BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN   VOL. 41   987—992 (1968)

Reaction Rates in Binary Mixed Solvents. IV[1]

Yasuhiko KONDO, Yoshitoshi HONJO and Niichiro TOKURA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Higashinoda, Miyakojima-ku, Osaka

(Received October 18, 1967)

Three cases of combinations of the solvation free-energy differences in two solvents, with respect to a reactant and an activated complex, have been proposed. The theoretical expressions for the rate constant and for the activation energy in binary mixed solvents have been derived for each model. From the theoretical calculations based on these models, it has been demonstrated that the behavior of a system in which the reaction rates are mainly dependent on the difference in the solvation energies of an activated complex can be distinguished from behavior of a system where the reaction rates are controlled by the difference in the solvation energies of a reactant. The reaction rates of the Menschutkin reaction in binary mixed solvents containing liquid sulfur dioxide as one component of the mixed solvent have been analyzed on the basis of these models.

According to the theory of the absolute reaction rates,[2] a rate constant is expressed as the difference in the free energies between reactants and activated complexes. Therefore, the rate constants in a solution would be affected not only by the individual solvation of the reactants or an activated complex, but also by the combinations of these factors in several ways. In the theoretical treatment of the effects of solvents on reaction rates, these facts should be taken into consideration.

Some of the factors which influence the rates of a reaction in solution might be made clear by an analysis of the rate constants measured in pure solvents, but the study of other factors might have to depend on investigations of the rate constants measured in mixed solvents.

In previous studies[1] the present authors have reported the theoretical treatment of the reaction rates in binary mixed solvents.

In this paper we will discuss theoretically what information can be obtained on the solvation of a solute from an analysis of the reaction rates measured in binary mixed solvents.

Discussion

The Model of a Solvation and Reaction Rates in Solution. The effects of solvents on the rates of a reaction in solution can be replaced by the dependence of the activation free energies on the nature of a solvent. If the influence of a solvent on the reaction rates in solution is assumed to be caused by its influence on the solvation of reactants and an activated complex, then the following combinations of the solvation free-energy differences (Fig. 1) can be considered as factors which make the reaction rates different in two solvents; the solvent in which the reaction proceeds more rapidly is expressed by the subscript 1. $\Delta F_4^{\neq}$ and $\Delta F_1^{\neq}$ stand for the activation free energy in the solvents 4 and 1 respectively.

Model I represents a system in which both a reactant and an activated complex are more solvated in the solvent 1 than in the solvent 4.

Model II is a system where an activated complex is more solvated in the solvent 1, while a reactant is more solvated in the solvent 4.

Model III stands for a system where both a

---

[1] Part III: Y. Kondo and N. Tokura, This Bulletin, **40**, 1438 (1967).

[2] S. Glasstone *et al.*, "The Theory of Rate Processes," McGraw-Hill Book Company, New York (1941).

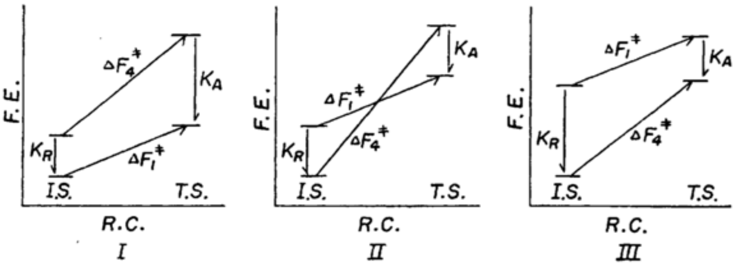

Fig. 1. The model of a solvation.

reactant and an activated complex are more solvated in the solvent 4 than in the solvent 1.

Any combination of the two solvents in which the rates of the same reaction are differentiated from each other should correspond to one of the three solvation models represented in Fig. 1.

Now, let us consider what variations should be introduced into the theoretical expressions for the rate constants and the activation energies in binary mixed solvents according to the solvation models presented above.

