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Solvation of Anions in Solvent Mixtures as Deduced from the Rates of the Finkelstein Reaction

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The Finkelstein reaction has been studied in five dipolar aprotic–dipolar aprotic solvent mixtures and one protic–dipolar aprotic solvent mixture. The theoretical equations for the rate constant as a function of solvent composition derived previously have been reformulated in terms of the solvent exchange model on the solvation site, taking into account the two main features of solvation: the number of the solvation sites on the solvent molecule and the equilibrium constant for the solvent exchange process. The results obtained previously, together with present results, are comprehensively discussed and the solvent mixtures are classified into four groups from the viewpoint of solute-solvent interaction in the region near the ion, using derived theoretical equations.

Thermodynamics of transfer of a single ion from one solvent to another as expressed in terms of a solvent activity coefficient has been accepted as an important criteria, when discussing solvent effects on reaction rates and mechanisms in solution.[1,2] In the course of the development of the concept, most attention seems to have been paid to the hydrogen bonding interaction, and polarizability effects, between solute and solvent. Even though this is quite useful in discussing the gross features of a solute in pure solvents, more sophisticated versions on the solute-solvent interactions in the vicinity of an ionic solute are required, when analyzing chemical phenomena in mixed solvents.[3,4]

In previous papers[5,6] we have dealt with the analysis of reaction rates of the Finkelstein reaction in acetonitrile–protic solvent mixtures from the viewpoint of the specific solvation of the anion in the solvent mixtures. In the present work we set up a generalized model for describing the cluster distribution of anion solvates in solvent mixtures, and derive the theoretical equations for the reaction rate in solvent mixtures on the basis of the model. By the mathematical analysis of reaction rates in solvent mixtures, solvent mixtures are classified into four groups from the viewpoint of ion-solvent interactions in the region near the ion.

Experimental

Materials: *N,N*-Dimethylacetamide, Wako's guaranteed reagent, was distilled from barium oxide and from calcium hydride under reduced pressure. Ethyl methyl ketone, Wako's extra pure reagent, was distilled twice after storage over anhydrous sodium sulfate. γ-Butyrolactone, Wako's extra pure reagent, was distilled twice under reduced pressure after storage over calcium hydride. Sulfolane, Wako's reagent, was distilled three times under reduced pressure after storage over sodium hydroxide. Propylene carbonate, Wako's extra pure reagent, was stored over freshly activated molecular sieves and distilled twice under reduced pressure. Other materials were treated as described elsewhere.[5]

Kinetic measurements and calculations were carried out as described elsewhere.[5]

Density measurements were performed with a glass dilatometer consisting of a bulb and two graded stems (*ca.* 40 ml capacity).

Densities and rate constants are summarized in Tables 1 and 2.

Results and Discussion

Activation Parameters in Pure Solvents and the Solvent Activity Coefficients of Bromide Ion. Rate constants and activation parameters in pure solvents are summarized in Table 3. They change according to solvents

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

N,N-Dimethylacetamide –acetonitrile mixtures		Ethyl methyl ketone –sulfolane mixtures		Ethyl methyl ketone –propylene carbonate mixtures		Ethyl methyl ketone –acetonitrile mixtures		Ethyl methyl ketone –γ-butyrolactone mixtures	
$x_{\rm DMA}$	d	$x_{\rm EMK}$	d	$x_{\rm EMK}$	d	$x_{\rm EMK}$	d	$x_{\rm EMK}$	d
1.0	0.9319	1.0	0.7948	1.0	0.7948	1.0	0.7948	1.0	0.7948
0.90	0.9232	0.90	0.8487	0.90	0.8345	0.80	0.7927	0.90	0.8251
0.80	0.9133	0.75	0.9262	0.75	0.8952	0.65	0.7906	0.75	0.8716
0.70	0.9022	0.50	1.0480	0.50	0.9951	0.50	0.7878	0.50	0.9516
0.60	0.8899	0.25	1.1604	0.25	1.0951	0.35	0.7842	0.25	1.0341
0.50	0.8761	0.0	1.2622	0.0	1.1945	0.15	0.7778	0.0	1.1192
0.40	0.8604					0.0	0.7713		
0.30	0.8426								
0.20	0.8221								
0.10	0.7986								
0.0	0.7713								

Table 2. Rate constants in solvent mixtures (30 °C)

