into closer agreement with the observed velocity, but this does not seem necessary, for the main object of these experiments is to show that the presence of inert salts makes no difference to the general character of the results which are obtained for mixtures of a weak acid and the corresponding salt.

Since the v–log $[H^+]$ curve for such mixtures with constant acid concentration is a catenary, it follows that the plot of the reaction velocity against log x should also yield a catenary curve, for $[H^+]$ is inversely proportional to x provided that the acetate concentration is not too small. The v–log x curve has, for certain purposes, an obvious advantage over the v–p_H curve in that it involves the correlation of the directly measured quantities v and x. When the data recorded in Table III are plotted in this way, a series of catenary curves is obtained. The symmetry of these curves facilitates the determination of the minimum reaction velocity v_i and the acetate concentration x_i which correspond with the respective isocatalytic points. From x_i, the value of $[H^+]_i$ is given by $[H^+]_i = 0{\cdot}1K/x_i$, where K is the ionisation constant of the acetic acid in the solvent concerned.

The observed minimum velocities are shown in col. 2 of Table IV, whilst the calculated velocities derived from the equation

$$v_i = 2\sqrt{(k_h - k_m)k_aKc} + k_mc \quad . \quad . \quad . \quad . \quad (4)$$

are shown in col. 3. Col. 4 gives the values of the acetate concentration at the *M.V.* point, and col. 5 the corresponding values of $(p_H)_i$. The calculated values of $(p_H)_i$ in col. 6 are those which follow from the general equation

$$[H^+]_i = \sqrt{k_aKc/(k_h - k_m)} \text{ or } (p_H)_i = \tfrac{1}{2}\{\log(k_h - k_m) - \log k_aKc\} \quad (5)$$

For the derivation of these equations reference may be made to Part II (Dawson and Dean, J., 1926, 2872).

TABLE IV.

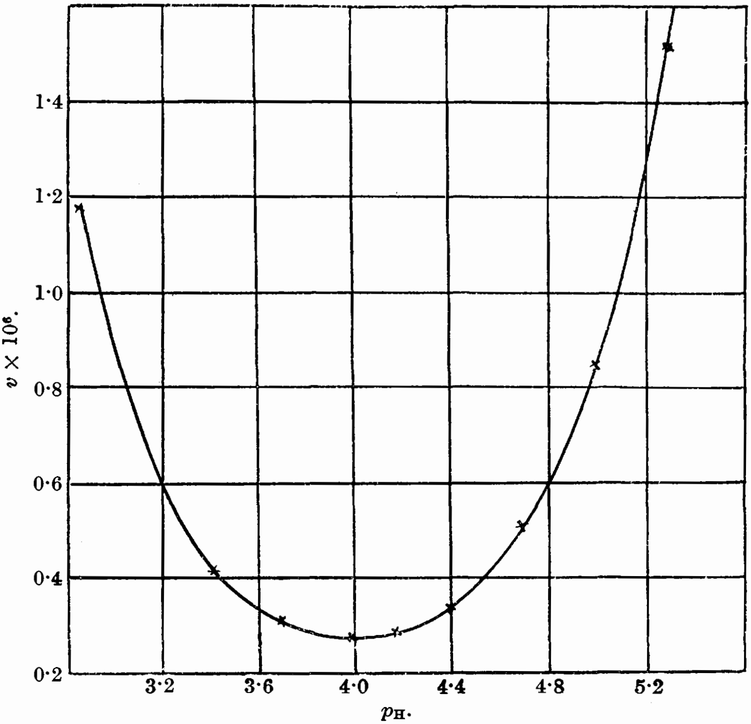
Isocatalytic data for $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$.

Solvent.	$v_i \cdot 10^6$ (obs.).	$v_i \cdot 10^6$ (calc.).	x_i.	$(p_H)_i$ (obs.).	$(p_H)_i$ (calc.).
Water	0·267	0·256	0·0165	3·95	3·90
0·1*N*-NaCl	0·278	0·277	0·0175	3·88	3·86
0·5*N*-NaCl	0·288	0·288	0·0190	3·83	3·85
2·0*N*-NaCl	0·280	0·283	0·0205	3·99	4·00
4·0*N*-NaCl	0·237	0·243	0·0190	4·35	4·30

In reference to the above table it may be noted that the quantity of sodium acetate which is required to reduce the catalytic activity to a minimum increases with the concentration of the inert salt, reaches a maximum and then diminishes. In general, the agreement between the observed and calculated isocatalytic data is sufficient to indicate the applicability of the theory to all the solvents investigated, but it may be noted that the greatest difference between the observed and calculated minimum velocities is shown by the data for water as solvent. It is probable that this is connected with the inert-salt action of the sodium acetate, for in the absence of sodium chloride this may be expected to produce a greater effect than in those solutions which already contain sodium chloride. It has indeed been shown that the inert-salt effect, as measured by $dv/d[\mathrm{NaCl}]$, diminishes with increase in the concentration of the inert salt and ultimately becomes negative (compare Dawson and Key, *loc. cit.*). The fact that the observed value of v_i for the pure aqueous solvent is greater than the calculated value, accords completely with this view in the sense that the addition of acetate to the salt-free solution should correspond with an increase in the ionisation constant of the acid. There is reason to believe,

FIG. 2.

Catalytic catenary (v–p_{H}) *for* $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$ *in a solution of* 2·0M-*sodium chloride.*



however, that the inert-salt effect produced by the sodium acetate will not be so large as that produced by an equivalent amount of sodium chloride.