In previous papers¹⁾ the authors have represented a system in which there are no specific interactions among the components by the construction of a regular solution, and have assumed the formation of an addition product as the model for a system in which attractive interactions are observed between the components. With the object of applying the above models to the three models mentioned previously, the following two assumptions will be made hereafter: 1) A system in which no specific interactions can be observed among the components constructs a regular solution, and 2) In the systems where a substantial difference in the solvation energies of a solute exists between the two solvents, we assume that the solute reacts to form an addition product with the solvent having the stronger solvating power, whereas the solute forms a regular solution with the other solvent, with the weaker solvating power.

Insofar as the above assumptions are adopted, the theoretical expressions for the rate constants and the activation energies in binary mixed solvents can be derived from suitable combinations of the expressions for Henry's constant in a regular solution and in an associated solution for all of the three models described previously.

The theoretical expressions for Henry's constant in binary mixed solvents and the relations between Henry's constants in pure solvents may be summarized as follows.

Shown below is a system in which the solute 2 constructs a regular solution with both of the two solvents, 1 and 4:³⁾

$$\ln H_{2,\mathrm{mix}} = x_1 \ln H_{2,1} + x_4 \ln H_{2,4} - x_1 x_4 \alpha_{14} \quad (1)$$

$$(H_{2,1}/H_{2,4}) = \exp(\alpha_{21} - \alpha_{24}) \quad (2)$$

Shown below is a system in which the solute 2 reacts to form an addition product with the solvent 1, whereas it constructs a regular solution with the solvent 4:¹⁾

$$\ln H_{2,\mathrm{mix}} = x_1 \ln H_{2,1} + x_4 \ln H_{2,4} + x_1 \ln(K+1) - \ln(x_1 K + 1) - x_1 x_4 \alpha_{14} \quad (3)$$

$$(H_{2,1}/H_{2,4}) = \frac{1}{(K+1)} \exp(-\alpha_{24}) \quad (4)$$

Shown below is a system in which the solute 2 reacts to form an addition product with the solvent 4, whereas it constructs a regular solution with the solvent 1:

$$\ln H_{2,\mathrm{mix}} = x_1 \ln H_{2,1} + x_4 \ln H_{2,4} + x_4 \ln(K+1) - \ln(x_4 K + 1) - x_1 x_4 \alpha_{14} \quad (5)$$

$$(H_{2,4}/H_{2,1}) = \frac{1}{(K+1)} \exp(-\alpha_{21}) \quad (6)$$

The Theoretical Expressions for the Reaction Rate in Binary Mixed Solvents. In this paper the theoretical expressions will be derived for the general second-order reaction:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{M}^{*} \rightarrow \text{Products}$$

For the sake of simplicity, the reactant A will be assumed to construct a regular solution with both of the two solvents, 1 and 4.

According to previous discussions,¹⁾ the rate constant in a binary mixed solvent and the ratio of the rate constant in two sorts of pure solvents are expressed by Eqs. (7) and (8) respectively:

$$k_{\mathrm{mix}} = k_0 \left(\frac{H_{\mathrm{A,mix}} \times H_{\mathrm{B,mix}}}{H_{\mathrm{M}^{\neq},\mathrm{mix}}} \right) \left(\frac{V_{\mathrm{mix}}}{\boldsymbol{RT}} \right) \quad (7)$$

$$(k_1/k_4) = \left(\frac{H_{\mathrm{A},1}}{H_{\mathrm{A},4}} \right) \left(\frac{H_{\mathrm{B},1}}{H_{\mathrm{B},4}} \right) \left(\frac{H_{\mathrm{M}^{\neq},4}}{H_{\mathrm{M}^{\neq},1}} \right) \left(\frac{V_1}{V_4} \right) \quad (8)$$

Model I. Since, in this system, both a reactant and an activated complex are more solvated in the solvent 1, we assume that both the reactant B and an activated complex react to form addition products with the solvent 1.

