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Reaction Rates in Binary Mixed Solvents. III

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The expressions for the activation energies in binary mixed solvents have been derived from the differentiation of the expressions for the rate constants in binary mixed solvents obtained in Part II of this series [Y. Kondo and N. Tokura, *Bull. Chem. Soc. Japan*, **40**, 1433 (1967).] with respect to the temperature. The activation energies in mixed solvents have been expressed in terms of the activation energies of the pure solvents, the equilibrium constant, and the composition of the solvent. From comparison with the experimental results, the model used by the authors has been proved to be valid for a consideration of the effects of solvents on the reaction rates and the activation parameters in binary mixed solvents.

In Part II of this series[1] devoted to the study of the effects of solvation on the reaction rates in a solution, the authors proposed two sorts of molecular models, and for the each model they developed a theoretical expression for the rate constant in binary mixed solvents.

These two models are: i), each of the reactants and the transition complex constructs a regular solution with both of the two solvents used in the reaction, and ii), the reactants behave much as in the first model, but the activated complex reacts with one of the two solvents to form an addition product. The latter model has been shown to be valid for the representation of the effects of the specific solvation on the reaction rates in mixed solvents.

If the molecular models offered by the authors have validity in representing the behavior of the reaction in the binary mixed solvents, the theoretical expressions for the activation parameters as well as for the rate constants derived on the basis of the molecular models should accurately describe the variation in these parameters with the composition of the mixed solvent.

In this paper the theoretical expressions for the activation energies in binary mixed solvents will be developed from the equations for the rate constant, and the experimental results for three examples will be compared.

Theoretical Expressions for the Activation Energies

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

The rate constant of a general bimolecular reaction in mixed solvents consisting of 1 and 4 components, k_{mix}, is given by the equations for each model.[1]

For the first model:

$$\ln k_{mix} = x_1 \ln k_1 + x_4 \ln k_4 - x_1 x_4 \alpha_{14} \tag{1}$$

For the second model:

$$\ln k_{mix} = x_1 \ln k_1 + x_4 \ln k_4 - \{x_1 \ln(K+1) - \ln(x_1 K + 1) + x_1 x_4 \alpha_{14}\} \tag{2}$$

where k_i, x_i, and α_{ij} refer to the rate constant in a pure solvent, i; the mole fraction of a solvent, i, and the empirical coefficient obtained from the vapor pressure data respectively.

Since the activation energy of the reaction carried out in a solvent, i, $\Delta E_i^{\neq}$, is defined by:

$$\left(\frac{\mathrm{d}\ln k_i}{\mathrm{d}T}\right)_p = \frac{\Delta E_i^{\neq}}{\boldsymbol{R}T^2} \tag{3}$$

the activation energy in the mixed solvent for these models, $\Delta E^{\neq}_{mix}$, should be given by the differentiation between Eqs. (1) and (2) with respect to the temperature.

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[1] Part II: Y. Kondo and N. Tokura, This Bulletin, **40**, 1433 (1967).

Then, for the first model:

$$\Delta E^{\neq}_{mix} = \boldsymbol{R}T^2\left(\frac{\mathrm{d}\ln k_{mix}}{\mathrm{d}T}\right)_p = x_1\Delta E_1{}^{\neq} + x_4\Delta E_4{}^{\neq} - x_1x_4 \times \boldsymbol{R}T^2\left(\frac{\mathrm{d}\alpha_{14}}{\mathrm{d}T}\right)_p \tag{4}$$

For the second model:

$$\Delta E^{\neq}_{mix} = \boldsymbol{R}T^2\left(\frac{\mathrm{d}\ln k_{mix}}{\mathrm{d}T}\right)_p = x_1\Delta E_1{}^{\neq} + x_4\Delta E_4{}^{\neq} - \boldsymbol{R}T^2\left\{x_1\left(\frac{\mathrm{d}\ln(K+1)}{\mathrm{d}T}\right)_p - \left(\frac{\mathrm{d}\ln(x_1K+1)}{\mathrm{d}T}\right)_p + x_1x_4\left(\frac{\mathrm{d}\alpha_{14}}{\mathrm{d}T}\right)_p\right\} \tag{5}$$