In Fig. 2 the observed reaction velocities for $2N$-sodium chloride as solvent are plotted against the p_H values derived in the usual way from the value of K tabulated for this solvent in Table I, *viz.*, $K = 2{\cdot}09 \times 10^{-5}$. The symmetrical catenary distribution of the points is obvious. In this connexion, it is of interest to compare the p_H values of the pure acid solutions with the p_H values of the acetic–acetate mixtures which exhibit the same catalytic activity as the acetate-free solutions. The concentration of the acetate (x_e) for such mixtures can be read off directly from the v–x curves. The corresponding hydrogen-ion concentration is given by $[H^+]_e = 0{\cdot}1K/x_e$. If $[H^+]_0$, derived from $[H_0^+] = \sqrt{0{\cdot}1K}$, represents the hydrogen-ion concentration of the acetate-free solution, we have, as previously shown,

$$[H^+]_0 \cdot [H^+]_e = [H^+]_i^2$$

or

$$(p_H)_i = \tfrac{1}{2}\{(p_H)_0 + (p_H)_e\}$$

In Table V, col. 2 gives the values of x_e, cols. 3 and 4 the values of $(p_H)_0$ and $(p_H)_e$, col. 5 the arithmetic mean of these, and col. 6 the value of $(p_H)_i$ derived by calculation from equation (5).

TABLE V.

Symmetry of the Catalytic Catenaries.

Solvent.	x_e.	$(p_H)_0$.	$(p_H)_e$.	$\frac{(p_H)_0+(p_H)_e}{2}$.	$(p_H)_i$.
Water	0·16	2·86	4·94	3·90	3·90
0·1N-NaCl	0·184	2·82	4·90	3·86	3·86
0·5N-NaCl	0·24	2·78	4·93	3·86	3·85
2·0N-NaCl	0·292	2·84	5·15	4·00	4·00
4·0N-NaCl	0·310	3·04	5·57	4·30	4·30

The almost complete identity of the figures in the last two columns may be to some extent fortuitous, but when due allowance is made for this, the results must be regarded as affording strong evidence for the view that the presence of sodium chloride does not affect the nature of the relations which find expression in the symmetrical catenary curves. The main object with which this series of experiments was planned has thus been attained. This was to show that the catalytic phenomena described and co-ordinated in earlier papers of this series are not effects which can be explained in terms of those environmental factors which are associated with the concept of "activity" in its application to solutions of electrolytes. It is true that inert-salt effects may in certain circumstances play an important part in modifying the velocities of acid-catalysed reactions.

This is the case, for instance, when inert salts are added to a salt-free solution of a weak electrolyte, and the conditions are such that any change in the degree of ionisation of the catalysing acid is reflected in a corresponding change in the reaction velocity. On the other hand, it is equally clear that when these particular conditions do not obtain, the importance of such inert-salt effects may be relatively small and entirely insufficient to affect the general nature of the results which are conveniently expressed in terms of the catalytic catenary. It may indeed be anticipated that the generalised catalytic equation $r = \cosh \log_e n$, which expresses the connexion between the reduced ionic velocity r and the reduced hydrogen-ion concentration n, will be applicable with greater precision to salt-containing solutions than it is to solutions which are free from catalytically inert salts.

In conclusion, attention may be directed to the circumstance that equation (3) may be derived from a comparison of the equations for the velocity (v_0) of the salt-free acid solution and for the velocity (v_e) of the catalytically conjugate acid–salt mixture $c\text{HA} + x_e\text{MA}$. We have

$$v_0 = k_h[\text{H}^+]_0 + k_m c = k_h\sqrt{Kc} + k_m c$$

$$v_e = k_a x_e + k_m c$$

and since $v_0 = v_e$, we obtain

$$k_h\sqrt{Kc} = k_a x_e = v_e - k_m c = v_0 - k_m c$$

or

$$k_h\sqrt{K} = v_0/\sqrt{c} - k_m\sqrt{c}$$

which is the same as the relation previously derived from a consideration of the catalytic effects produced by the pure acid at different concentrations. From $k_h\sqrt{Kc} = k_a x_e$, we derive $K = (k_a x_e/k_h)^2/c$. If the tabulated values of k_a, k_h, and x_e are substituted in this equation, we obtain $K = 1{\cdot}89$, $2{\cdot}36$, $2{\cdot}93$, $1{\cdot}87$, and $0{\cdot}90$ for the series of five solvents examined. These differ somewhat from the K values recorded in Table I, but show the same general relations.

Summary.

The influence of catalytically inert salts on the velocity of the acetone–iodine reaction has been examined when the reaction is catalysed by a weak acid in the presence and in the absence of the corresponding salt.

The relations in sodium chloride solutions (0·1 to 4·0 molar) are closely similar to those which are exhibited by pure aqueous solutions.

The coefficients which measure the catalytic activity of the acetic acid molecule and of the acetate ion are but slightly affected by the presence of sodium chloride. On the other hand, it would seem that

the catalytic activity of the hydrogen ion and the degree of ionisation of acetic acid vary considerably with the salt concentration.

The v–p_H curves approximate in all cases to a true catenary. The isocatalytic data vary with the salt concentration, but the variations are small.

The results show that the catalytic phenomena described and co-ordinated in previous papers are not affected to any great extent by the changes in ionic environment which are associated with the replacement of water as the solvent by solutions of catalytically inert salts.

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