The theoretical expression for the rate constant in a binary mixed solvent can then be derived by the substitution of Eq. (3) into Henry's constants of the solutes B and $\mathrm{M}^{\neq}$ in Eq. (7).

---

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

Accordingly, Eqs. (1) and (2) will be used for a solute, A, in all the equations.

$$\ln k_{\text{mix}} = x_1 \ln k_1 + x_4 \ln k_4 + \left\{ x_1 \ln\left(\frac{K_R+1}{K_A+1}\right) - \ln\left(\frac{x_1K_R+1}{x_1K_A+1}\right) - x_1x_4\alpha_{14} \right\} + \ln V_{\text{mix}} - x_1 \ln V_1 - x_4 \ln V_4 \tag{9}$$

In Eq. (9), K_R and K_A stand for the equilibrium constants of a reactant and an activated complex respectively, when they form addition products with a particular solvent.

The ratio of the rate constant, (k_1/k_4), is given by the substitution of Eq. (4) into Henry's constants of solutes, B and $M^{\neq}$ in Eq. (8):

$$(k_1/k_4) = \exp(\alpha_{A1} - \alpha_{A4}) \times \exp(\alpha_{M^{\neq}4} - \alpha_{B4}) \times \left(\frac{K_A+1}{K_R+1}\right)\left(\frac{V_1}{V_4}\right) \tag{10}$$

The expressions for an activation energy are given by the differentiation of Eqs. (9) and (10) with respect to the temperature:

$$\Delta E^{\neq}_{\text{mix}} = x_1 \Delta E_1{}^{\neq} + x_4 \Delta E_4{}^{\neq} - x_1x_4 \left\{ \frac{\Delta H^\circ{}_R}{(1+1/K_R)(x_1+1/K_R)} - \frac{\Delta H^\circ{}_A}{(1+1/K_A)(x_1+1/K_A)} \right\} \tag{11}$$

$$(\Delta E_1{}^{\neq} - \Delta E_4{}^{\neq}) = \left\{ \frac{\Delta H^\circ{}_A}{(1+1/K_A)} - \frac{\Delta H^\circ{}_R}{(1+1/K_R)} \right\} \tag{12}$$

where $\Delta H^\circ{}_R$ and $\Delta H^\circ{}_A$ stand for the enthalpy change of a reactant and an activated complex respectively, accompanied by the formation of addition products with a particular solvent.

Model II. Since an activated complex is more solvated in the solvent 1, while a reactant is more solvated in the solvent 4, we assume that an activated complex forms an addition product with the solvent 1 and that the reactant B forms an addition product with the solvent 4.

Thus, the theoretical expression for a rate constant is given by the substitution of Eqs. (3) and (5) for Henry's constants of an activated complex and the reactant B in Eq. (7):

$$\ln k_{\text{mix}} = x_1 \ln k_1 + x_4 \ln k_4 + \{x_4 \ln(K_R+1) - \ln(x_4K_R+1) - x_1 \ln(K_A+1) + \ln(x_1K_A+1) - x_1x_4\alpha_{14}\} + \ln V_{\text{mix}} - x_1 \ln V_1 - x_4 \ln V_4 \tag{13}$$

The ratio of the rate constant is given by the combination of Eqs. (2), (4), (6), and (8) as follows:

$$(k_1/k_4) = \exp(\alpha_{A1} - \alpha_{A4}) \times \exp(\alpha_{B1} + \alpha_{M^{\neq}4}) \times (K_A+1)(K_R+1)\left(\frac{V_1}{V_4}\right) \tag{14}$$

