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The Finkelstein Reaction in Acetonitrile-Alcohol Mixtures. An Approach to an Anion Solvation by Means of a Multi-step Solvation Model*

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The rate constants were determined for both processes of the Finkelstein reaction in acetonitrile–alcohol mixtures at 30 °C:

$$CH_3Br + I^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_3I + Br^-$$

Theoretical equations were derived describing the dependence of the rate constant on the composition changes in the solvent mixtures. These equations describe the change in the rate constant in terms of changes in the activity coefficient. The results were analyzed by means of the equations; they lead to the conclusion that anions have multiple solvation equilibria with alcohols. The relative magnitudes of the step-by-step association constants and of the solvation numbers thus determined agreed with the results determined spectrophotometrically.

In various fields of solution chemistry, quantitative discussions of solvation phenomena are often based on the concept of multi-step solvation processes. The present authors developed a theoretical expression in terms of multi-step solvation for the activity coefficient when a solute is dissolved in a binary mixed solvent. The solvation behavior of a proton in methanol–water mixtures[1] was discussed in terms of such processes. Even though it is intuitively reasonable, however, the weakness of the concept lies in the lack of experimental evidence directly pertaining to the phenomenon.

According to Parker,[2] protic and dipolar aprotic solvents most clearly manifest their characteristics on anion solvation. Recent spectroscopic investigations of the anion-protic solvent interactions successfully support the idea, and quantitative data have been accummulated.[3,4] The Finkelstein reaction, for which reaction rates have been extensively reviewed,[5,6] can be expected to be a good probe for searching into the relation between solute-solvent interactions and reaction rates in solution.

In the present work, the authors have measured the reaction rates in alcohol–acetonitrile mixtures. After analyzing the results on the basis of theoretical expressions derived by the authors, the anion-alcohol interactions and reaction rates in solvent mixtures are discussed.

Experimental

Materials: The tetra-*n*-butylammonium bromide and iodide were prepared by refluxing tri-*n*-butylamine and the corresponding halide in methyl ethyl ketone. The crude products were recrystallized three times from an acetone–ether mixture and dried *in vacuo* at 65 °C for a few days before use.

The methyl iodide was shaken with a dilute potassium carbonate solution, washed with water, dried over anhydrous calcium chloride for one day, and distilled.

The methyl bromide was washed with concentrated sulfuric acid in a pressure vessel, distilled twice, and kept over phosphorus pentoxide in a pressure vessel.

The acetonitrile was refluxed over calcium hydride and distilled, and then distilled two times from phosphorus pentoxide and calcium hydride.

The methanol, ethanol, 2-propanol, and *t*-amyl alcohol were treated as has been described elsewhere.[7]

Kinetic Procedure: The solutions of alkyl halide and tetraalkylammonium salt were prepared by weight. 5 ml aliquots from each stock solution were mixed in a glass test tube, a capacity of 20 ml: and with a ground glass stopper; the reaction was then carried out in a thermostated bath held at 30.0±0.05 °C. After a given period of time, the reaction mixture was poured into a mixture of petroleum ether and water. The electrolytes were extracted from the organic layer, and the concentrations were determined by potentiometric titration using a silver nitrate solution.

Calculation of Rate Constants: The reaction scheme is as follows:

$$\begin{array}{cccc} \mathrm{MeBr} + & \mathrm{I}^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} & \mathrm{MeI} + & \mathrm{Br}^- \\ a-x & b-x & x & x \end{array} \qquad (1)$$

$$K = \frac{x^2}{(a-x)(b-x)}$$

where a and b are the initial concentrations of the reactants.

