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Reaction Rates in Binary Mixed Solvents. II*[1]

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In order to study the effects of solvents on reaction rates, the theoretical expression for the rate constant has been introduced using Henry's constant. The Henry constant of the solute in a chemically-reacting mixture has been calculated thermodynamically. The theoretical expressions for the rate constants in mixed solvents have been derived on the basis of the molecular models; the application of these equations showed that one model accurately illustrates the behavior of the reaction rates in solvent mixtures.

A number of solvent parameters have recently been introduced with the intent of providing an empirical measure of the effect on an organic reaction in a variety of solvents.[1] However, no theoretical correlation has yet been established between these empirically-determined parameters and the theory of an absolute reaction rate.

On the basis of the view that, when two sorts of solvents with different selectivities[2] are mixed, the selectivities of the solvents may be expected to vary continuously with the composition of the solvent, the present authors have previously discussed the general behavior of the reaction rate in binary mixed solvents.[3]

It has long been accepted that the solvation of the solute is one of the most important factors determining the rate of the reaction in solution.[4]

Although the rates and activation parameters in mixed solvents have been investigated in connection with the specific solvation of the solute, they themselves have been nothing but speculation.[2,5-7] In this report, therefore, the authors have treated the rate of reaction in binary mixed solvents on the basis of the theory of the non-electrolyte solution and applied a theoretical expression to the experimental results.

Theoretical Expression for the Rate Constants in a Solution. According to the theory of an absolute reaction rate, the rate constant of a general reaction,

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{M}^{\neq} \rightarrow \mathrm{X} + \mathrm{Y}$$

where $M^{\neq}$ is the activated complex and X and Y are the final products, is expressed by Eq. (1).[3]

$$k = k_0\left(\frac{\beta_A \times \beta_B}{\beta_{M^{\neq}}}\right) \tag{1}$$

where k_0 is the rate constant in the gas phase at the ideal gas state of 1 atm, and β_i is the appropriate activity coefficient defined by Eq. (2) at a sufficiently low concentration of the solute, i:

$$\beta_i = \left(\frac{m_{gi}}{m_{li}}\right) \tag{2}$$

where m_{gi} stands for the concentration of the solute i in the vapor above the solution and m_{li} the concentration of the solute i in the solution.

The Henry constant for a solute, 2, in solvent 1 is defined by:

$$H_{2,1} = \operatorname*{limit}_{x_2 \to 0}\left(\frac{f_2}{x_2}\right) \tag{3}$$

where f_2 and x_2 stand for the fugacity and the mole fraction of the solute 2 respectively.

At sufficiently low pressures,

$$f_i = P_i \tag{4}$$

$$P_i = \left(\frac{n_i}{V}\right)\boldsymbol{RT} = m_{gi}\boldsymbol{RT} \tag{5}$$

The concentration of the solute i in the solution, m_{li} is expressed by:

$$m_{li} = \frac{n_i}{\sum_i n_i V_i} = \frac{n_i}{(\sum_i n_i) \times V_{\mathrm{soln.}}} = x_i \times V^{-1}{}_{\mathrm{soln.}} \tag{6}$$

where n_i, V_i and x_i stand for the moles, the partial molar volume, and the mole fraction of the component i respectively, and where $V_{\mathrm{soln.}}$ stands for the molar volume of the solution.

At a sufficiently low concentration of the solute, from a combination of Eqs. (3), (4), (5) and (6), Eq. (2) reduces to:

$$\beta_i = \left(\frac{H_i \times V_{\mathrm{solv.}}}{\boldsymbol{RT}}\right) \tag{7}$$

[*1] Part I: Y. Kondo and N. Tokura, This Bulletin, **37**, 1148 (1964).

1) For a recent review, C. Reichart, *Angew. Chem.*, **77**, 30 (1965).

2) J. B. Hine, *J. Am. Chem. Soc.*, **82**, 5129 (1960).