The expressions for an activation energy are given by the differentiation of Eqs. (13) and (14) with respect to the temperature:

$$\Delta E^{\neq}_{\text{mix}} = x_1 \Delta E_1{}^{\neq} + x_4 \Delta E_4{}^{\neq} + x_1x_4 \left\{ \frac{\Delta H^\circ{}_A}{(1+1/K_A)(x_1+1/K_A)} - \frac{\Delta H^\circ{}_R}{(1+1/K_R)(x_4+1/K_R)} \right\} \tag{15}$$

$$(\Delta E_1{}^{\neq} - \Delta E_4{}^{\neq}) = \left\{ \frac{\Delta H^\circ{}_R}{(1+1/K_R)} + \frac{\Delta H_A{}^\circ}{(1+1/K_A)} \right\} \tag{16}$$

Model III. Since both a reactant and an activated complex are more solvated in the solvent 4, we assume that both the reactant B and an activated complex form addition products with the solvent 4.

The theoretical expressions for a rate constant and for the ratio of rate constants are given by combinations of Eqs. (1), (5), and (7) and of Eqs. (2), (6), and (8), respectively:

$$\ln k_{\text{mix}} = x_1 \ln k_1 + x_4 \ln k_4 + \left\{ x_4 \ln\left(\frac{K_R+1}{K_A+1}\right) - \ln\left(\frac{x_4K_R+1}{x_4K_A+1}\right) - x_1x_4\alpha_{14} \right\} + \ln V_{\text{mix}} - x_1 \ln V_1 - x_4 \ln V_4 \tag{17}$$

$$(k_1/k_4) = \exp(\alpha_{A1} - \alpha_{A4}) \times \exp(\alpha_{B1} - \alpha_{M^{\neq}1}) \times \left(\frac{K_R+1}{K_A+1}\right)\left(\frac{V_1}{V_4}\right) \tag{18}$$

The expressions for an activation energy are given by the differentiation of Eqs. (17) and (18) with respect to the temperature:

$$\Delta E^{\neq}_{\text{mix}} = x_1 \Delta E_1{}^{\neq} + x_4 E_4{}^{\neq} + x_1x_4 \left\{ \frac{\Delta H^\circ{}_A}{(1+1/K_A)(x_4+1/K_A)} - \frac{\Delta H_R{}^\circ}{(1+1/K_R)(x_4+1/K_R)} \right\} \tag{19}$$

$$(\Delta E_1{}^{\neq} - \Delta E_4{}^{\neq}) = \left\{ \frac{\Delta H^\circ{}_R}{(1+1/K_R)} - \frac{\Delta H^\circ{}_A}{(1+1/K_A)} \right\} \tag{20}$$

Since in the three sorts of combination the solvation of an activated complex and that of a reactant are taken into consideration at the same time, in the theoretical expressions for the rate constants, as well as those for the activation energies, there exist two sorts of parameters, which represent the solvations of a reactant and of an activated complex, *i. e.*, K_R and K_A for the rate constants, $\Delta H^\circ{}_R$ and $\Delta H^\circ{}_A$, for the activation energies. However, these two parameters are related to one another by the theoretical expressions for the ratio of the rate constant, (k_1/k_4), or by those for the difference in the activation energies in pure solvents, $(\Delta E_1{}^{\neq} - \Delta E_4{}^{\neq})$.

Thus, there exists only one independent variable for the rate constant and for the activation energy in binary mixed solvents. In order to compare the characteristics of these models, calculations have been made for the system where $(k_1/k_4)=100$, $(\Delta E_1^{\ne}-\Delta E_4^{\ne})=(-6.0)$ [kcal·mol^{-1}], $V_1=V_4=V_{\text{mix}}$, and all the interaction coefficients, α_{ij}, are zero. The results are shown in Figs. 2 and 3, while the parameters used in the calculations are summarized in Table 1.

In the limiting case of $K_R=0$, both the differences in the rate constants and in the activation energies in pure solvents should be dependent on the difference between the two solvents in the solvation of an activated complex.

Therefore, in this case the differences between the I and II models should vanish.