Acetonitrile–methanol mixtures			N,N-Dimethylacetamide–acetonitrile mixtures		
x_{AN}	$\mathrm{EtI+Br^-}$ $k\times10^5$	$\mathrm{EtBr+I^-}$ $k\times10^5$	x_{DMA}	$\mathrm{EtI+Br^-}$ $k\times10^2$	$i\text{-}\mathrm{PrI+Br^-}$ $k\times10^4$
1.0	1050	59.3	1.0	62.5	154.2
0.90	70.7	18.5	0.90	—	107.4
0.80	24.1	9.67	0.80	27.8	—
0.60	7.60	5.42	0.70	—	45.0
0.40	3.78	3.69	0.60	12.1	—
0.20	1.89	2.39	0.50	—	22.3
0.0	1.01	2.05	0.40	5.01	—
			0.30	—	10.6
			0.20	2.37	—
			0.10	—	5.42
			0.0	1.05	3.98

Ethyl methyl ketone–propylene carbonate mixtures		Ethyl methyl ketone–sulfolane mixtures	
x_{EMK}	$\mathrm{EtI+Br^-}$ $k\times10^2$	x_{EMK}	$\mathrm{EtI+Br^-}$ $k\times10^2$
1.0	58.1	1.0	58.1
0.90	19.2	0.90	34.5
0.75	7.98	0.75	24.9
0.50	3.84	0.50	16.9
0.25	2.92	0.25	13.0
0.0	2.21	0.0	10.5

Ethyl methyl ketone–acetonitrile mixtures		Ethyl methyl ketone–γ-butyrolactone mixtures	
x_{EMK}	$\mathrm{EtI+Br^-}$ $k\times10^2$	x_{EMK}	$\mathrm{EtI+Br^-}$ $k\times10^2$
1.0	58.1	1.0	58.1
0.80	23.2	0.90	37.0
0.65	11.6	0.75	26.2
0.50	5.98	0.50	16.2
0.35	3.57	0.25	13.1
0.15	1.80	0.0	8.83
0.0	1.05		

k; 1.0 $\mathrm{mol^{-1}\cdot s^{-1}}$.

without any clear pattern, except for methanol solvent, in which the enthalpy term is the predominant factor responsible for the much reduced rate.

As summarized in Table 4, logarithmic relative rates are well correlated with the single ion solvent activity coefficient of bromide ion, for both protic and dipolar aprotic solvents.[7–9] The transition state anion-neutral molecule assumption[1,7] was used to obtain the bromide ion activity coefficient.[1]

The sensitivity of a bulky transition state to a change in solvent is believed to be less than that of a compact reactant anion in solvent mixtures as well as in pure solvents.[1] The principal feature of the log k_{mix} *vs.* composition profile (Figs. 1, 2, and 3) should be ascribed to the change in the solvation of a reactant anion, even though there must be differences in the solvent activity coefficient of the transition state.

Table 3. Rate constants and activation parameters for the reaction of ethyl iodide with bromide ion (30 °C)

Solvents	k ($\mathrm{l\cdot mol^{-1}\cdot s^{-1}}$)	$\Delta H^{\ddagger}$ ($\mathrm{kcal\cdot mol^{-1}}$)	$\Delta S^{\ddagger}$ ($\mathrm{cal\cdot K^{-1}\cdot mol^{-1}}$)
N,N-Dimethylacetamide	6.25×10^{-1}	16.6	−4.74
Ethyl methyl ketone	5.81×10^{-1}	17.4	−2.25
γ-Butyrolactone	8.83×10^{-2}	16.3	−9.62
Propylene carbonate	2.21×10^{-2}	17.0	−10.06
Acetonitrile	1.05×10^{-2}	18.3	−7.25
Methanol	1.01×10^{-5}	22.7	−6.54

Table 4. Relative rates and solvent activity coefficients

Solvents	$\log(k/k_{\mathrm{AN}})$	$\log {}^{0}\gamma^{\mathrm{S}}_{\mathrm{Br^-}}$
N,N-Dimethylacetamide	1.77	2.0[7]
Ethyl methyl ketone	1.74	2.5,[a,7] 2.35[a,8] 1.90,[a,9] 2.93[b]
Sulfolane	1.00	0.4,[7] 1.90[9]
γ-Butyrolactone	0.925	—
Propylene carbonate	0.323	0.5,[7] 0.367[9]
Acetonitrile	0	0
Methanol	−3.01	−2.3[7]

a) $\log {}^{0}\gamma^{\mathrm{S}}_{\mathrm{Br^-}}$ for acetone. b) Private communication from Dr. M. H. Abraham.