The rate law and the forward rate constant, k_f, are given by these equations:

$$(\mathrm{d}x/\mathrm{d}t) = k_f(a-x)(b-x) - k_r x^2 \qquad (2)$$

$$k_f = \frac{1}{2(K^{-1}-1)Bt} \ln\left\{\frac{1+x/(A+B)}{1+x/(A-B)}\right\} \qquad (3)$$

$$K = (k_f/k_r) \qquad (4)$$

$$A = \frac{(a+b)}{2(K^{-1}-1)} \qquad (5)$$

$$B = \frac{\{(a-b)^2+4K^{-1}ab\}^{1/2}}{2(K^{-1}-1)} \qquad (6)$$

When the contribution from the reverse reaction is negligibly small, the rate constant is given by this equation:

$$K_f = \frac{1}{(a-b)t} \ln\left\{\frac{b(a-x)}{a(b-x)}\right\} \qquad (7)$$

The reaction rates were followed starting from the appropriate direction; *i.e.*, for the measurement of k_f we started

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* This should be referred to as "Reaction Rates in Binary Mixed Solvents, VII," part VI; Y. Kondo, K. Uosaki, and N. Tokura, This Bulletin, **44**, 2548 (1971).

TABLE 1. DENSITIES OF SOLVENT MIXTURES (30 °C)

Mole fraction of MeCN	MeCN–MeOH	MeCN–EtOH	MeCN–2-PrOH	MeCN–*t*-AmOH
0.0	0.782	0.781	0.777	0.800
0.2	0.782	0.780	0.775	0.797
0.4	0.779	0.778	0.773	0.792
0.6	0.777	0.775	0.771	0.785
0.8	0.774	0.773	0.770	0.778
0.9	0.772	0.772	0.770	0.775
1.0	0.771	0.771	0.771	0.771

from methyl bromide and tetra-*n*-butylammonium iodide, and *vice versa*.

All the calculations were performed on the basis of Eqs. (3) and (7) with a NEAC 2200-700 computer.

Measurements of Density: The densities of the solvent mixtures, *i.e.*, acetonitrile–methanol, –ethanol, –2-propanol, and –*t*-amyl alcohol, were measured with a single-stem pycnometer with a capacity of *ca.* 30 ml. The interpolated values are summarized in Table 1.

Results

Rate measurements were carried out for both forward and reverse processes; the results are summarized in Table 2. They are the average values for duplicate or triplicate runs; the experimental uncertainty was estimated to be less than ±2%.

In 2-propanol and its mixtures with acetonitrile, the rate constants showed a slight dependence on the initial concentration of the tetra-*n*-butylammonium salts used as a nucleophile. This might be partly due to the partial dissociation of the electrolytes. For such a case, the data were determined over a four-fold change of the initial concentration of the salt at *ca.* 0.001—0.01 M; the listed average values differed by *ca.* 4—5% from the extrapolation to a zero concentration of the salt, but not more. Usually rate measurements were carried out at concentrations of 0.001—0.01 M for both reactants.

TABLE 2. RATE CONSTANTS IN PURE AND MIXED SOLVENTS (30 °C)

Mole fraction of MeCN	$k_f \times 10^4$ ($l \cdot mol^{-1} \cdot s^{-1}$)			
	MeCN–MeOH	MeCN–EtOH	MeCN–2-PrOH	MeCN–*t*-AmOH
0.0	17.3	48.8	144	445
0.2	25.4	63.0	168	600
0.4	38.2	80.5	194	692
0.6	58.6	112	225	627
0.8	120	187	292	593
0.9	209	281	374	604
1.0	705	705	705	705

Mole fraction of MeCN	$k_r \times 10^4$ ($l \cdot mol^{-1} \cdot s^{-1}$)			
	MeCN–MeOH	MeCN–EtOH	MeCN–2-PrOH	MeCN–*t*-AmOH
0.0	1.36	4.80	20.8	112
0.2	2.86	9.51	37.9	286
0.4	5.85	17.4	59.9	422
0.6	13.6	34.2	99.2	514
0.8	47.9	93.7	216	727
0.9	150	259	485	1100
1.0	2580	2580	2580	2580

Solvent	$k_f \times 10^4$	$k_r \times 10^4$
n-PrOH	—	6.0
i-BuOH	79.4	8.33
t-BuOH	—	127
n-AmOH	—	9.3

Discussion

Equilibrium Constants and Rate Constants in Single Solvents. It is important to determine whether or not the Finkelstein reaction proceeds exactly as indicated by this equation:

$$\mathrm{MeBr} + \mathrm{I}^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{MeI} + \mathrm{Br}^-$$

That is, it is important to determine whether or not the reaction has only one transition state.