In the model I the curves approach Curve 3 in the order of 1→2→3, while in the model II they do so in the order of 5→4→3, as the values of K_R and $(-\Delta H_R{}^{\circ})$ approach zero.

Similarly, in the limiting case of $K_A=0$, the influences of the solvents on the reaction rates in solution should be attributed to the differences between the two solvents in the solvation of a reactant.

Therefore, the differences between the models II and III should disappear. Then, in the model II the curves approach curve 9 in the order of 7→8→9, while in the model III they do so in the order of 11→10→9, as the values of K_A and $(-\Delta H^{\circ}{}_A)$ approach zero.

Curve 6 represents a system where $K_A=K_R$, and $\Delta H^{\circ}{}_A=\Delta H^{\circ}{}_R$. This is a system in which the solvation of an activated complex makes an contribution equivalent to that of a reactant to the

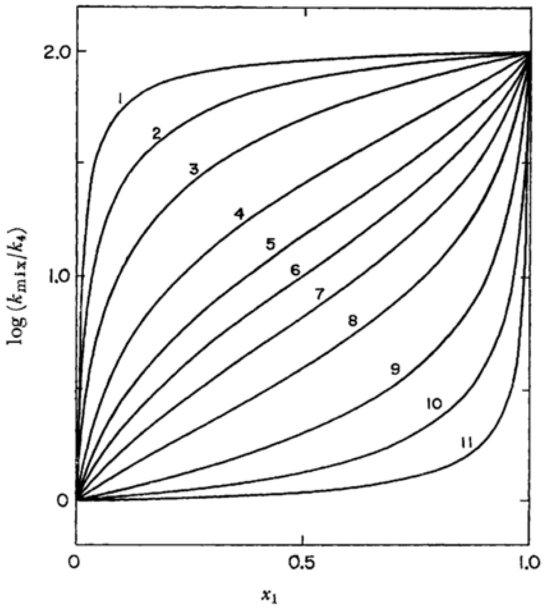

Fig. 2. The calculated values of log (k_{mix}/k_4) as a function of x_1.

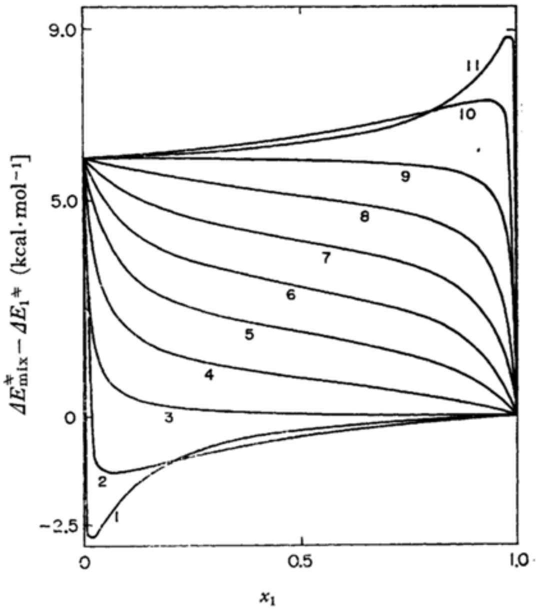

Fig. 3. The calculated values of $(\Delta E^{\ne}_{\text{mix}}-\Delta E_1^{\ne})$ as a function of x_1.

TABLE 1. THE PARAMETERS USED IN THE CALCULATIONS
$(k_1/k_4)=100$, $(\Delta E_1^{\ne}-\Delta E_4^{\ne})=(-6.0)$ [kcal·mol]

No.	The Model	K_A	K_R	$\Delta H^{\circ}{}_A/(1+1/K_A)$	$\Delta H^{\circ}{}_R/(1+1/K_R)$
1	I	1099	10.0	−10.0	−4.0
2	I	299	2.0	−8.0	−2.0
3	I or II	99	0	−6.0	0
4	II	32.33	2.0	−5.0	−1.0
5	II	15.66	5.0	−4.0	−2.0
6	II	9.0	9.0	−3.0	−3.0
7	II	5.0	15.66	−2.0	−4.0
8	II	2.0	32.33	−1.0	−5.0
9	II or III	0	99	0	−6.0
10	III	2.0	299	−2.0	−8.0
11	III	10.0	1099	−4.0	−10.0

The dimensions, $\Delta H^{\circ}{}_A$ and $\Delta H^{\circ}{}_R$: [kcal·mol] differences in the rate constants and the activation energies between the two solvents.