Reaction Rates in Binary Mixed Solvents. Thermodynamic Treatments: In the previous papers of this series[5,6] it was shown that the chemical equilibria and the reaction rates in binary mixed solvents could be reproduced by treating the solvation change of the respective solute in terms of m successive solvent exchange processes.

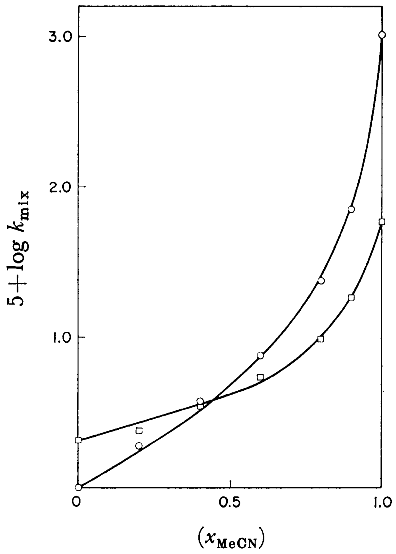


Fig. 1. Plots of log k_{mix} *vs.* mole fraction of acetonitrile (in MeOH–MeCN mixtures).
○; Experimental results for $\mathrm{EtI+Br^-}$, ——; calculated at $K_{\mathrm{se,1}}=75.0$, $K_{\mathrm{se,2}}=7.16$, $K_{\mathrm{se,3}}=1.49$ in Eq. 5. □; Experimental results for $i\text{-}\mathrm{PrI+I^-}$, ——; calculated at $K_{\mathrm{se,1}}=22.3$ in Eq. 5.

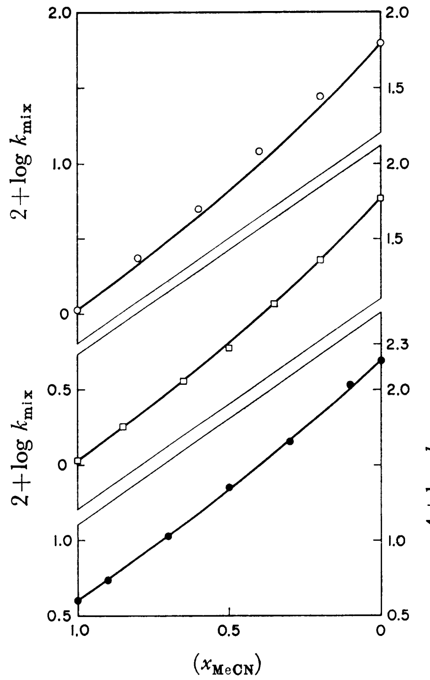


Fig. 2. Plots of log k_{mix} vs. mole fraction of acetonitrile. ○: Experimental results for EtI+Br⁻ in DMA–AN mixtures, ——: calculated at $K_{se,1}=1.80$ in Eq. 7. □: Experimental results for EtI+Br⁻ in EMK–AN mixtures, ——: calculated at $K_{se,1}=1.79$ in Eq. 7. ●: Experimental results for *i*-PrI+Br⁻ in DMA–AN mixtures, ——: calculated at $K_{se,1}=1.68$ in Eq. 7.

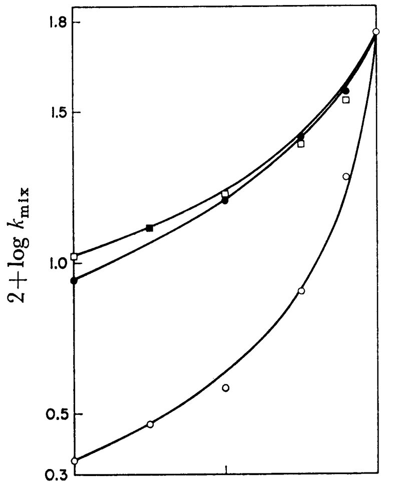
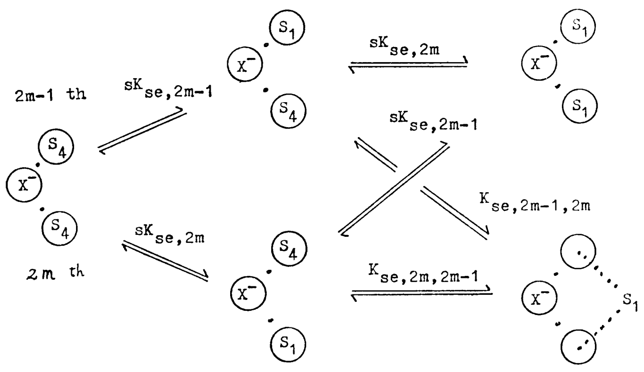


