[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Acid-catalyzed Hydrolysis of Methylal. II. Kinetic and Equilibrium Salt Effects and Correlation with H_0

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Studies have been made on the influence of electrolytes on the activity coefficient of methylal in aqueous solutions and on the kinetic salt effects for the hydrolysis of methylal in aqueous solutions containing 0.371 *M* hydrochloric acid as catalyst. The influence of salts on the activity coefficient of the neutral indicator, *p*-nitroaniline, has been determined and some extensions have been made of Paul's data for salt effects on the Hammett acidity function. All of the salts studied increase the rate of hydrolysis of methylal. The hydrolysis rates in the salt solutions do not correlate at all well with H_0 for the salt solutions even though with strong acids a good correlation of rate and H_0 had previously been obtained. Neither do the salt effects correlate well with f_M, the activity coefficient of methylal. However, a fairly good correlation is obtained if one assumes that the rate is given by $\log k_h/k_{h_0} = -\Delta H_0 + \log f_M/f_B$ where f_M and f_B are activity coefficients of methylal and *p*-nitroaniline, respectively. This can be interpreted as meaning that the rate does indeed depend on H_0 but that a correction must be made for the different effects of salts on methylal and on the neutral base used to determine H_0. This same procedure also removes the slight discrepancy noted earlier in the correlation of rate and H_0 for solutions of strong acids.

In the previous paper[1] it was shown that the rate of the acid-catalyzed hydrolysis of methylal in concentrated solutions of strong acids follows the Hammett H_0 acidity function fairly closely. This result was interpreted as support for the "unimolecular" mechanism which has been proposed for the hydrolysis of acetals.[2,3] However, it was also noted that the parallelism between rate and H_0 was not exact in that a plot of $\log k_h$ *vs.* $-H_0$ showed a slope of 1.15 rather than unity. This small discrepancy was tentatively ascribed to "salt effects," *i.e.*, to a difference in the effect of the strong acids on f_M and on f_B where these are the activity coefficients of methylal and of a neutral base indicator used for the determination of H_0.

In the present paper we give the results of a study of kinetic salt effects on the rate of hydrolysis of methylal and also a study of equilibrium salt effects on the activity coefficients of methylal in aqueous solutions. One of the objects of this work was to determine whether the H_0 function could be correlated with kinetic salt effects in the same way that it can be with effects of concentrated solutions of acids. If feasible, this would make salt effect studies useful for determination of reaction mechanisms and hence greatly broaden the applicability of the H_0 function.

Experimental

The kinetic salt effects on the hydrolysis of methylal were mostly made by dilatometric techniques using the equipment and procedures described in the previous paper.[1] As before the rates were checked in a few cases by the somewhat less accurate titration of the formaldehyde which is produced by the hydrolysis. All measurements were at 25°.

The activity coefficients of methylal in aqueous solutions of electrolytes were determined by the partition of methylal between the aqueous solutions and benzene. For studies with salt solutions the two phase mixtures of benzene, salt solution and methylal were equilibrated for 24 hours in a 25° water-bath with occasional stirring. With hydrochloric acid solutions, equilibrium was obtained by continuous and vigorous stirring for ten minutes. After equilibration the phases were separated and aliquots of each phase were removed. The methylal in the aliquots was then hydrolyzed with 3 *M* hydrochloric acid and the formaldehyde produced was determined by the bisulfite method. Primarily because of the volatility of methylal, the accuracy of this analysis was probably not over 2 or 3%, although the precision of the method is considerably better than this. In all of the distribution experiments the concentration of methylal in the aqueous phase was kept below 0.07 *M*. This minimized the contribution from a "self interaction" term of the sort discussed by Long and McDevit.[4]

Most of the necessary data on the influence of salts on H_0 was available from the recent studies by Paul[5] but additional measurements on the influence of salts on the H_0 value for 0.1 *M* hydrochloric acid were made with two salts, sodium perchlorate and sodium *p*-toluenesulfonate. As in Paul's studies, the neutral base indicator was *p*-nitroaniline and ratios of the concentrations of neutral and acid forms of the indicator were measured with a Beckman DU spectrophotometer. Finally the influence of several salts on the activity coefficient of *p*-nitroaniline was determined by measuring the solubility of the neutral molecule in water and in salt solutions. Analysis was again made with a spectrophotometer.