As the solvation of an activated complex exceeds that of a reactant in the contribution to the reaction rate, the positive deviation from linearity increases in the rate constants, while the negative deviation from linearity increases in the activation energies *i. e.*, in the order of 6→5→4. In contrast, as the solvation of a reactant exceeds that of an activated complex, the negative deviation from linearity increases in the rate constant, while the positive deviation from linearity increases in the activation energies, *i. e.*, in the order of 6→7→8.

In principle, it should be possible to determine, from the analysis of the reaction rates in binary mixed solvents, whether the differences in the rate constants and in the activation energies are due to the differences in the solvation of an activated complex or in the solvation of a reactant.

Comparison of the Theory with the Experimental Results. In previous papers[1,4] the

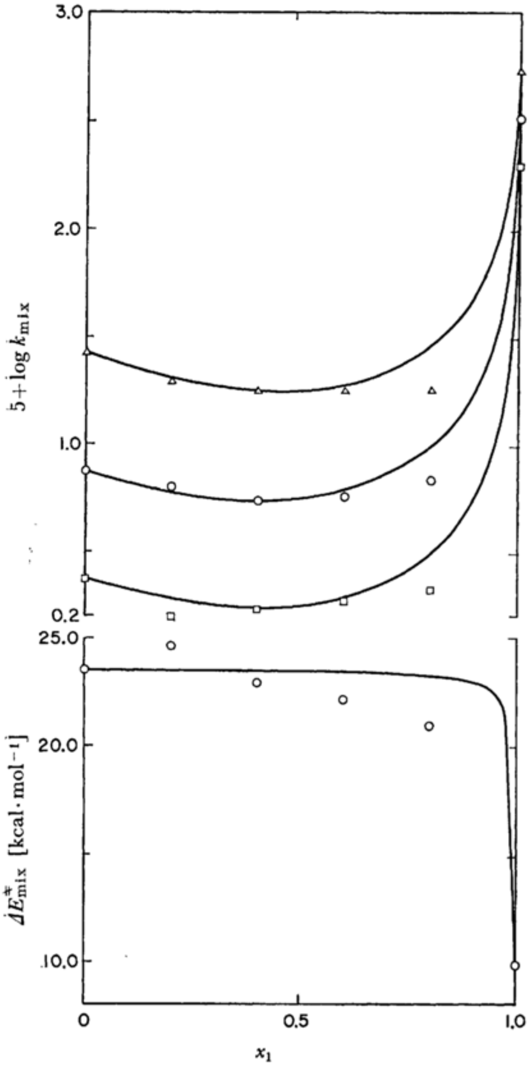

Fig. 4. Dependence of $\log k_{\mathrm{mix}}$ and $\Delta E^{\ddagger}_{\mathrm{mix}}$ for the reaction of triethylamine with methyl iodide in liq. SO_2 - benzene mixture upon mole fraction of benzene (x_1).
$K_R=357$, 30°C; $K_R=186$, 40°C; $K_R=106$, 50°C
$\alpha_{14}=0.973$ (refered to the value for liq. SO_2-isoprene mixture[5])
□ (30°C), ○ (40°C), △ (50°C): experimental results, ——: calculated results based on model 9.