The equilibrium constants as determined from the rate constants presented in Table 2 ($K=k_f/k_r=0.273$ in acetonitrile) and by approaching equilibrium from both directions ($K=\{(\mathrm{MeI})_e (\mathrm{Br}^-)_e\}/\{(\mathrm{MeBr})_e (\mathrm{I}^-)_e\}=0.274$ in acetonitrile, where the equilibrium concentrations were determined after letting the reaction mixture stand over four half lives) were in excellent agreement. The present result is a necessary corollary of the postulated mechanism.

The rate constants in methanol are much smaller than in acetonitrile, as was pointed out by Parker *et al.*[2] Even in the series of protic solvents, the rate constant shows a marked dependence on the solvent characteristics.

In the classical treatment of the solvent effect on the reaction rate,[8] the logarithmic rate constants are plotted against the reciprocal dielectric constants of the solvents. Such a plot is presented for our data in

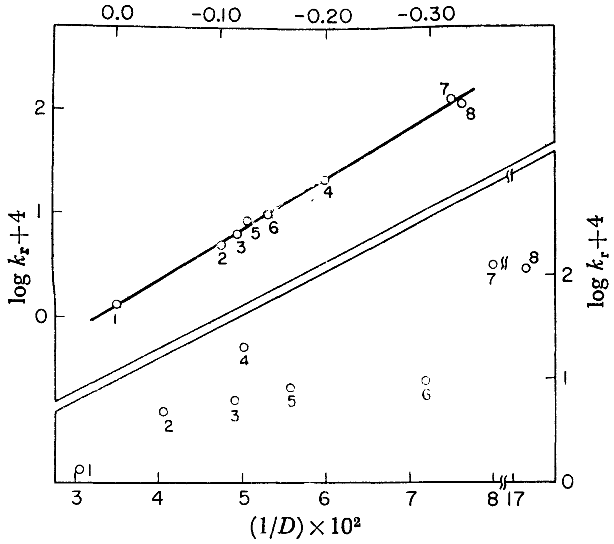

Fig. 1. Plots of log k_r *vs.* $(1/D)$ and of log k_r *vs.* σ*
1: MeOH, 2: EtOH, 3: *n*-PrOH, 4: 2-PrOH
5: *i*-BuOH, 6: *n*-AmOH, 7: *t*-BuOH, 8: *t*-AmOH

Fig. 1. Also, the same data are plotted against the Taft σ^* values.[9]

For the Finkelstein reaction, even for a homologous series of solvents, the dielectric constant does not seem to be an adequate solvent parameter. The Taft σ^* values correlate much better with the rate data. Further, it should be noted that the Taft σ^* values are fairly well correlated to the E_t values[10] for the present series of alcohols.

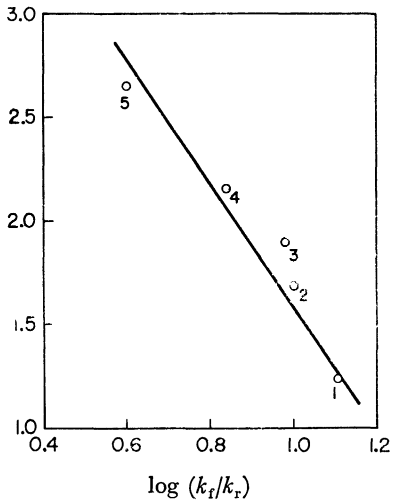

Fig. 2. Plots of log k_f vs. log (k_f/k_r)
1: MeOH, 2: EtOH, 3: *i*-BuOH, 4: 2-PrOH, 5: *t*-AmOH.

The logarithmic forward-rate constants, which reveal a marked solvent dependence, are plotted against the logarithmic equilibrium constants in Fig. 2. The slope is *ca.* −3.0. Since the solvent effect on the equilibrium constant is suspected to come mainly from the perturbation in the solvation free energies of the reactants and products due to the change in solvent, the abscissa may be taken as reflecting the sensitivity to the environmental change of the differential solvation energy between the two anions. In a similar way, the ordinate would serve as a measure of the solvent effect on the differential solvation energy between the reactant, the iodide ion, and an activated complex. Thus, the slope of −3.0 corresponds to an indication that the charge density difference between the iodide and the activated complex is considerably larger than the difference between bromide and iodide ions. In addition, the negative sign of the slope indicates that the charge density is more less in the transition state than in the initial state.