Fig. 3. Plots of log k_{mix} vs. mole fraction of methyl ethyl ketone.
□: Experimental results for EtI+Br⁻ in EMK–TMSO$_2$ mixtures, ——: calculated at $K_{bs,2}=4.81$ in Eq. 11. ●: Experimental results for EtI+Br⁻ in EMK–γ-BL mixtures, ——: calculated at $K_{bs,2}=4.58$ in Eq. 11. ○: Experimental results for EtI+Br⁻ in EMK–PC mixtures, ——: calculated at $K_{bs,2}=23.8$ in Eq. 11.

For formal simplicity of the derived equations it is necessary to assume that the true solvation number of a solute,[5] or the number of a solvation site Z° is an even integral value and that these sites are grouped into adjacent pairs of sites which are independent of each other in the respective pair, as well as of the members of other pairs.



Scheme 1. Solvent exchange scheme on $2m-1$ th and $2m$ th solvation sites.

As was suggested previously[6] and will be suggested also later, in some cases it is feasible that a solvent molecule can interact with a solute by simultaneously occupying a pair of solvation sites, if the solvent molecule contains multiple functional solvating groups. In the following treatment we will deal with the cluster distribution in solvent mixtures in which a component solvent, 4, has only one functional group, whereas a solvent, 1, has s equivalent functional groups.

Consider the frequencies of occupation of a given pair of sites which are referred to as $2m-1$ th and $2m$ th solvation site on the basis of the above solvent exchange scheme, where $K_{se,2m-1}$ and $K_{se,2m}$ refer to the equilibrium constants for the solvent exchange process on the $2m-1$ th and the $2m$ th solvation site, and $K_{se,2m-1,2m}$ refers to that of the bidentate solvent exchange process.

The number of ways of occupation of the solvation site is given as follows:

S_4 on both $2m-1$ th and $2m$ th site; x_4^2

S_4 on $2m-1$ th and S_1 on $2m$ th site; $sK_{se,2m}x_1x_4$

S_1 on $2m-1$ th and S_4 on $2m$ th site; $sK_{se,2m-1}x_1x_4$

different S_1 molecules on both $2m-1$ th and $2m$ th site; $s^2K_{se,2m-1}K_{se,2m}x_1^2$

same S_1 molecule on both $2m-1$ th and $2m$ th site; $sK_{se,2m-1}K_{se,2m-1,2m}x_1=sK_{se,2m}K_{se,2m,2m-1}x_1$

When the average monodentate and bidentate solvation equilibrium constants, $K_{ms,2m}$ and $K_{bs,2m}$ are defined by the equations,

$$K_{ms,2m} = (K_{se,2m-1}K_{se,2m})^{1/2}$$

$$K_{bs,2m} = (K_{se,2m-1,2m}K_{se,2m,2m-1})^{1/2}$$

the distribution of cluster as defined by the way of occupation of Z° solvation sites on a solute, M, is given by the equation,

$$\prod_{m=1}^{Z^\circ/2}\{(x_4+sK_{se,2m-1}x_1)(x_4+sK_{se,2m}x_1)+sK_{ms,2m}K_{bs,2m}x_1\}. \qquad (1)$$

The activity coefficient of a solute, M, in the solvent mixture, $\beta_{M,mix}$, is given by the equation derived in the previous paper,[5]

$$\lim_{x_M\to 0}\beta_{M,mix} = f_M^\circ/[1+K_0\prod_{m=1}^{Z^\circ/2}\{(x_4+sK_{se,2m-1}x_1)(x_4+sK_{se,2m}x_1) + sK_{ms,2m}K_{bs,2m}x_1\}](V_{mix}/RT) \qquad (2)$$

where f_{M}° is the fugacity of equibrated vapor of a pure solute, M,[5] and V_{mix} is the mean molar volume of the mixed solvent; K_0 is the equilibrium constant for the reaction,

$$\mathrm{M} + Z^{\circ}\mathrm{S}_4 = \mathrm{M}\cdot(\mathrm{S}_4)_{Z^{\circ}}.$$