3) Y. Kondo and N. Tokura, This Bulletin, **37**, 1148 (1964).

4) S. Glasstone *et al.* "The Theory of Rate Processes," McGraw Hill, New York (1941), Chap. 8.

5) J. B. Rossell, *J. Chem. Soc.*, **1963**, 5183.

6) H. S. Venkataraman and S. C. Hinshelwood, *ibid.*, **1960**, 4986.

7) See references in Ref. 2.

where H_i is the Henry constant of the solute i and $V_{\mathrm{solv.}}$, the molar volume of the solvent.
By using Eq. (7), the rate constant in the j solvent is expressed by:

$$k_j = k_0\left(\frac{H_{\mathrm{A},j} \times H_{\mathrm{B},j}}{H_{\mathrm{M}^{\neq},j}}\right)\left(\frac{V_j}{\boldsymbol{R}T}\right) \tag{8}$$

Similarly, the rate constant in mixed solvents is:

$$k_{mix} = k_0\left(\frac{H_{\mathrm{A},mix} \times H_{\mathrm{B},mix}}{H_{\mathrm{M}^{\neq},mix}}\right)\left(\frac{V_{mix}}{\boldsymbol{R}T}\right) \tag{9}$$

where $H_{i,mix}$ is the Henry constant of a component, i, in a mixed solvent and V_{mix}, the molar volume of a mixed solvent.

The Henry Constant in A Binary Mixed Solvent. *I) The Henry Constant in A Regular Solution.* In order to be consistent with the notation introduced by Lewis and Randall,[8] we designate the solute by the subscript 2, and the solvent, by the subscripts 1 and 4.

If the molar excess free energies of the three binaries are written in the one-parameter Margules expressions:

$$(g_{12}^E/\boldsymbol{R}T) = \alpha_{12}x_1x_2 \tag{10}$$

$$(g_{14}^E/\boldsymbol{R}T) = \alpha_{14}x_1x_4 \tag{11}$$

$$(g_{24}^E/\boldsymbol{R}T) = \alpha_{24}x_2x_4 \tag{12}$$

where the α's are empirical coefficients obtained from binary data, the molar excess free energy of the ternary solution cosisting of the three component 1, 2 and 4 is assumed to be:

$$(g_{124}^E/\boldsymbol{R}T) = \alpha_{12}x_1x_2 + \alpha_{14}x_1x_4 + \alpha_{24}x_2x_4 \tag{13}$$

The Henry constant in this mixture has been theoretically proved by O'connell and Prausnitz to be:[9]

$$\ln H_{2,mix} = x_1 \ln H_{2,1} + x_4 \ln H_{2,4} - \alpha_{14}x_1x_4 \tag{14}$$

II) The Henry Constant in a Chemically Reacting Mixture. Expressions for the Activity Coefficients. In order to consider a system in which a specific interaction exists between the solute and the solvent molecules, we assume that the solute, 2, reacts with one of the two components, 1 and 4, to construct the mixed solvent, that is, a component 1, to produce an addition product, 3.

Let us consider a system which contains, in all, N_1 molecules of the component, 1, in all, N_2 molecules of the component, 2 and, in all, N_4 molecules of the component, 4. We suppose that the equilibrium system contains also M_3 molecules of the addition products, so that:

$$N_1 = M_1 + M_3 \tag{15}$$

$$N_2 = M_2 + M_3 \tag{16}$$

$$N_4 = M_4 \tag{17}$$

where M_i refers to the free molecules in solution.