Generally speaking, the rate constants of the reaction in alcohol–acetonitrile mixtures show a marked negative deviation from the line connecting the values in pure solvents, *i.e.*, $x_1 \ln k_1 + x_4 \ln k_4$. According to a previous publication by the present authors,[11] this type of behavior can be expected where a solvent effect on the reaction rate mainly originates from the specific solvation of the reactant by the solvent slowing the reaction.

The above features appear to substantiate the position that, for the present system, the specific solvation of halide ions by alcohols is the major factor in producing such a big solvent influence on the reaction rate.

Reaction Rates in Binary Mixed Solvents: For the quantitative treatment of the solvent effects on the rate constants, the activity coefficient of a solute, M, in a solvent, s, was defined by Eq. (8):[12]

$$\beta_{M,\mathrm{s}} = (m_{gM}/m_{1M})_{\mathrm{s}} \tag{8}$$

where m_{gM} and m_{1M} stand for the molar concentration of a solute, M, in a gas phase over the solution and that of the solute, M, in solution.

Let us consider a case where a solute, M, exists in equilibrium with such a cluster as $\mathrm{M}\cdot(\mathrm{S}_4)_{Z^\circ-n}\cdot(\mathrm{S}_1)_n$, where Z° is the true solvation number, where S_4 and S_1 stand for the 4 and 1 solvents, where these clusters are related to each other by the equations, and where the unsolvated solute, M, is in a vapor-liquid equilibrium:

$$\mathrm{M} + Z^\circ\mathrm{S}_4 = \mathrm{M}\cdot(\mathrm{S}_4)_{Z^\circ} \qquad ; K_0$$
$$\mathrm{M}\cdot(\mathrm{S}_4)_{Z^\circ-j+1}\cdot(\mathrm{S}_1)_{j-1} + \mathrm{S}_1$$
$$= \mathrm{M}\cdot(\mathrm{S}_4)_{Z^\circ-j}\cdot(\mathrm{S}_1)_j + \mathrm{S}_4\ ;\ K_j$$

When the mixture forms an ideal associated solution, the activity coefficient of a solute, M, in a solvent mixture composed of the 1 and 4 solvents, $\beta_{M,\mathrm{mix}}$, is given by this equation:[1]

$$\lim_{x_M\to 0} \beta_{M,\mathrm{mix}} = [f_M^\circ/\{1+\sum_{i=0}^{Z^\circ}(\prod_{j=0}^{i} K_j)x_4^{Z^\circ-i}x_1^{i}\}](V_{\mathrm{mix}}/RT) \tag{9}$$

where x_1 and x_4 stand for the mole fraction of the 1 and 4 solvents respectively; f_M° is the fugacity of a pure solute, M, and V_{mix} is the molar volume of the mixed solvent.

Strictly speaking, all the solvation sites might not necessarily be equivalent to each other. In other words, the equilibrium constant on one solvation site might not be equal to that on the other site. We denote by $K_{\mathrm{se},m}$ the equilibrium constant for the solvent-exchange process on the mth solvation site. The $\sum_{i=0}^{Z^\circ}(\prod_{j=0}^{i} K_j)x_4^{Z^\circ-i}x_1^{i}$ term in Eq. (9) expresses the distribution of the clusters as a function of the solvent composition. In the solvent mixture each solvation site is occupied either by 1 or 4 solvents and, with respect to the mth solvation site, the ratio of the frequency of the occupation by the 4 solvent to that by the 1 solvent is x_4 to $K_{\mathrm{se},m}x_1$. Since there are Z° solvation sites around the solute, the distribution of such clusters as is specified by the occupation of the respective site either by the 1 solvent or the 4 solvent is given by the $K_0\prod_{m=1}^{Z^\circ}(x_4+K_{\mathrm{se},m}x_1)$ term. The activity coefficient of a solute, M, in the solvent mixture is given by this equation:

$$\lim_{x_M\to 0} \beta_{M,\mathrm{mix}} = [f_M^\circ/\{1+K_0\prod_{m=1}^{Z^\circ}(x_4+K_{\mathrm{se},m}x_1)\}](V_{\mathrm{mix}}/RT) \tag{10}$$