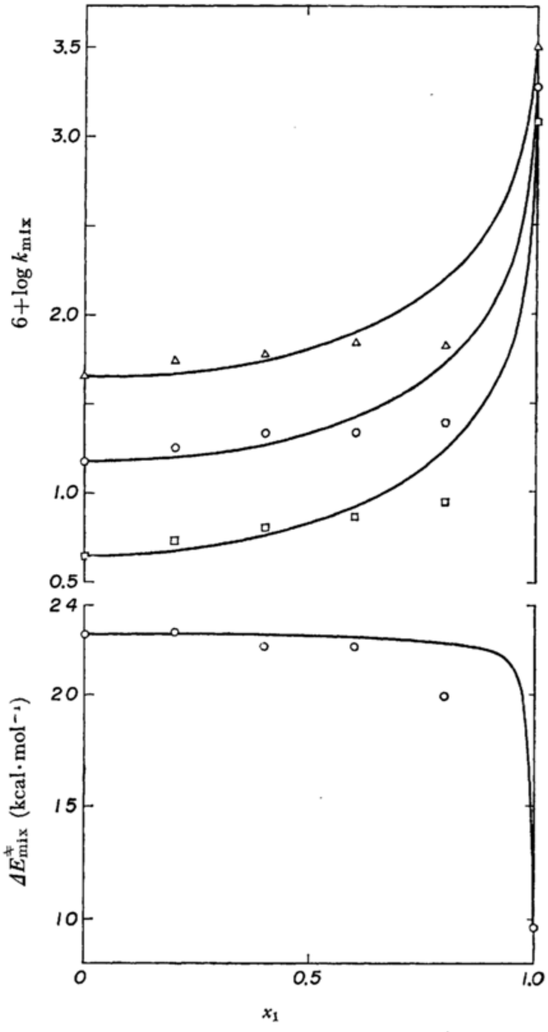

Fig. 5. Dependence of $\log k_{\mathrm{mix}}$ and $\Delta E^{\ddagger}_{\mathrm{mix}}$ for the reaction of dimethylbenzylamine with methyl iodide in liq. SO_2 - toluene mixture upon mole fraction of toluene (x_1).
$K_R=287$, 30°C; $K_R=148$, 40°C; $K_R=80.2$, 50°C
$\alpha_{14}=0.973$ (refered to the value for liq. SO_2-isoprene mixture[5])
□ (30°C), ○ (40°C), △ (50°C): experimental results, ——: calculated results based on model 9.

---

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

5) P. B. Ayscough, K. J. Ivin and J. H. O'Donnell, *Trans. Faraday Soc.*, **61**, 1601 (1965).

present authors have reported that, in most cases, positive deviations from linearity have been observed in the plots of $\log k_{\mathrm{mix}}$ *vs.* the composition of a solvent, and that these positive deviations from linearity should correspond to a significant specific solvation of an activated complex due to a more polar solvent.

According to the models proposed by the present authors, large negative deviations from linearity should be observed in systems where there exists a significant specific solvation of a reactant due to a less polar solvent.

The experimental results of the Menschutkin reaction in mixtures of liquid sulfur dioxide and aromatic solvents are shown in Figs. 4 and 5.

These results can be explained semiquantitatively by Model No. 9 in Table 1, as shown by the smooth curves of Figs. 4 and 5. Since, in that model, only the interaction between a reactant and liquid sulfur dioxide has been taken into consideration, only one parameter, that is, K_R, can be determined from the analysis of the experimental results.

It has been suggested by two of the present authors⁶⁾ that the rate of the Menschutkin reaction in liquid sulfur dioxide is mainly dependent on the specific solvation of amines by liquid sulfur dioxide. The semiquantitative agreement of the experimental results in binary mixed solvents with the calculated results based on Model No. 9 would then be reasonable, since in that model the specific interaction between a reactant and liquid sulfur dioxide is emphasized as the main source of the effects of the solvent on reaction rates.

---

6) N. Tokura and Y. Kondo, This Bulletin, **37**, 133 (1964).