If the molar-excess free energies of the six binaries are given by:

$$(g_{i\,j}^E/\boldsymbol{R}T) = \alpha_{ij}y_iy_j \tag{18}$$

where y_i is the mole fraction of the species i in solution, $M_i/\sum_i M_i$, the chemical potential of the species i in a tetramorous solution consisting of the species 1, 2, 3, and 4, μ_{il}, should be expressed by:

$$\begin{aligned}\mu_{1l} = \mu_{1\,l}^\circ + \boldsymbol{R}T \ln y_1 + \boldsymbol{R}T\{&y_2(1-y_1)\alpha_{12} \\ &+ y_3(1-y_1)\alpha_{13} + y_4(1-y_1)\alpha_{14} \\ &- y_2y_3\alpha_{23} - y_2y_4\alpha_{24} - y_3y_4\alpha_{34}\}\end{aligned} \tag{19}$$

$$\begin{aligned}\mu_{2l} = \mu_{2\,l}^\circ + \boldsymbol{R}T \ln y_2 + \boldsymbol{R}T\{&y_1(1-y_2)\alpha_{12} \\ &+ y_3(1-y_2)\alpha_{23} + y_4(1-y_2)\alpha_{24} \\ &- y_1y_3\alpha_{13} - y_1y_4\alpha_{14} - y_3y_4\alpha_{34}\}\end{aligned} \tag{20}$$

$$\begin{aligned}\mu_{3l} = \mu_{3\,l}^\circ + \boldsymbol{R}T \ln y_3 + \boldsymbol{R}T\{&y_1(1-y_3)\alpha_{13} \\ &+ y_2(1-y_3)\alpha_{23} + y_4(1-y_3)\alpha_{34} \\ &- y_1y_2\alpha_{12} - y_1y_4\alpha_{14} - y_2y_4\alpha_{24}\}\end{aligned} \tag{21}$$

Further, we assume that an addition product presents only in the liquid phase and the gas phase constructs an ideal gas mixture consisting of 1, 2, and 4 components. Then, in an equlibrium the following relations should be satisfied:

$$\mu_{1g} = \mu_{1l} \tag{22}$$

$$\mu_{2g} = \mu_{2l} \tag{23}$$

$$\mu_{4g} = \mu_{4l} \tag{24}$$

$$\mu_{1l} + \mu_{2l} = \mu_{3l} \tag{25}$$

where μ_{ig} is the chemical potential of a componet i in the gas phase. From the combination of Eqs. 20 and 23, the fugacity of a component 2, f_2, is given by:

$$\begin{aligned}\ln f_2 = \ln f_2^\circ + \ln y_2 &+ y_1(1-y_2)\alpha_{12} \\ &+ y_3(1-y_2)\alpha_{23} + y_4(1-y_2)\alpha_{24} \\ &- y_1y_3\alpha_{13} - y_1y_4\alpha_{14} - y_3y_4\alpha_{34}\end{aligned} \tag{26}$$

where f_2° stands for the fugacity of the pure component 2. If the mole fraction is defined in terms of the moles of the pure component, so that $x_i = N_i/\sum N_i$, the activity coefficient of the solvent standard state is given by:

$$\gamma_i = \frac{f_i}{f_1^\circ \times x_i} \tag{27}$$

and, from Eqs. (26) and (27),

$$\begin{aligned}\ln \gamma_2 = \ln(y_2/x_2) &+ y_1(1-y_2)\alpha_{12} \\ &+ y_3(1-y_2)\alpha_{23} + y_4(1-y_2)\alpha_{24} \\ &- y_1y_3\alpha_{13} - y_1y_4\alpha_{14} - y_3y_4\alpha_{34}\end{aligned} \tag{28}$$

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[8] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill, New York (1923); 2nd Ed. (revised by K. S. Pitzer and L. Brewer, 1961).

[9] J. P. O'connell and J. M. Prausnitz, *Ind. & Eng. Chem. Fundamentals,* **3,** 347 (1964).