As was mentioned above and discussed elsewhere,[1,5] the rate of the Finkelstein reaction seems to be predominantly controlled by the solvation of a nucleophile. Thus, by the same procedure as described in the previous paper,[5] the rate constants in solvent mixtures, k_{mix}, and the ratio of the rate constants in solvent 4 and 1, (k_4/k_1), are given by the equations,

$$\begin{aligned}\ln k_{\mathrm{mix}} = \ln k_1 &+ \ln \prod_{m=1}^{Z^{\circ}/2} (s^2K_{\mathrm{se},2m-1}K_{\mathrm{se},2m} + sK_{\mathrm{ms},2m}K_{\mathrm{bs},2m}) \\ &- \ln \prod_{m=1}^{Z^{\circ}/2} \{(x_4 + sK_{\mathrm{se},2m-1}x_1)(x_4 + sK_{\mathrm{se},2m}x_1) \\ &+ sK_{\mathrm{ms},2m}K_{\mathrm{bs},2m}x_1\} + \ln (V_{\mathrm{mix}}/V_1) \qquad (3)\end{aligned}$$

$$(k_4/k_1) = \prod_{m=1}^{Z^{\circ}/2} (s^2K_{\mathrm{se},2m-1}K_{\mathrm{se},2m} + sK_{\mathrm{ms},2m}K_{\mathrm{bs},2m}) \times (V_4/V_1) \qquad (4)$$

where V_4 and V_1 stand for the molar volumes of solvents 4 and 1.

Comparisons with the Experimental Results. Case I. Alcohol and Acetonitrile Mixtures (Fig. 1): Both alcohol and acetonitrile contain only one functional group each. Thus, by setting s equal to unity, and $K_{\mathrm{bs},2m}$ equal to zero, Eqs. 3 and 4 reduce to Eqs. 5 and 6, which are the same formulae as derived previously.[5]

$$\begin{aligned}\ln k_{\mathrm{mix}} = \ln k_1 &+ \ln \prod_{m=1}^{Z^{\circ}} K_{\mathrm{se},m} - \ln \prod_{m=1}^{Z^{\circ}} (x_4 + K_{\mathrm{se},m}x_1) \\ &+ \ln (V_{\mathrm{mix}}/V_1) \qquad (5)\end{aligned}$$

$$(k_4/k_1) = \prod_{m=1}^{Z^{\circ}} K_{\mathrm{se},m}(V_4/V_1) \qquad (6)$$

Equation 6 gives the boundary conditions for $\prod_{m=1}^{Z^{\circ}} K_{\mathrm{se},m}$. Under these conditions, the theoretical values of the rate constants were obtained as a function of the solvent compositions on the basis of Eq. 5 for a definite set of Z° and $K_{\mathrm{se},2m}$'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°.

In applying Eqs. 5 and 6 to the experimental data, only those equilibrium constants which are larger than unity are detectable from the solvent exchange studies,[5] since the term $x_4 + K_{\mathrm{se},m}x_1$ reduces to unity when $K_{\mathrm{se},m}$ becomes unity.[5]

One noticeable trend observed in the solvent mixtures is a large attenuation effect in $K_{\mathrm{se},m}$ as described previously.[5] Similar effects were observed in Ag^+ solvation exchange studies in *N*,*N*-dimethylthioformamide–propylene carbonate, $-\mathrm{H_2O}$, and –acetonitrile mixtures.[10] Similar but rather smaller attenuation effects were also observed in NMR chemical shift studies in solvent mixtures.[11] Throughout these studies, the solvent exchange processes with up to four steps are sufficient to reproduce the data.[5,10,11]

In alcoholic and dipolar aprotic solvents, only proton and first row elements can interact with the anion. These have respective Slater orbital exponents which crucially effect the interaction distances between ion and solvents. The variation in the interaction distances, which would alternatively be stated as a change in the degree of covalency in the interaction,[10] is the predominant feature with regard to the inequivalence of the respective solvation sites.

Case II. Acetonitrile–Ethyl Methyl Ketone, and N,N-*Dimethylacetamide Mixtures (Fig. 2)*: These component solvents contain only one solvation site each as in case I. In contrast, experimental results were reproduced by taking the same equilibrium constant throughout the solvent exchange processes concerned and by taking the number of solvation site as equal to a normal coordination number, *i.e.*, six,[12] as expressed in Eqs. 7 and 8.

$$\begin{aligned}\ln k_{\mathrm{mix}} = \ln k_1 &+ \ln (K_{\mathrm{se},1})^6 - \ln (x_4 + K_{\mathrm{se},1}x_1)^6 \\ &+ \ln (V_{\mathrm{mix}}/V_1), \qquad (7)\end{aligned}$$

$$(k_4/k_1) = (K_{\mathrm{se},1})^6(V_4/V_1). \qquad (8)$$

Similar patterns of solution phenomena *vs.* composition profile were observed previously,[10,13] where the pattern was designated as binomial distribution of cluster.