For a given solvent pair, there would exist a critical value, z, within the range, $1 \leqq z \leqq Z^\circ$, beyond which the equilibrium constant, $K_{\mathrm{se},m}$, could approximately be equal to unity; that is to say, $K_{\mathrm{se},m} \doteqdot 1$ for $z+1 \leqq m \leqq Z^\circ$, when the solvation sites are arranged and numbered in decreasing order of the equilibrium constant, for example, from the inner site to the outer site. Under these conditions, the $\prod_{m=1}^{Z^\circ}(x_4+K_{\mathrm{se},m}x_1)$ term can be approximated by $\prod_{m=1}^{z}(x_4+K_{\mathrm{se},m}x_1)$. When the term is expanded in series, Eq. (10) reduces to Eq. (11) and the K_j's are related to $K_{\mathrm{se},m}$'s by the following equations:

$$\lim_{x_M\to 0}\beta_{M,\mathrm{mix}} = [f_M^\circ/\{1+\sum_{i=0}^{z}(\prod_{j=0}^{i}K_j)x_4^{z-i}x_1^{i}\}](V_{\mathrm{mix}}/RT) \qquad (11)$$

$$K_1 = \sum_{m=1}^{z}K_{\mathrm{se},m},\ K_1K_2 = \sum_{m>n}^{z}K_{\mathrm{se},m}K_{\mathrm{se},n},\ \cdots \prod_{j=1}^{z}K_j = \prod_{m=1}^{z}K_{\mathrm{se},m}$$

The z value means the "experimentally detectable" solvation number for the solvent pair or, in other words, the number of solvent molecules responsible for bringing about the observed difference in the solvation energy; it will be referred to as "specific solvation number", in contrast to the true solvation number.

For the following bimolecular reaction, the rate constant in a mixed solvent is given by this equation:[12]

$$\mathrm{X}^- + \mathrm{RY} \longrightarrow \mathrm{M}^{\neq} \longrightarrow \mathrm{RX} + \mathrm{Y}^-$$

$$k_{\mathrm{mix}} = k_g(\beta_{\mathrm{x}^-,\mathrm{mix}}\beta_{\mathrm{RY},\mathrm{mix}}/\beta_{\neq,\mathrm{mix}}) \qquad (12)$$

where $\beta_{\mathrm{X},\mathrm{mix}}$, $\beta_{\mathrm{RY},\mathrm{mix}}$, and $\beta_{\neq,\mathrm{mix}}$ stand for the activity coefficients of X^-, of RY, and of the activated complex in the mixed solvent respectively, and where k_g is the rate constant in an ideal gas.

As was described above, and as will be discussed below, there are indications that the rate of the Finkelstein reaction is mainly controlled by the specific solvation of the anion by a protic solvent and the concept of multi-step solvation should be taken into account in the quantitative treatment of the anion solvation in protic solvents.

In the following treatment, we assume that Eq. (11) applies only to the anion and that the other systems, *i.e.*, alkyl halide-solvent mixtures, and activated complex-solvent mixtures, are to be considered ideal mixtures; that is, $\beta_{\mathrm{RY},\mathrm{mix}}=\beta_{\neq,\mathrm{mix}}=1$.

For electrolytes, the $K_0 \gg 1$ condition will be satisfied; as a result, K_0 drops out of the equations, giving these approximate formulas, *i.e.*, Eqs. (13) and (14):

$$\ln k_{\mathrm{mix}} = \ln k_1 + \ln(\prod_{j=1}^{z}K_j) - \ln\{\sum_{i=1}^{z}(\prod_{j=1}^{i}K_j)x_4^{z-i}x_1^{i}+x_4^{z}\} + \ln(V_{\mathrm{mix}}/V_1) \qquad (13)$$

$$(k_4/k_1) = (\prod_{j=1}^{z}K_j)(V_4/V_1) \qquad (14)$$

The ratio of rate constants in pure solvents, Eq. (14), is mainly controlled by the $\prod_{j=1}^{z}K_j$ term, since the values of (k_4/k_1) lie *ca.* 10—10^3, whereas the values of (V_4/V_1) are *ca.* 1—2. The rate constant in acetonitrile is usually larger than in alcohols. We identify acetonitrile as the 4 solvent and alcohol as the 1 solvent.