Relation between Symmetric and Asymmetric Activity Coefficients. Prigogine and Defay[10] showed that, in a binary solution, the activity coefficient of the solvent standard state, γ_2, is related to that of the solute standard state, γ_2^*, by:

$$(\gamma_2/\gamma_2^*) = (H_2/f_2^\circ) \tag{29}$$

where H_2 is the Henry constant for a component 2 in the mixture and where f_2° is the fugacity of pure liquid 2. From[9]

$$\operatorname*{Limit}_{x_2\to 0} \gamma_2 = (H_2/f_2^\circ) \tag{30}$$

substitution gives:[9]

$$(\gamma_2/\gamma_2^*) = \operatorname*{Limit}_{x_2\to 0} \gamma_2 \tag{31}$$

For the binary containing components 1 and 2, the definition of the activity coefficient of the component 2 is the same as that for the ternary, so that[9]:

$$(\gamma_2/\gamma_2^*) = \frac{\gamma_{2,1}}{\gamma^*_{2,1}} = \frac{H_{2,1}}{f_2^\circ} = \operatorname*{Limit}_{x_2\to 0} \gamma_{2,1} \tag{32}$$

For the binary containing components 2 and 4, the limit of the activity coefficient of the component 2 as defined in Eq. (30) is different from that of the ternary (Eq. (32))[9]:

$$(\gamma_{2,4}/\gamma^*_{2,4}) = (H_{2,4}/f_2^\circ) = \operatorname*{Limit}_{x_2\to 0} \gamma_{2,4} \tag{33}$$

But

$$\begin{aligned}(\gamma_2/\gamma_2^*) &= (H_{2,4}/f_2^\circ)(H_{2,1}/H_{2,4}) \\ &= (\gamma_{2,4}/\gamma^*_{2,4})(H_{2,1}/H_{2,4}) \\ &= (\operatorname*{Limit}_{x_2\to 0} \gamma_{2,4})(H_{2,1}/H_{2,4}) \end{aligned} \tag{34}$$

or

$$\operatorname*{Limit}_{x_2\to 0} \gamma_{2,1} = (\operatorname*{Limit}_{x_2\to 0} \gamma_{2,4})(H_{2,1}/H_{2,4}) \tag{35}$$

If the molar-excess free energy for the 2-4 binary is given by:

$$(g^E_{2,4}/\boldsymbol{R}T) = \alpha_{24}x_2x_4 \tag{36}$$

then;

$$\ln \gamma_{2,4} = \alpha_{24}x_4{}^2 \tag{37}$$

From Eq. (37),

$$\operatorname*{limit}_{x_2\to 0} \gamma_{2,4} = \exp(\alpha_{2,4}) \tag{38}$$

In order to calculate the left-hand side of Eq. (35), we consider a mixture consisting of components 1 and 2, that is, a chemically-reacting mixture similar to that mentioned above, though not equal in the absence of the component 4.
Much as in Eqs. (15), (16), (19), (20), (21), and (28),

$$N_1 = M_1 + M_3 \tag{39}$$

$$N_2 = M_2 + M_3 \tag{40}$$

$$\begin{aligned}\mu_{1l} = \mu^\circ_{1l} + \boldsymbol{R}T\ln y_1 + \boldsymbol{R}T\{y_2(1-y_1)\alpha_{12} \\ + y_3(1-y_1)\alpha_{13} - y_2y_3\alpha_{23}\}\end{aligned} \tag{41}$$

$$\begin{aligned}\mu_{2l} = \mu^\circ_{2l} + \boldsymbol{R}T\ln y_2 + \boldsymbol{R}T\{y_1(1-y_2)\alpha_{12} \\ + y_3(1-y_2)\alpha_{23} - y_1y_3\alpha_{13}\}\end{aligned} \tag{42}$$

$$\begin{aligned}\mu_{3l} = \mu^\circ_{3l} + \boldsymbol{R}T\ln y_3 + \boldsymbol{R}T\{y_1(1-y_3)\alpha_{13} \\ + y_2(1-y_3)\alpha_{23} - y_1y_2\alpha_{12}\}\end{aligned} \tag{43}$$