In the solvent mixtures of this class, all the component solvents retain first row elements as a binding site with the anion. Their Slater orbital exponents resemble each other in magnitude, thus leading to a similar interaction distance with the anion. This can be considered as a major factor in indiscriminating the essentially inequivalent solvation sites.

Case III. Glycol–Acetonitrile Mixtures: In glycol two hydroxyl groups are available for interaction with the anion, so that s is equal to 2. When a pair of sites are considered as approximately equivalent to one another, and only one pair of sites contribute predominantly to the total solvation exchange, that is to say the contributions from the remaining sites are minor and masked by the much larger terms from the first pair of sites, then Eqs. 3 and 4 reduce to Eqs. 9 and 10, since for the other pair of sites, the term, $\{(x_4 + 2K_{\mathrm{ms},2m}x_1)^2 + 2K_{\mathrm{ms},2m}K_{\mathrm{bs},2m}x_1\}$, should be equal to unity irrespective of the value, x_1.

$$\begin{aligned}\ln k_{\mathrm{mix}} = \ln k_1 &+ \ln \{2K_{\mathrm{ms},2}(2K_{\mathrm{ms},2} + K_{\mathrm{bs},2})\} \\ &- \ln \{(x_4 + 2K_{\mathrm{ms},2}x_1)^2 + 2K_{\mathrm{ms},2}K_{\mathrm{bs},2}x_1\} \\ &+ \ln (V_{\mathrm{mix}}/V_1). \qquad (9)\end{aligned}$$

$$(k_4/k_1) = 2K_{\mathrm{ms},2}(2K_{\mathrm{ms},2} + K_{\mathrm{bs},2})(V_4/V_1). \qquad (10)$$

Equations 9 and 10 are equivalent to those derived previously on a less sophisticated basis.[6] Rates *vs.* composition profile in five glycol–acetonitrile mixtures were satisfactorily reproduced by these equations.[6]

Case IV. Propylene Carbonate–, Sulfolane–, and γ-Butyrolactone–Ethyl Methyl Ketone Mixtures (Fig. 3): Propylene carbonate, sulfolane and γ-butyrolactone each have multiple solvation sites. When the same conditions as mentioned in case III also hold for the solvent mixtures of this class, Eqs. 9 and 10 would apply to the present cases. As a matter of fact, experimental results were satisfactorily reproduced by the simplest formulae *i.e.*, Eqs. 11 and 12 as obtained by setting $sk_{\mathrm{ms},2m} = 1$ for $m \geqq 1$ in Eqs. 9 and 10.

$$\ln k_{\mathrm{mix}} = \ln k_1 + \ln(1+K_{\mathrm{bs},2}) - \ln(1+K_{\mathrm{bs},2}x_1) + \ln(V_{\mathrm{mix}}/V_1), \tag{11}$$

$$(k_4/k_1) = (1+K_{\mathrm{bs},2})(V_4/V_1). \tag{12}$$

They are formally equivalent to the formulae as derived from Eqs. 5 and 6 under the conditions, $K_{\mathrm{se},m}=1$ for $m\geqq2$. Thus, on purely mathematical grounds, the present systems are indistinguishable from the systems stet case I. Other mechanistic criteria are necessary in order to establish the solvation pattern. On the basis of the results of model CNDO/2 calculations,[14] the present systems would preferably be classified as a special case of a concurrent monodentate-bidentate solvation system, *i.e.*, the special case of case III.

In acetonitrile and propylene carbonate, rate constants and activation parameters are quite similar in value (Table 3), and do not indicate any marked mechanistic difference for Finkelstein reactions in the two solvents; the activity coefficient for bromide ion (Table 4) is also nearly the same in these solvents.

However, logarithmic rate *vs.* composition profiles are quite different for systems containing acetonitrile or propylene carbonate (*e.g.* for the acetonitrile–ethyl methyl ketone and propylene carbonate–ethyl methyl ketone systems). The use of solvent mixtures and the mathematical analysis of the results have thus provided information on solute-solvent interactions in the vicinity of the bromide ion that cannot be obtained from studies of data in the two pure single solvents.

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