The methylal used in these studies was from the same sample described in paper I.[1] The quaternary ammonium salts and sodium *p*-toluenesulfonate were Eastman Kodak Co. chemicals and were recrystallized from absolute alcohol and water, respectively. All other salts were reagent grade and were used without further purification.

A. Activity Coefficients of Methylal in Electrolyte Solutions.—The distribution ratio, $K_0 = C_i^b/C_i^\circ$ where C_i^b and C_i° are molar concentrations of methylal in benzene and in pure water, is needed for the calculation of the activity coefficients and was measured by the method discussed in the previous section. Over the concentration range $C_i^\circ = 0.028$ to 0.135 *M* the value of K_0 is linear in C_i^b and follows the equation $K_0 = 3.85 - 1.6\, C_i^b$.

For seven salts and for hydrochloric acid the distribution of methylal between benzene and the aqueous solutions was measured for several concentrations of electrolyte ranging from 0.3 to 3 *M*. From these data the activity coefficients of the methylal were calculated using the usual procedure.[4] The resulting activity coefficients are for molar concentration, *i.e.*, $a = f_M C_M$ where C_M is molar concentration of methylal. In agreement with the expected equation

$$\log f_M = k_M C_s \qquad (1)$$

where C_s is concentration of electrolyte and k_M is the "salting out" parameter, plots of $\log f_M$ *vs.* C_s were linear in all cases. Figure 1 gives the plots for the eight electrolytes studied. Experimental

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[1] Donald McIntyre and F. A. Long, THIS JOURNAL, **76**, 3240 (1954).

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 334.

[3] J. M. O'Gorman and H. J. Lucas, THIS JOURNAL, **72**, 5489 (1950).

[4] F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

[5] M. Paul, THIS JOURNAL, **76**, 3236 (1954).

points are listed for four of the salts. Values of the salting out parameters are listed in Table I.

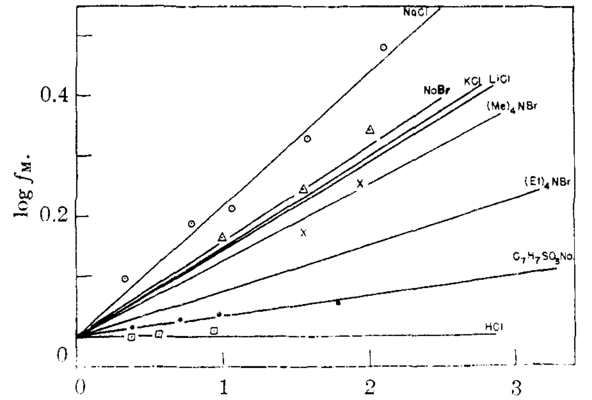

Fig. 1.—Salt effects on the activity coefficient of methylal in aqueous solutions, 25°.

The plot of Fig. 1 shows a pronounced dependence of f_M on the particular electrolyte used. This specificity of the electrolytes is quite normal,[4] but the particular order of the salts is somewhat surprising. The most unexpected result is the "salting out" shown by the salts of large ions, tetramethyl- and tetraethylammonium bromide and sodium p-toluenesulfonate, since these electrolytes salt in most non-electrolytes, both polar and non-polar. However, a somewhat unusual salt order seems to be characteristic of acetals as is seen in Table I which compares the results for methylal with some of the data of Olson and Tong[6] for other acetals. Clearly the general behavior of the several acetals is much the same. As would be expected there is a tendency toward an increase in the values of the salting out parameters with an increase in the size of the acetals.

Table I

Values of Salting Out Paramrters, k_s, for Acetals

Salt	Methylal, 25°	Dimethyl acetal, 25°	Acetal 25°	Acetal 0°	Dipropyl formal, 25°
NaCl	0.225	0.191	0.260	0.302	0.282
NaBr	0.158	...	...	...	...
NaNO$_3$	...	...	...	0.233	...
NaClO$_4$	...	...	...	.225	...
KCl	0.150	...	...	.300	0.279
LiCl	0.145	...	...	.194	...
KBr	...	...	...	...	0.264
KI	...	...	...	...	.121
HCl	0.00	...	...	...	.060
(Me)$_4$NBr	.127	...	...	...	...
(Et)$_4$NBr	.075	...	...	...	...
Na p-C$_7$H$_7$SO$_3$	.034	...	...	...	...