$$\begin{aligned}\ln \gamma_2 = \ln(y_2/x_2) + y_1(1-y_2)\alpha_{12} \\ + y_3(1-y_2)\alpha_{23} - y_1y_3\alpha_{13}\end{aligned} \tag{44}$$

where N_1 and N_2 are the total number of molecules of the components 1 and 2, M_1 and M_2, the number of free molecules of the components 1 and 2 in a solution, and M_3, the number of the addition product, y_i and x_i are, then, given by

$$y_i = \frac{M_i}{\sum_i M_i} \tag{45}$$

$$x_i = \frac{N_i}{\sum_i N_i} \tag{46}$$

Since, in equilibrium,

$$\mu_{1l} + \mu_{2l} = \mu_{3l} \tag{47}$$

$$\begin{aligned}-\Delta\mu^\circ_l = (\mu^\circ_{1l} + \mu^\circ_{2l} - \mu^\circ_{3l}) = \\ \boldsymbol{R}T\Big\{\ln\left(\frac{y_3}{y_1y_2}\right) - (y_1 + y_2 - y_1y_2)\alpha_{12} \\ + (y_1 - y_3 + y_1y_3)\alpha_{13} \\ + (y_2 - y_3 + y_2y_3)\alpha_{23}\Big\}\end{aligned} \tag{48}$$

Since, at a sufficiently low concentration of the component 2, the terms below the second on the right-hand side of Eq. (48) lead to a constant of:

$$\boldsymbol{R}T\ln K = \ln\left(\frac{y_3}{y_1y_2}\right) \tag{49}$$

Under the conditions of Eqs. (39), (40), (45), (46), and (49), the limit of Eq. (44) yields:

$$\operatorname*{limit}_{x_2\to 0} \gamma_{2,1} = \frac{1}{(K+1)} \tag{50}$$

Therefore, α_{12} can be omitted from the equation. From Eqs. (35), (38), and (50),

$$\frac{1}{(K+1)} = \left(\frac{H_{2,1}}{H_{2,4}}\right)\exp(\alpha_{24}) \tag{51}$$

The Henry Constant in The Chemically-reacting Mixture. Recalling the definition of γ_2^*, in mixed solvents we have:[9]

$$\gamma_2^* = \left(\frac{f_{2\text{ in mixed solvent}}}{x_2H_{2,1}}\right) \tag{52}$$

The Henry constant for the solute 2 in a mixed solvent is given by:[9]

$$H_{2,\,mix} = \operatorname*{limit}_{x_2\to 0}\left(\frac{f_2}{x_2}\right)_{\text{mixed solvent}} \tag{53}$$

From Eqs. (52) and (53),[9]

$$\operatorname*{limit}_{x_2\to 0} \gamma_2^* = \left(\frac{H_{2,mix}}{H_{2,1}}\right) \tag{54}$$

The combination of Eqs. (32), (50), and (51) gives:

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[10] I. Prigogine and R. Defay, "Chemical Thermodynamics," Longmans, London (1954).

$$\begin{aligned}\gamma_2 &= \gamma_2{}^* \lim_{x_2\to 0} \gamma_{2,1} = \gamma_2{}^* \times \left(\frac{1}{K+1}\right)\\ &= \gamma_2{}^* \times \left(\frac{H_{2,1}}{H_{2,4}}\right) \exp(\alpha_{24}) \qquad (55)\end{aligned}$$

From Eqs. (28) and (55),

$$\begin{aligned}\ln \gamma_2 &= \ln \gamma_2{}^* + \ln\left(\frac{H_{2,1}}{H_{2,4}}\right) + \alpha_{24}\\ &= \ln(y_2/x_2) + y_1(1-y_2)\alpha_{12}\\ &\quad + y_3(1-y_2)\alpha_{23} + y_4(1-y_2)\alpha_{24}\\ &\quad - y_1y_3\alpha_{13} - y_1y_4\alpha_{14} - y_3y_4\alpha_{34} \qquad (56)\end{aligned}$$

