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The Finkelstein Reaction in Acetonitrile-Glycol Mixtures.* An Approach by a Concurrent Monodentate and Bidentate Solvation Model of the Halide Ion

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The rate constant of the reaction of methyl iodide with the bromide ion showed a characteristic dependence on the composition of solvent mixtures. In five solvent mixtures, *i.e.*, acetonitrile–ethylene glycol, –1,2-propanediol, –1,3-butanediol, –1,4-butanediol, and –2,3-butanediol, its dependence was fairly well reproduced by the theoretical equations derived on the basis of the concept of the concurrent monodentate and bidentate solvation of the halide ion by glycol. In contrast, the rate constants in acetonitrile–diethylene glycol and –triethylene glycol mixtures were better reproduced by the modified theoretical equations allowing for a self-association of glycol.

In the previous paper1) the behavior of the rate constant of the Finkelstein reaction in acetonitrile–alcohol mixtures was discussed in terms of the multi-step solvation of anions in solvent mixtures. Several properties of the solvent which might influence the solvation energy of the anion changed simultaneously from one system to another, and this introduced extracomplexities into the treatment. In the present work, in order to understand better the concept of the multi-step solvation of anions, we intended to reduce the number of exposed parameters involved in the treatment as far as possible and to set up a visualized model of the solvation of anions in solvent mixtures.

In this paper the rate of the reaction of methyl iodide with the bromide ion in acetonitrile–glycol mixtures will be discussed on the basis of the concept of the concurrent monodentate and bidentate solvation of the anion.

Experimental

The tetrabutylammonium bromide, methyl iodide, and acetonitrile were treated as has been described elsewhere.1) Commercial ethylene glycol, 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, and diethylene glycol (all of purity>99% by GLPC) were dried over anhydrous sodium sulfate and distilled twice under reduced pressure. Commercial 2,3-butanediol (*dl*: 52.3%, *meso*: 46.6% by GLPC) and triethylene glycol (>96% by GLPC) were treated similarly.

The densities of the solvent mixtures were measured with a single-stem pycnometer with a capacity of *ca.* 30 ml; the interpolated values are summarized in Table 1.

The rate measurements were performed as has been described elsewhere.1)

The experimental uncertainties of the rate constant were estimated to be less than ±2% from duplicate or triplicate runs. The average values are summarized in Table 2.

Table 1. Densities of solvent mixtures (30 °C)

$X_{\mathrm{CH_3CN}}$a)	MeCN –Ethylene glycol	MeCN –1,2-Propanediol	MeCN –2,3-Butanediol	MeCN –1,3-Butanediol	MeCN –1,4-Butanediol	MeCN –Diethylene glycol	MeCN –Triethylene glycol	pure MeCN
0.95	0.7902	0.7892	0.7894	0.7897	0.7920	0.8030	0.8156	0.77111)
0.90	0.8092	0.8066	0.8061	0.8072	0.8112	0.8318	0.8529	
0.80	0.8461	0.8395	0.8371	0.8390	0.8461	0.8831	0.9140	
0.60	0.9174	0.8977	0.8880	0.8841	0.9031	0.9638	0.9977	
0.40	0.9870	0.9483	0.9288	0.9349	0.9480	1.0254	1.0520	
0.20	1.0489	0.9918	0.9618	0.9692	0.9824	1.0727	1.0893	
0	1.1066	1.0288	0.9892	0.9976	1.0093	1.1097	1.1163	

a) $X_{\mathrm{CH_3CN}}$ stands for the mole fraction of acetonitrile.