Equation (14) gives the boundary conditions for $\prod_{j=1}^{z}K_j$. Under these conditions, the theoretical values of the rate constants were obtained as a function of the solvent compositions on the basis of Eq. (13) for a definite set of z and K_j's. The calculations were repeated by a trial and error-method, systematically changing the equilibrium constants for the respective solvation number and afterwards for the different values of z. These calculations were performed by hand.

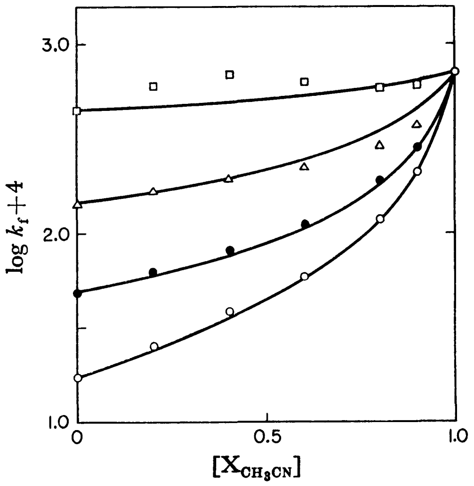

Fig. 3. Comparisons of the experimental results with the calculated values.
——: calculated.
○: MeCN-MeOH, ●: MeCN-EtOH
△: MeCN-2-PrOH, □: MeCN-*t*-AmOH.

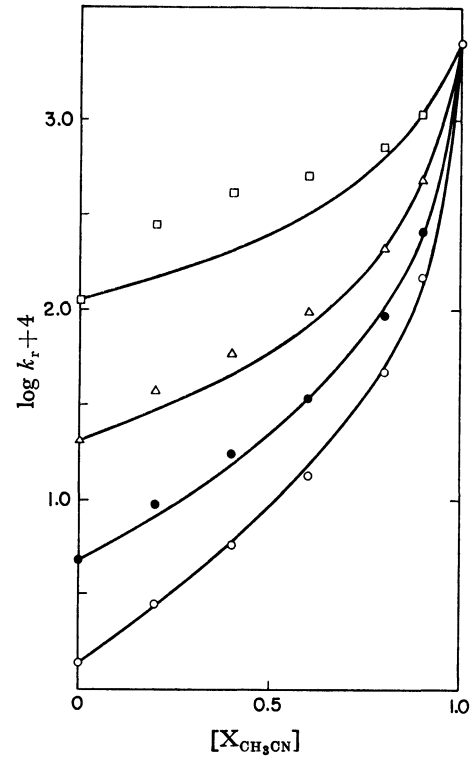

Fig. 4. Comparisons of the experimental results with the calculated values.
——: calculated.
○: MeCN-MeOH, ●: MeCN-EtOH,
△: MeCN-2-PrOH, □: MeCN-*t*-AmOH.

The calculated results are compared with the experimental data in Figs. 3 and 4. The parameters used in the calculations are summarized in Table 3.

The results in Table 3 indicate that the specific solvation number decreases with an increase in the size of the hydrocarbon moieties and of the anion. For the present systems, the specific solvation number, z, obtained above would correspond to the number of alcohol molecules interacting with the anion in a

Table 3. Experimentally determined parameters

Alcohols	I^-				Br^-					
	Z	$\prod_{j=1}^{z} K_j$	K_1	K_2	Z	$\prod_{j=1}^{z} K_j$	K_1	K_2	K_3	K_4
MeOH	2	31.36	24.1	1.30	4	1460	133	6.97	1.50	1.05
EtOH	1	16.00	16.0	—	3	595.4	75.5	4.23	1.86	—
2-PrOH	1	7.11	7.11	—	2	180.2	33.0	5.46	—	—
t-AmOH	1	3.28	3.28	—	2	47.67	14.0	3.40	—	—

different way from acetonitrile. As the protic solvent becomes more bulky, fewer protic solvent molecules can be in close proximity to the anion. This will lead to a decrease in the specific solvation number, z, that is, to a decrease in the number of protic solvent molecules interacting in a "protic" way.