Since, when the solute is extremely dilute, we can let $y_2=y_3=0$, the combination of Eqs. (19), (20), (21), and (25) yields:

$$\begin{aligned}-\Delta\mu_l^\circ &= (\mu^\circ_{1l} + \mu^\circ_{2l} - \mu^\circ_{3l})\\ &= \boldsymbol{R}T \ln\left(\frac{y_3}{y_1y_2}\right) + \boldsymbol{R}T\{y_1(\alpha_{13} - \alpha_{12})\\ &\quad + y_4(\alpha_{34} - \alpha_{24} - \alpha_{14}) + y_1y_4\alpha_{14}\} \qquad (57)\end{aligned}$$

Since the second term on the right-hand side of Eq. (57) is negligibly small, much as in Eq. (49),[*2]

$$\boldsymbol{R}T \ln K = \boldsymbol{R}T \ln\left(\frac{y_3}{y_1y_2}\right) \qquad (58)$$

Under the conditions of Eqs. (15), (16), (17), and (58),

$$\lim_{x_2\to 0}\left(\frac{y_2}{x_2}\right) = \left(\frac{1}{x_1K+1}\right) \qquad (59)$$

Since

$$y_2, y_3 \to 0,\ y_1 \to x_1, \text{ and } y_4 \to x_4 \text{ as } x_2 \to 0$$

by the substitution of Eq. (59) into Eq. (56), and after rearrangement, a limit of Eq. (56) gives:

$$\begin{aligned}\lim_{x_2\to 0} \ln \gamma_2{}^* &= \ln\left(\frac{H_{2,4}}{H_{2,1}}\right) + \ln\left(\frac{1}{x_1K+1}\right)\\ &\quad + (x_4-1)\alpha_{24} - x_1x_4\alpha_{14} \qquad (60)\end{aligned}$$

therefore, α_{12} can be omitted from the equation. The combination of Eqs. (51), (54), and (60) gives the desired result:

$$\begin{aligned}\ln H_{2,mix} &= x_1 \ln H_{2,1} + x_4 \ln H_{2,4}\\ &\quad + \{x_1 \ln(K+1) - \ln(x_1K+1) - x_1x_4\alpha_{14}\} \qquad (61)\end{aligned}$$

III) Theoretical Expressions for the Rate Constants. In order to analyze the rates of reaction in binary mixed solvents, let us consider the reaction in solution on the bases of the molecular models.

The first model is the system in which all the solutes, the two reactants, A and B, and a transition complex, $M^{\neq}$, yield regular solutions with both of the solvents, 1 and 4.

The theoretical expression for the rate constant in a binary mixed solvent, k_{mix}, can be obtained by the substitution of Eq. (14) into Eq. (9) for every solute:

$$\begin{aligned}\ln k_{mix} &= x_1 \ln k_1 + x_4 \ln k_4 - \alpha_{14}x_1x_4\\ &\quad + \ln V_{mix} - (x_1 \ln V_1 + x_4 \ln V_4) \qquad (62)\end{aligned}$$

where k_i stands for the rate constant in a pure solvent, i. If $V_{mix}=V_1=V_4$,

$$\ln k_{mix} = x_1 \ln k_1 + x_4 \ln k_4 - \alpha_{14}x_1x_4 \qquad (63)$$

The second model is a system in which the solutes A and B yield a regular solution with both solvents, 1 and 4, but a transition complex reacts with the solvent 1 to form an addition complex. In the second case, the expression for the rate constant can be given by the substitution of Eq. (14) into the numerator of Eq. (9), and by that of Eq. (61) into the denominator of Eq. (9);

$$\begin{aligned}\ln k_{mix} &= x_1 \ln k_1 + x_4 \ln k_4\\ &\quad - \{x_1 \ln(K+1) - \ln(x_1K+1) + x_1x_4\alpha_{14}\}\\ &\quad + \ln V_{mix} - x_1 \ln V_1 - x_4 \ln V_4 \qquad (64)\end{aligned}$$