Table 2. Rate constants for the reaction of the bromide ion with methyl iodide in solvent mixtures at 30 °C; $k \times 10^4$ l mol^{-1} s^{-1} (in pure MeCN $k \times 10^4$: 25801))

$X_{\mathrm{CH_3CN}}$	MeCN –Ethylene glycol	MeCN –1,2-Propandiol	MeCN –2,3-Butanediol	MeCN –1,3-Butanediol	MeCN –1,4-Butanediol	MeCN –Diethylene glycol	MeCN –Triethylene glycol
0.95	93.0	122	199	172	217	244	386
0.90	38.7	52.0	91.5	72.9	91.6	114	218
0.80	17.6	23.1	40.9	31.8	40.3	60.1	128
0.60	8.51	11.5	22.8	17.5	18.5	32.9	90.3
0.40	5.75	7.99	15.0	10.8	12.6	28.8	85.8
0.20	4.49	5.89	10.8	7.70	8.13	27.9	92.7
0	3.76	4.34	8.32	5.62a)	6.03a)	30.4	109

a): value estimated from the plot of log k_{mix} *vs.* X_4

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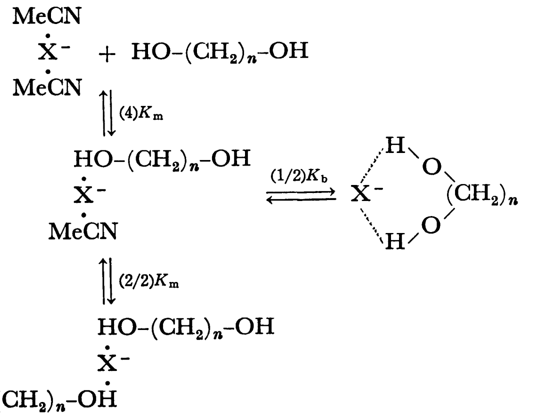
* This should be referred to as "Reaction Rates in Binary Mixed Solvents. VIII."

Results and Discussion

Rate Constants in Acetonitrile–Glycol Mixtures. In acetonitrile–glycol mixtures the logarithmic rate constants show a marked negative deviation from the line connecting the values in pure solvents, *i.e.*, $x_1 \ln k_1 + x_4 \ln k_4$, where k_1 and k_4 stand for the rate constant in Solvents 1 and 4, while x_1 and x_4 correspond to the mole fractions of Solvents 1 and 4. This type of behavior can be ascribed to the specific solvation of a reactant by the solvent, tending to lower the rate of reaction.[1,2]

For the purpose of reducing the complexity of the derived final equations, we set up the following scheme for the solvation of the halide ion in acetonitrile–glycol mixtures:



Scheme 1.

where K_m and K_b stand for the parameters corresponding to a monodentate and bidentate interaction of the glycol molecule with the halide ion and where the numbers in parentheses are the statistical factors of the reaction. Two such factors are combined to give the equilibrium constant of the reaction.

According to the same line of treatment as has been described in the previous papers,[1,3] the rate constants of

$$CH_3I + Br^- \longrightarrow CH_3Br + I^-$$

the reaction in mixed solvents, k_{mix}, are given by these equations:

$$\ln k_{mix} = \ln k_1 + \ln\{2K_m(2K_m+K_b)\} - \ln\{(x_4+2K_m x_1)^2+2K_m K_b x_1\} + \ln(V_{mix}/V_1) \quad (1)$$

$$(k_4/k_1) = 2K_m(2K_m+K_b)(V_4/V_1) \quad (2)$$

where V_1, V_4, and V_{mix} stand for the molar volumes of pure Solvent 1, of pure Solvent 4, and of a mixed solvent respectively. In the present series of solvent mixtures, k_4 is always the rate constant in acetonitrile.

Two parameters are included in these equations as a consequence of the proposed model. Since Eq. 2 serves as a boundary condition for the parameters, there is only one parameter left to be adjusted in reproducing the data. In Figs. 1 and 2 the theoretical values are compared with the experimental values.

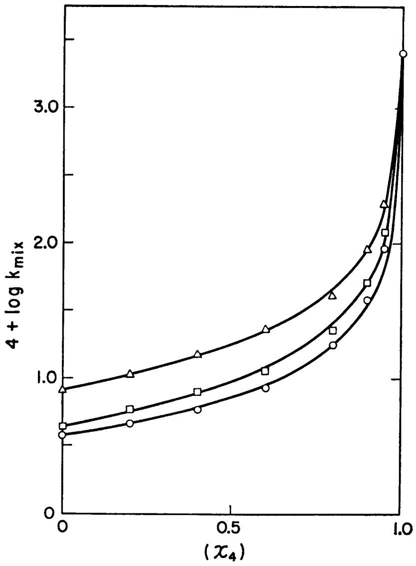


Fig. 1. Comparison of experimental and calculated data. ——; calculated, ○; MeCN–ethylene glycol, □; MeCN–1,2-propanediol, △; MeCN–2,3-butanediol.