B. Influence of Salts on H_0 and on the Activity Coefficient of p-Nitroaniline.—Paul[5] has measured the influence of several salts on the Hammett acidity, H_0, of 0.1 M hydrochloric acid using p-nitroaniline as the neutral indicator base. The results are given in Fig. 2 which also includes data for the effects of two additional salts, which have been studied in this investigation. In Fig. 2 $-\Delta H_0$ is the *increase* in acidity caused by the salt and is defined by

$$\Delta H_0 = (H_0)_{0.1\,M\ \mathrm{HCl}\,+\,\mathrm{salt}} - (H_0)_{0.1\,M\ \mathrm{HCl}} \qquad (2)$$

For all of the salts of Fig. 2 plots of $-\Delta H_0$ *vs.* C_s are quite linear and the second column of Table II gives the values of α, the slope of the straight line defined by

$$-\Delta H_0 = \alpha C_s \qquad (3)$$

A combination of eq. 2 and 3 and the value of $H_0 = 0.99$ for 0.1 M hydrochloric acid permits easy calculation of H_0 for any of the salt–acid mixtures.

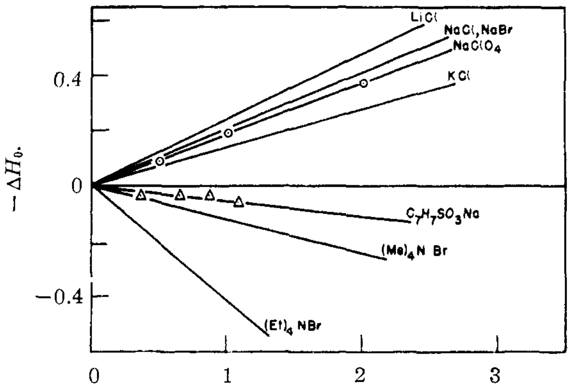

Fig. 2.—Influence of salts on H_0 of 0.1 M hydrochloric acid, 25°. Indicator is p-nitroaniline.

The most striking thing about Fig. 2 is the pronounced specificity in the salt effects on H_0. Although the more ordinary salts increase the "indicator acidity," the three salts with large ions actually decrease the acidity of the solutions. The general character of Fig. 2 is in fact quite similar to a typical plot of log f_i *vs.* C_s for the effect of salts on the activity coefficient of a neutral molecule. From the basic definition of the Hammett acidity function, ΔH_0 can be written as

$$-\Delta H_0 = \log\,(f_{\mathrm{H}^+}f_{\mathrm{B}}/f_{\mathrm{BH}^+})$$

where the reference state for the activity coefficients is 0.1 M hydrochloric acid. This raises the question of how much of the effects of Fig. 2 are due to the salt effects on f_B, the activity coefficient of the base used, which for these experiments is p-nitroaniline.

Data on the activity coefficient of p-nitroaniline in salt solutions are available from the studies of Kruyt and Robinson[7] but only for 0.2 M salt solutions and for only three of the salts of Fig. 2. Consequently we have extended these data by measuring the solubility of p-nitroaniline in water and in 0.5 and 1 M solutions of the following salts: lithium chloride, sodium chloride, potassium chloride, sodium bromide, sodium perchlorate, sodium p-toluenesulfonate, tetramethylammonium bromide and tetraethylammonium bromide.[8] Activity coefficients and values of the salting out parameter, k_B, were calculated from the equations

$$\log f_B = \log\,(S_B{}^\circ/S_B) = k_B C_s$$

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[6] A. R. Olson and L. K. J. Tong, This Journal, **66**, 1555 (1944).

[7] H. R. Kruyt and C. Robinson, *Proc. Acad. Sci., Amsterdam*, **29**, 1244 (1926).

[8] We acknowledge with thanks the assistance of R. L. Bergen in these measurements.

where S_B^0 and S_B are solubilities of *p*-nitroaniline in water and in a salt solution of concentration C_s. The resulting data are given in Fig. 3. The plots of $\log f_B$ *vs.* salt concentration are all satisfactorily linear and lead to the values of k_B listed on the right of Fig. 3. The agreement between the present results and those of Kruyt and Robinson for lithium, sodium and potassium chloride is fairly good. The salt order of Fig. 3, ranging from salting out by lithium chloride to pronounced salting in by tetraethylammonium bromide and sodium *p*-toluenesulfonate, is the expected one for a nitro aromatic[4] and is in fact quite similar to that of nitrobenzene.[9] Table II which lists the values of k_B contains estimated values for the acids, hydrochloric and perchloric. These estimates are based on comparisons of the data for *p*-nitroaniline with salt effect data for nitrobenzene,[9] benzene[9,10] and aniline[11] using the known regularities of salt orders[4]; they are probably correct to ±0.03 unit.