This trend is observed in the equilibrium constants: $K_1 > K_2 > K_3 > K_4 \cdots$. This same trend was observed in proton solvation in methanol–water mixtures.[1]

A final point to be noticed is that, in the respective K_j values, the general trend in the interaction energy with a halide ion, *i.e.*, MeOH>EtOH>2-PrOH>*t*-AmOH, is retained.

According to the features summarized in Table 3, the solvation energy of a halide ion in a pure alcohol seems to be a composite quantity determined by two factors, a specific solvation number and the acidity of the alcohol.

Conclusions Reached by a Kinetic Procedure and by Spectroscopic Measurements. One conclusion about anion solvation has been drawn from the association equilibrium studies between phenol and halide ions by Taylor and Kuntz.[4] Both the static and dynamic procedures substantiate the concept of a multi-step solvation of anions due to protic solvents. The generalization about the interaction coefficient, *i.e.*, $K_1 > K_2 > K_3$, and the specific solvation number, *i.e.*, $z(Br^-) > z(I^-)$, are also supported by the two procedures. In addition, three independent studies, *i.e.*, the present work, IR studies,[4] and NMR studies,[3] give coincident results concerning the order of the interaction coefficients between the alcohol and the anion: $K_j(Br^-) > K_j(I^-)$.

From these results, a smaller anion seems to be better solvated in a less bulky solvent. The specific solvation number is larger as well. Among the multiple steps, the first solvent-exchange process makes an extraordinarily large contribution to the overall difference in the solvation energy.

Recently NMR studies of halide-alcohol association have been performed under conditions where one-to-one complex formation is favored (K_{eq}).[3] These results are shown in Fig. 5 as a function of the Taft σ^* values. The similarity in the slopes of the plots, *i.e.*, 2.8 and 2.5 for $\log K_1$ *vs.* σ^* and $\log K_{eq}$ *vs.* σ^*, lends support to the internal consistency of the assumptions involved in the above procedure.

As may be inferred from Figs. 3 and 4, with an increase in the size of the alcohols the plot of $\log k_{mix}$ *vs.* x tends to reveal an **S**-shape character. This type of behavior can not be simulated by the equations shown above. In such low dielectric solvents as *t*-amyl alcohol or its mixture with acetonitrile, electrolytes are only slightly dissociated; this might have some influence on the observed reaction rates. The possibility of the exchange of solvents in the transition state has been ignored in this treatment. The present work is incapable of confirming these possibilities.

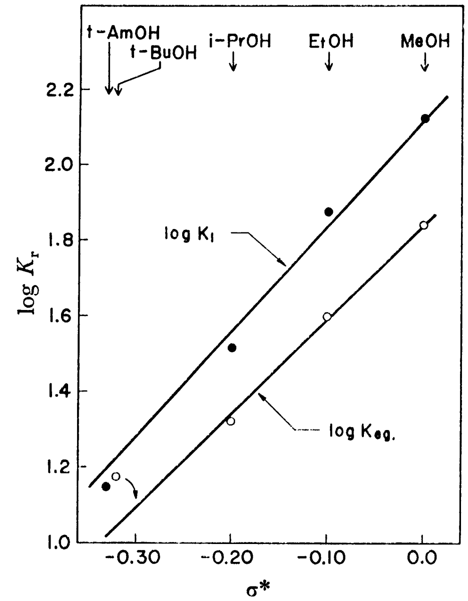

Fig. 5. Correlations of $\log K_1$ and $\log K_{eq}$ values with Taft σ^*

From the results of our studies, it seems safe to regard the anion-alcohol interaction as taking place by means of a multi-step process; in a qualitative sense, the results obtained by several procedures are consistent.

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