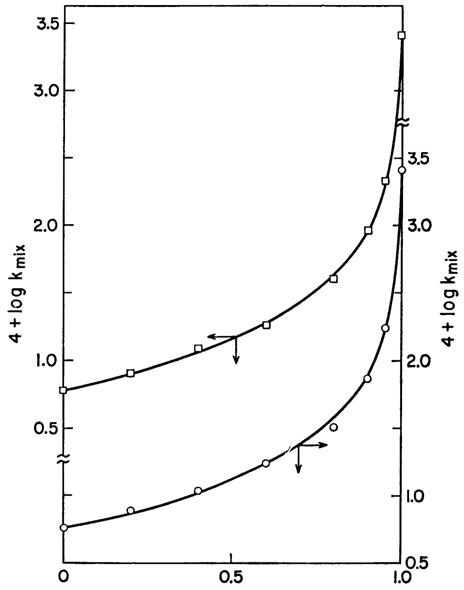


Fig. 2. Comparison of experimental and calculated data. ——; calculated, ○; MeCN–1,3-butanediol, □; MeCN–1 4-butanediol.

Table 3. Experimentally determined parameters in acetonitrile–glycol mixtures at 30 °C

Glycol	$2K_m \cdot (2K_m+K_b)$	K_m	K_b	(K_b/K_m)
Ethylene glycol	723	0.5	722	1444
1,2-Propanediol	826	10.0	21.3	2.1
2,3-Butanediol	531	8.7	13.1	1.5
1,3-Butanediol	779	11.5	10.9	0.9
1,4-Butanediol	717	11.5	8.19	0.7

One noticeable trend shown in Table 3 is that, as the distance between the hydroxyl groups gets larger and as the hydrocarbon moiety around the hydroxyl group becomes more bulky, the unidentate solvation mode takes the place of a bidentate solvation mode. This

TABLE 4. EXPERIMENTALLY DETERMINED PARAMETERS AT 30 °C

	$\frac{2K_m\{2K_m+K_b(1+K)\}}{(1+K)^3}$	K	K_m	K_b	(K_b/K_m)
MeCN–Diethylene glycol	152	1.2	18.6	2.92	0.16
MeCN–Triethylene glycol	59.8	1.2	10.7	3.8	0.3

feature is in accord with our chemical intuitions.

Rate Constants in Acetonitrile–Diethylene Glycol and –Triethylene Glycol Mixtures. In contrast to the results shown above, the rate constants in diethylene glycol and triethylene glycol–acetonitrile mixtures exhibit marked negative deviations from the values estimated on the basis of the above treatment (Fig. 3).

One of the factors not taken into account in the above treatment, but which is likely to be operating in the present systems, is a self-association of the glycol through the hydrogen bonding of a hydroxyl group to an ether linkage.

For the system in which a glycol forms acyclic long-chain polymers through self-association,[4] the mole fractions of a monomer glycol and of acetonitrile, defined in terms of moles in solution, *i.e.*, y_1 and y_4, are related to the stoichiometric mole fractions of glycol and of acetonitrile, *i.e.*, x_1 and x_4, by the following equations, as will be described in the Appendix:

$$y_1 = \frac{1}{2K(1+K)x_1}\{2Kx_1+1-(4Kx_1x_4+1)^{1/2}\} \tag{3}$$

$$y_4 = \frac{1-(K+1)y_1}{1-Ky_1} \tag{4}$$

where K stands for the equilibrium constant of the self-association.

$$[HO-(CH_2CH_2O)_m-H]_{n-1} + HO-(CH_2CH_2O)_m-H \rightleftarrows [HO-(CH_2CH_2O)_m-H]_n$$