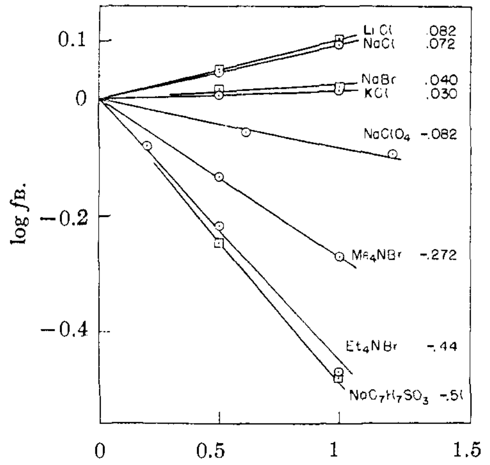

Fig. 3.—Salt effects on the activity coefficient of *p*-nitroaniline, 25°.

The last two columns of Table II compare values of k_B with the slope, α, of $-\Delta H_0$ *vs.* C_s and show that a large fraction of the effects of salts on H_0 is indeed due to effects on the term f_B. The general order of the values of α and k_B are similar and those salts which markedly salt in the indicator lead to negative values of α. In all cases the k_B value for a given salt is smaller than the value of α, very roughly by 0.15 unit. This difference must be attributed to the term f_{H^+}/f_{BH^+} and the comparative constancy of this term indicates that, in contrast to ΔH_0 and k_B, its value is not very dependent on the particular salt involved.

A point which is of consequence for subsequent discussions is that Paul has found essentially the same effects of salts on H_0 for 0.01, 0.1 and 1.0 *M* hydrochloric acid. This means that the results of Fig. 2 will apply to any solution of hydrochloric acid in the range 0.01 to 1 *M*. In contrast to this, for a given acid concentration the apparent effect of a salt on H_0 is distinctly dependent on the particular indicator used since Paul has found roughly 20% higher values of the slope, α, using diphenylamine rather than *p*-nitroaniline. This dependence on indicator used is consistent with the conclusion that f_B makes an important contribution since the values of f_B will be expected to be different for different neutral molecules. In fact, Paul has shown that a large part of the differences in ΔH_0 observed for the two indicators is due to changes in f_B which suggests that the ratio f_{H^+}/f_{BH^+} is not very dependent on the choice of indicator.

C. Kinetic Salt Effects for Methylal Hydrolysis.—The acid-catalyzed hydrolysis of methylal follows the equation

$$\mathrm{CH_2(OCH_3)_2 + H_2O \xrightarrow{H^+} HCHO + 2CH_3OH}$$

and the reaction is pseudo first-order at a given concentration of catalyst acid. The influence of salts on the hydrolysis rates was studied at 25° for eight salts at concentrations ranging from 0.2 to 3 *M*. For all experiments the catalyst acid and concentration was the same, 0.371 *M* hydrochloric acid. For a salt-free solution of acid at this concentration the first-order rate constant was $k_{h0} = 0.749 \times 10^{-3}$ min.$^{-1}$. Figure 4 gives the observed salt effects as plots of $\log k_h/k_{h0}$ *vs.* C_s where k_h is the first-order rate constant for the salt–acid mixtures.

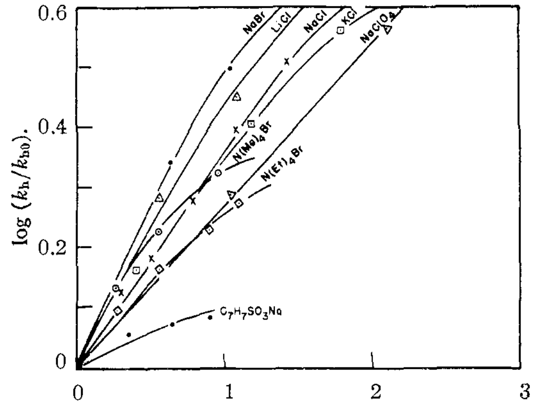

Fig. 4.—Kinetic salt effects for the acid-catalyzed hydrolysis of methylal, 25°.