If $V_{mix} = V_1 = V_4$,

$$\begin{aligned}\mathrm{In}\quad k_{mix} &= x_1 \ln k_1 + x_4 \ln k_4 - \{x_1 \ln(K+1)\\ &\quad - \ln(x_1K+1) + x_1x_4\alpha_{14}\} \qquad (65)\end{aligned}$$

From Eq. (9) and (51),

$$\begin{aligned}(k_1/k_4) &= \left(\frac{H_{\mathrm{A},1} \times H_{\mathrm{B},1}}{H_{\mathrm{M}^{\neq},1}}\right)\left(\frac{H_{\mathrm{M}^{\neq},4}}{H_{\mathrm{A},4} \times H_{\mathrm{B},4}}\right)\left(\frac{V_1}{V_4}\right)\\ &= \left(\frac{H_{\mathrm{A},1}}{H_{\mathrm{A},4}}\right)\left(\frac{H_{\mathrm{B},1}}{H_{\mathrm{B},4}}\right)\left(\frac{V_1}{V_4}\right)(K+1) \exp(\alpha_{\mathrm{M}^{\neq}4}) \qquad (66)\end{aligned}$$

Since, in a regular solution,[9)]

$$\left(\frac{H_{2,1}}{H_{2,4}}\right) = \exp(\alpha_{21} - \alpha_{24}) \qquad (67)$$

the value for (k_1/k_4) mainly depends on the value of the equilibrium constant, K. If the α's values can not be refered to the literature, it seems reasonable to decide that the solvent in which the reaction proceeds more rapidly is to be designated by the subscript 1, as the solvent with which the transition complex reacts to form an addition product.

In order to test the validity of the derived equations, applications have been made to the popular second-order reactions, the Menschutkin reactions and the benzoylation reaction. The rate constants measured by Hinshelwood *et al.*[6,11)] are used in the following calculations.

Since these reactions proceed more rapidly in nitrobenzene, nitrobenzene has been taken for a component 1 in these systems.

In the second model the values for K have been so determined that the value calculated for k

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[*2] The equilibrium constant, K, in Eq. (58) slightly differs from that in Eq. (49) because of the presence of the emipirical coefficients, α_{ij}, in Eqs. (48) and (57). However, as a first approximation the present authors have ignored the difference between them, since the terms containing these coefficients are negligibly small.

11) H. C. Raine and C. N. Hinshelwood, *J. Chem. Soc.*, **1939**, 1379.

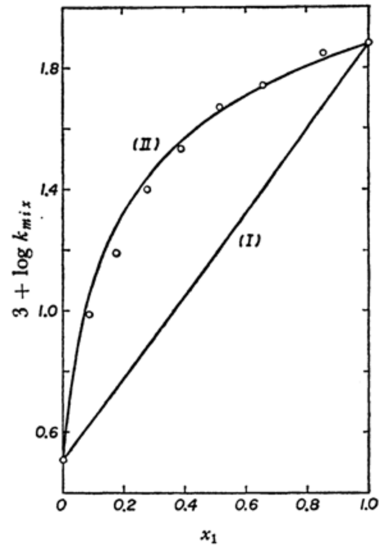

Fig. 1. Plot of log k_{mix} vs. x_1.
The Menschutkin reaction of methyliodide with triethylamine in benzene-nitrobenzene mixture at 40°C.
x_1: mole fraction of nitrobenzene, $K=43$, $\alpha_{14}=0.10$ (estimated from the equilibrium vapour pressure data)
○: experimental results in Ref. 11
—: calcd., (I): the first model, (II): the second model