According to a line of treatment described elsewhere,[1,3] except for the additional assumption that only a monomer glycol, and not polymers, can participate in the specific solvation of the halide ion, the activity coefficient of a halide ion in a solvent mixture, $\beta_{2,\text{mix}}$ is given by Eq. 5 (see Appendix). The rate constant in these mixtures, k_{mix}, is given by Eq. 6, and the k_4/k_1 ratio is now defined by Eq. 7:

$$\beta_{2,\text{mix}} = \frac{1+\dfrac{Ky_1^2}{(1-Ky_1)^2}}{[1+K_0\{(y_4+2K_my_1)^2+2K_mK_by_1\}]}\left(\frac{f_2^\circ V_{\text{mix}}}{RT}\right) \tag{5}$$

$$\begin{aligned}\ln k_{\text{mix}} = {} & \ln k_1 + \ln[2K_m\{2K_m+K_b(1+K)\}/(1+K)^3] \\ & - \ln\{(y_4+2K_my_1)^2+2K_mK_by_1\}/ \\ & [1+\{Ky_1^2/(1-Ky_1)^2\}] + \ln(V_{\text{mix}}/V_1)\end{aligned} \tag{6}$$

$$(k_4/k_1) = \frac{2K_m\{2K_m+K_b(1+K)\}}{(1+K)^3}(V_4/V_1) \tag{7}$$

The calculations were performed as follows: (1) the values of y_1 and y_4 were calculated as functions of x_1 and x_4 from Eqs. 3 and 4, using an assumed value of K; (2) making use of these values, the rate constants were calculated by means of Eqs. 6 and 7 for an assumed value of (K_b/K_m), and (3) the procedures were repeated until the optimum fit to the experimental results was obtained.

The value found for the equilibrium constant, *i.e.*, $K=1.2$, is not unexpected, since, for the hydrogen bonding between ethanol and ether, an equilibrium constant of the same order of magnitude can be estimated from the pK_{Hb} values after correcting for its solvent dependence.[5–7]

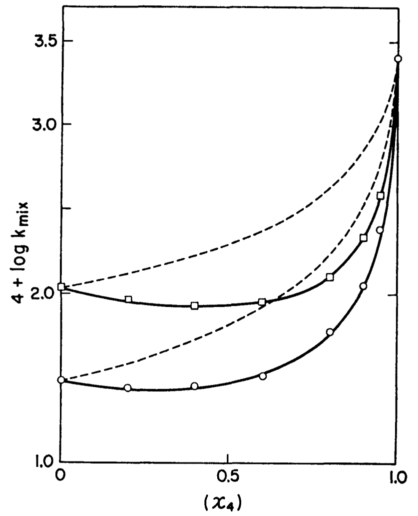


Fig. 3. Comparison of experimental and calculated data. ----; estimated values on the basis of Eqs. (1) and (2) assuming $(K_b/K_m)=0.7$, ——; calculated, ○; MeCN–diethylene glycol, □; MeCN–triethylene glycol.

As has been shown above, the values of the rate constant derived theoretically, on the basis of the solvation of the halide ion and the self-association of glycol, are in good agreement with the values observed in the various solvent mixtures. Even the phenomenon of a shallow minimum in the rate plots given in Fig. 3 is accounted for. However, although such features can be reproduced using the particular model, this does not constitute proof of the model. We feel, though, that the model is useful in accounting for the general trends observed.

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Appendix

The material balances, mole fractions and equilibrium constants used in the treatment are given by these equations. (1). Material balances,

$$N_1 = M_1 + \sum_{j=0}^{2} jM_{j2} + M_{b2} + \sum_{k=2}^{n} kM_{Ak} \tag{A-1}$$

$$N_2 = M_2 + \sum_{j=0}^{2} M_{j2} + M_{b2} \tag{A-2}$$

$$N_4 = M_4 + \sum_{j=0}^{2}(2-j)M_{j2} \tag{A-3}$$

where N_i, M_i, M_{j2}, M_{b2}, and M_{Ak} stand for the number of moles of species i before mixing, of species i in solution, of the halide ion solvated by j mol of glycol in a monodentate way, of the halide ion solvated by glycol in a bidentate way, and of acyclic k-mer of glycol respectively.