From Fig. 4 it is evident that all of the salts studied lead to an increase in hydrolysis rate and that the salt effects are quite large for most of the salts. Qualitatively these results are quite similar to those of Riesch and Kilpatrick[12] for the acid-catalyzed hydrolysis of acetal. In contrast to the salt effects on H_0 and on $\log f_M$ and $\log f_B$, the plots of $\log k_h$ *vs.* C_s show departures from linearity at the higher salt concentrations. However, the plots are approximately linear up to salt concentrations of one molar and over this limited concentration range one can assume a constant slope, b, without too much error. The values of b are given in Table II, which also gives values of the slopes of $-\Delta H_0$, $\log f_B$ and $\log f_M$ *vs.* C_s.

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(9) J. H. Saylor, A. I. Whitten, I. Claiborne and P. M. Gross, THIS JOURNAL, **74**, 1778 (1952).

(10) W. F. McDevit and F. A. Long, *ibid.*, **74**, 1773 (1952).

(11) S. Glasstone, J. Bridgman and W. R. P. Hodgson, *J. Chem. Soc.*, 635 (1927).

(12) L. Riesch and M. Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935).

TABLE II

COMPARISON OF SALT EFFECTS

Salt	Slope b, log k_h *vs.* C_s	Slope k_M, log f_M *vs.* C_s	Slope α, $-\Delta H_0$ *vs.* C_s	Slope k_B, log f_B *vs.* C_s
NaBr	0.49	0.158	0.205	0.040
LiCl	.42	.145	.245	.082
NaCl	.36	.225	.205	.072
KCl	.33	.150	.145	.030
Me_4NBr	.33	.127	− .12	− .272
Et_4NBr	.26	.075	− .41	− .44
$C_7H_7SO_3Na$	.11	.034	− .06	− .51
$NaClO_4$	.29	...	.180	− .082
HCl	..	.00	.....	− .10 est.
$HClO_4$	..	...	.....	− .18 est.

From the mechanism of the paper I, the Brönsted salt effect equation for the rate of the reaction at a constant concentration of catalyst acid is

$$k_h = k_{h_0}(f_{H^+}f_M/f^*_{M^+}) \qquad (5)$$

where k_{h_0} is the rate constant in a salt-free solution and f_M and $f^*_{M^+}$ are activity coefficients for methylal and activated complex, respectively. The arguments of paper I led to the prediction that log k_h would closely parallel H_0 and this was found to be true for the three strong acids studied. However, it is evident from Table II that a similar parallelism is not found for the salt effects on the rate. The agreement between b and α is poor for all salts and for the salts of large ions which actually decrease H_0, there is a marked *increase* in rate.

An alternate approach for the salt effects is to assume in eq. 5 that $f_{H^+} = f^*_{M^+}$ and thus attribute all of the salt effects to f_M. However, for the methylal hydrolysis this is also a poor approximation as a comparison of the slopes b and k_M of Table II shows.

A final suggestion which was tentatively made in paper I and which is developed in the next section, is to assume that the reaction rate does indeed parallel H_0 but that explicit account must be taken of the differences in the salt effects on methylal and on the indicator, *p*-nitroaniline.

D. Salt Effects and H_0.—The condition for a linear relation between log k_h and H_0 is apparent if eq. 5 is written in logarithmic form and ΔH_0 is added to each side of the equation. The result is

$$\log \frac{k_h}{k_{h_0}} = -\Delta H_0 + \log\left(\frac{f_M f_{BH^+}}{f^*_{M^+} f_B}\right) \qquad (6)$$

showing that for a plot of log k_h *vs.* $-\Delta H_0$ to be linear with unit slope, the activity coefficient ratio $f_M f_{BH^+}/f^*_{M^+} f_B$ must be unity. However, from the data of earlier sections we know that f_M and f_B for the particular cases of methylal and *p*-nitroaniline are markedly different for a given solution of electrolyte. In contrast, the previously mentioned lack of dependence of f_{H^+}/f_{BH^+} on the nature of B suggests that $f_{BH^+}/f^*_{M^+}$ may in fact be close to unity. We are thus led, as a first approximation, to rewrite eq. 6 as

$$\log \frac{k_h}{k_{h_0}} = -\Delta H_0 + \log \frac{f_M}{f_B} \qquad (7)$$

and to suggest that in general the effects of electrolytes on log k_h and on H_0 will be different due to variations in the ratio f_M/f_B. Finally, since both f_M and f_B can be expressed by equations of the type of eq. 1, the above equation can be written

$$\log k_h/k_{h_0} = -\Delta H_0 + (k_M - k_B)C_s \qquad (8)$$

where C_s is electrolyte concentration and k_M and k_B are the salting out parameters for methylal and *p*-nitroaniline, respectively.