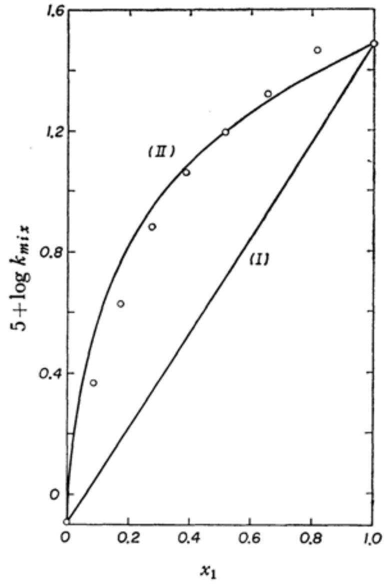

Fig. 2. Plot of log k_{mix} vs. x_1.
The Menschutkin reaction of isopropyliodide with pyridine in benzene-nitrobenzene at 99.8°C.
x_1: mole fraction of nitrobenzene, $K=37$, $\alpha_{14}=0.10$ (estimated from the equilibrium vapor pressure data)
○: experimental results in Ref. 11
—: calcd., (I): the first model, (II): the second model

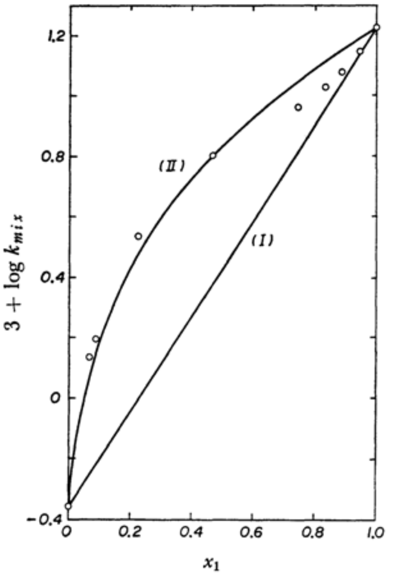

Fig. 3. Plot of log k_{mix} vs. x_1.
Benzoylation of *m*-nitroaniline in benzene-nitrobenzene at 25°C.
x_1: mole fraction of nitrobenzene $K=23.5$, $\alpha_{14}=0.10$ (estimated from the equilibrium vapor pressure data)
○: experimental results in Ref. 6
—: calcd., (I): the first model, (II): the second model

from Eq. (64) is equal to the experimental results at $x_1=x_5=0.5$.

Comparisons with the experimental results are shown in Figs. 1, 2, and 3.

From these figures it may be concluded that the second model, which takes interactions between a transition complex and solvent molecules into consideration, accurately illustrates the behavior of these reactions in mixed solvents.

It has generally been accepted that, in these reactions, the activated complexes have polar structures and that these are solvated to a considerable extent in such polar solvents as nitrobenzene, whereas the reactants are unsolvated.[3,6,11)]

Considering that regular solutions are characterized by the absence of any such specific interactions between molecules as the hydrogen bonding and acid-base association,[8)] the first model would not be suitable for these reactions.

The large values of K which have been calculated

TABLE 1. REACTIONS IN A BENZENE-NITROBENZENE MIXTURE

Reaction	k_1/k_4	$K+1$	$(k_1/k_4)/(K+1)$
MeI + Et_3N	23.6[11)]	44	0.54
i-PrI + Pyridine	38.5[11)]	38	1.01
m-Nitroaniline + Benzoylchloride	39.0[6)]	24.5	1.59

from the comparison of the theory with the experimental results show that specific interactions exist between the activated complex and the nitrobenzene molecules.

The authors have assumed, on the basis of Eqs. (66) and (67), that the values of (k_1/k_4) mainly depend upon the equilibrium constant, K.

Since the values of $(k_1/k_4)/K+1$ are close to unity, as is shown in the table, the above assumption may be proved.

Although these simplified pictures of such aspects of liquid solutions as the construction of a regular solution or the formation of an addition product can not be expected to have general validity, these should be good approximations for the study of the solvent effects on the reaction rate.