(2). Mole fractions.

$$x_i = N_i/(N_1+N_2+N_4) \tag{A-4}$$

$$y_i = M_i/M_t \tag{A-5}$$

$$y_{j2} = M_{j2}/M_t \tag{A-6}$$

$$y_{b2} = M_{b2}/M_t \tag{A-7}$$

$$y_{Ak} = M_{Ak}/M_t \tag{A-8}$$

$$\begin{aligned} M_t &= M_1 + M_2 + M_4 + M_{b2} \\ &\quad + \sum_{j=0}^{2} M_{j2} + \sum_{k=2}^{n} M_{Ak} \end{aligned} \tag{A-9}$$

(3). Equilibrium constants.

$$K_0 = y_{02}/(y_2 y_4^2) \tag{A-10}$$

$$4K_m = y_{12} y_4/(y_{02} y_1) \tag{A-11}$$

$$(2/2)K_m = y_{22} y_4/(y_{12} y_1) \tag{A-12}$$

$$(1/2)K_b = y_{b2} y_4/(y_{12}) \tag{A-13}$$

$$K = y_{Ak}/(y_1 y_{Ak-1}) \tag{A-14}$$

When $N_2=0$, the following relations are obtained:

$$\sum_{k=2}^{n}(k-1)y_{Ak} = Ky_1^2/(1-Ky_1)^2 \quad (\because\ n\rightarrow\infty) \tag{A-15}$$

$$y_1 + \sum_{k=2}^{n} k y_{Ak} = y_1/(1-Ky_1)^2 \quad (\because\ n\rightarrow\infty) \tag{A-16}$$

Combining Eqs. A-1, A-3, A-4, A-5, A-9, A-14, A-15, and A-16, two kinds of mole fraction are related to each other by these equations:

$$x_1 = N_1/(N_1+N_4) = y_1/\{(1-Ky_1)^2+Ky_1^2\} \tag{A-17}$$

$$\begin{aligned} x_4 &= N_4/(N_1+N_4) = y_4(1-Ky_1)^2/ \\ &\quad \{(1-Ky_1)^2+Ky_1^2\} \end{aligned} \tag{A-18}$$

Solving Eqs. A-17, and A-18 under the condition $x_1+x_4=1$, y_1 and y_4 are given by:

$$y_1 = \frac{1}{2K(1+K)x_1}\{2Kx_1+1-(4Kx_1x_4+1)^{1/2}\} \tag{A-19}$$

$$y_4 = \{1-(K+1)y_1\}/(1-Ky_1) \tag{A-20}$$

From Eqs. A-2, A-5, A-9, A-10, A-11, A-12, A-13, and A-15, we obtain:

$$\begin{aligned} \lim_{x_2\to 0}(y_2/x_2) &= \{1+\sum_{k=2}^{n}(k-1)y_{Ak}\}/\{1+\sum_{j=0}^{2}(y_{j2}/y_2) \\ &\quad + (y_{b2}/y_2)\} \\ &= \frac{1+\dfrac{Ky_1^2}{(1-Ky_1)^2}}{1+K_0\{(y_4+2K_m y_1)^2+2K_m K_b y_1\}} \end{aligned} \tag{A-21}$$

According to the definition of $\beta_{2,\mathrm{mix}}$ previously described,[3] the activity coefficient of a solute in a solvent mixture is given by:

$$\begin{aligned} \beta_{2,\mathrm{mix}} &= \lim_{x_2\to 0}(y_2/x_2)(f_2^\circ V_{\mathrm{mix}}/RT) \\ &= \frac{1+\dfrac{Ky_1^2}{(1-Ky_1)^2}}{1+K_0\{(y_4+2K_m y_1)^2+2K_m K_b y_1\}}\left(\frac{f_2^\circ V_{\mathrm{mix}}}{RT}\right) \end{aligned} \tag{A-22}$$

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