It should be noted that for the kinetic salt effect studies the reference state is not the infinitely dilute solution but 0.371 *M* hydrochloric acid. Hence to apply eq. 8 we should really have k_M and k_B for the effect of salts on the non-electrolytes present in this reference solution. However, in view of the known additive properties of salt effects[1] it should certainly be satisfactory to use the k_M and k_B values of Table II.

Table III gives a comparison of calculated values of log k_h/k_{h_0} from eq. 8 with the experimental values of Fig. 4 for 1 *M* salt solutions. In general, the calculated k_h/k_{h_0} values agree quite well with the experimental. In all cases but one the effect of the f_M/f_B term is to improve the agreement of rate and ΔH_0. The only major discrepancy is for sodium *p*-toluenesulfonate. In this case the salt effects on the rate are markedly concentration dependent and this makes the calculations rather uncertain. The differences which exist between calculated and observed k_h/k_{h_0} values for the other salts may simply be due to an accumulation of errors in the various terms or may indicate that the term $f_{BH^+}/f^*_{M^+}$ which was neglected in the calculation does actually make a small contribution.[13] However, the generally good agreement of Table III supports the basic assumption of eq. 8, that the rate of the methylal hydrolysis varies with H_0 in salt solutions as well as in acid solutions but that explicit corrections must be made for the differences between the reacting molecule and the indicator used for H_0.

TABLE III

CALCULATED AND EXPERIMENTAL VALUES OF LOG k_h/k_{h_0} FOR 1 *M* SALT SOLUTIONS

Salt	$(k_M - k_B)C_s$	$-\Delta H_0$	log k_h/k_{h_0} Calcd.	Obsd.
NaBr	0.12	0.205	0.33	0.49
LiCl	.06	.245	.31	.42
NaCl	.15	.205	.36	.36
KCl	.12	.145	.27	.33
Me_4NBr	.40	− .12	.28	.33
Et_4NBr	.52	− .41	.11	.26
$C_7H_7SO_3Na$	.54	− .06	.48	.11
$NaClO_4$	(.22)[a]	+ .18	(.40)[a]	.29

[a] Calculated using estimated value of $k_M = 0.14$.

Calculations similar to those of Table III can be made from available data for two other acetals, diethyl acetal and dipropyl formal. The kinetic salt effects for diethyl acetal were measured at 0° by Riesch and Kilpatrick.[12] Calculated kinetic salt effects for the salts sodium perchlorate, sodium *p*-toluenesulfonate, lithium chloride, sodium chloride and potassium chloride can be obtained using eq. 8 by combining the 0° salting out data of Olson and Tong[6] and the k_B and ΔH_0 values of Table II

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(13) Another possibility, which is suggested by the results for sodium *p*-toluenesulfonate and which needs further investigation, is that the term $f_{BH^+}/f^*_{M^+}$ may be relatively independent of the nature of the *cation* of the added salt but much more dependent on the character of the *anion*.

(which are for 25°). Considering the uncertainties of the calculation the agreement between observed and calculated kinetic salt effects is quite satisfactory. A similar comparison can be made in the case of dipropyl formal for the two salts, sodium and potassium chloride, utilizing the 25° kinetic and salting out data of Olson and Tong.[6] The agreement for these cases is also good. It thus appears that the conclusions reached for methylal have general validity.

In the previous paper[1] it was shown that with the strong acids, hydrochloric and perchloric, plots of log k_h *vs.* $-H_0$ gave slopes of 1.25 and 1.08, respectively, and it was tentatively concluded that these departures from a slope of unity might be due to salt effects. If for these cases one proceeds as in eq. 6 to 8 for the kinetic salt effects and assumes that the discrepancies are due to the term f_B/f_M, one arrives at the equation

$$\log k = -H_0 + (k_M - k_B)C_A + \text{const.} \qquad (9)$$

where C_A is molar concentration of acid and k_M and k_B are again the salting out parameters. For hydrochloric acid k_M has the value 0.00 (Table I) and k_B is estimated in Table II as −0.10. Equation (9) then becomes

$$\log k_h = -H_0 + 0.10C_A + \text{const.}$$

A plot of log k_h *vs.* $(-H_0 + 0.10C_A)$ for the hydrochloric acid data of Table I of the previous paper results in a straight line of slope 1.04 showing that explicit recognition of salt effects improves the strong acid data just as it does the data for salts.

From these salt and acid results for methylal we conclude that quite generally when a correlation is sought between rate data and H_0 a correction should be made for differences in the effects of electrolytes on the activity coefficients of the reacting neutral molecule and the indicator used for H_0. One then can ask why in several cases involving strong acids have correlations which ignore the correction been quite satisfactory? A partial answer is that in some cases the reacting molecule and the indicator may fortuitously be such that the term f_M/f_B remains at unity. However, a more important point is that normally the salt effects of the strong acids hydrochloric, sulfuric and perchloric are quite small,[4] varying for a wide series of neutral molecules from only slight salting in to slight salting out. Because of this, the correction term f_M/f_B tends to be relatively unimportant for these acids.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Conductances of Some Salts and Ion-Pair Equilibria in Acetic Acid at 30°[1,2]

BY MARK M. JONES[3] AND ERNEST GRISWOLD

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The conductances in acetic acid at 30° of the bromides, acetates and formates of potassium, sodium and lithium in concentrations ranging roughly from 10^{-5} to 10^{-3} *M* have been determined. Values of the limiting equivalent conductance and of the ion-pair dissociation constant have been obtained. Values of the latter are of the order of 10^{-7}. It is shown that these results may be used to give an independent test of a hypothesis previously advanced to account for salt effects on the solubility of potassium bromide in this solvent. Constants calculated from the conductance data for the postulated ion-pair exchange reactions KBr + MX ⇄ MBr + KX agree reasonably well with those previously obtained from solubility data.

In a recently reported investigation[4] of neutral salt effects on the solubility of potassium bromide in anhydrous acetic acid at 30°, it was pointed out that the experimental results could be interpreted quantitatively by assuming (1) that potassium bromide and the other salts involved exist largely undissociated in this solvent, presumably as ion-pairs of the type proposed by Bjerrum,[5] and (2) that these undissociated salts enter into metathetical reactions of the type

$$\mathrm{KBr} + \mathrm{MX} \rightleftharpoons \mathrm{MBr} + \mathrm{KX} \qquad (a)$$

which proceed until equilibrium is attained. By introducing the additional assumption that the concentrations of free ions are negligible in comparison with those of the undissociated species, and that the activity coefficients of the latter are equal and remain constant throughout, the following equilibrium equations may be written

$$\frac{[\mathrm{MBr}][\mathrm{KX}]}{[\mathrm{MX}]} = \frac{(\Delta S)^2}{C - \Delta S} = K \qquad (1)$$

Here the brackets denote molal concentrations, C the initial molal concentration of added salt MX, and ΔS the increase in molal solubility of potassium bromide resulting from presence of added salt. In the solubility studies mentioned above it was indeed found that equation 1 was obeyed over a rather wide range in concentration of each of a number of heteroionic added salts.

An independent test of equation 1 is possible, based upon the following considerations. From the work of Fuoss and Kraus[6] with solvents of moderately low dielectric constant it seems probable that in acetic acid the dissociation of salts such as KBr and MX, although slight may nevertheless be described by equilibrium equations such as

$$\frac{(\mathrm{K}^+)(\mathrm{Br}^-)}{(\mathrm{KBr})}\,\frac{y_{\mathrm{K}^+}y_{\mathrm{Br}^-}}{y_{\mathrm{KBr}}} = K_{\mathrm{KBr}} \text{ and}$$

$$\frac{(\mathrm{M}^+)(\mathrm{X}^-)}{(\mathrm{MX})}\,\frac{y_{\mathrm{M}^+}y_{\mathrm{X}^-}}{y_{\mathrm{MX}}} = K_{\mathrm{MX}} \qquad (2)$$

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(1) From a thesis presented to the Graduate School of the University of Kansas by Mark M. Jones in partial fulfillment of the requirements for the Ph.D. degree, 1952.

(2) Presented at the 123rd meeting of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

(3) Du Pont Fellow, 1951–1952.

(4) E. Griswold, M. M. Jones and R. K. Birdwhistell, THIS JOURNAL, **75**, 5701 (1953).

(5) N. Bjerrum, *Det Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **7**, No. 9, 1 (1926).

(6) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476, 1019 (1933).