Since the temperature coefficient of the empirical coefficient, α_{ij}, is assumed to be small compared with the activation energies of the reaction in solution, Eq. (4) reduces to:

$$\Delta E^{\neq}_{mix} = x_1\Delta E_1{}^{\neq} + x_4\Delta E_4{}^{\neq} \tag{6}$$

From the well-known equation of van't Hoff;

$$\left(\frac{\mathrm{d}\ln K}{\mathrm{d}T}\right)_p = \frac{\Delta H^\circ}{\boldsymbol{R}T^2} \tag{7}$$

$$\left(\frac{\mathrm{d}\ln(K+1)}{\mathrm{d}T}\right)_p = \left(\frac{1}{1+(1/K)}\right)\left(\frac{\Delta H^\circ}{\boldsymbol{R}T^2}\right) \tag{8}$$

$$\left(\frac{\mathrm{d}\ln(x_1K+1)}{\mathrm{d}T}\right)_p = \frac{1}{\{1+(1/x_1K)\}}\left(\frac{\Delta H^\circ}{\boldsymbol{R}T^2}\right) \tag{9}$$

The substitution of Eqs. (8) and (9) into Eq. (5) gives:

$$\Delta E^{\neq}_{mix} = x_1\Delta E_1{}^{\neq} + x_4\Delta E_4{}^{\neq} + \frac{x_1x_4\Delta H^\circ}{\{1+(1/K)\}\{x_1+(1/K)\}} - x_1x_4\left(\frac{\mathrm{d}\alpha_{14}}{\mathrm{d}T}\right)_p \tag{10}$$

Since;

$$(k_1/k_4) = \left(\frac{H_{\mathrm{A},1}}{H_{\mathrm{A},4}}\right)\left(\frac{H_{\mathrm{B},1}}{H_{\mathrm{B},4}}\right)\left(\frac{V_1}{V_4}\right) \times (K+1)\exp(\alpha_{M^{\neq}4}) \tag{11}$$

$$(\Delta E_1{}^{\neq} - \Delta E_4{}^{\neq}) = \boldsymbol{R}T^2\left(\frac{\mathrm{d}\ln(k_1/k_4)}{\mathrm{d}T}\right)_p = \boldsymbol{R}T^2 \times \frac{\mathrm{d}}{\mathrm{d}T}\left(\ln\left(\frac{H_{\mathrm{A},1}}{H_{\mathrm{A},4}}\right) \times \left(\frac{H_{\mathrm{B},1}}{H_{\mathrm{B},4}}\right)\left(\frac{V_1}{V_4}\right)(K+1)\exp(\alpha_{M^{\neq}4})\right) \tag{12}$$

Since the temperature coefficients of the Henry constant and the emprical coefficient, α, are assumed to be negligibly small compared with the differences between the activation energies, except for the system in which there exists a large solvent-solute interaction, such as a hydrogen bonding or the formation of an addition product, Eq. (12) reduces to:

$$(\Delta E_1{}^{\neq} - \Delta E_4{}^{\neq}) = \frac{\Delta H^\circ}{1+(1/K)} \tag{13}$$

The substitution of Eq. (13) into Eq. (10) gives:

$$\Delta E^{\neq}_{mix} = x_1\Delta E_1{}^{\neq} + x_4\Delta E_4{}^{\neq} + \frac{x_1x_4(\Delta E_1{}^{\neq} - \Delta E_4{}^{\neq})}{x_1+(1/K)} \tag{14}$$

The parameter, K, appearing in Eq. (14) is the equilibrium constant, which has already been determined from a comparison of Eq. (2) with the experimental results shown in Part II of this series.

Then, if the activation energies in a pure solvent are given, the activation energy in a binary mixed solvent can be determined definitely for each model from Eqs. (6) and (14).

When the rate constant and the activation energy have been calculated from Eqs. (1) and (6), or from Eqs. (2) and (14), the activation entropy in a binary mixed solvent can be obtained immediately from the relation:

$$\Delta G^{\neq}_{mix} = \Delta H^{\neq}_{mix} - T\Delta S^{\neq}_{mix} \tag{15}$$

From a comparison of Eqs. (1) and (2), it may be understood that Eq. (2) successively approaches Eq. (1) with the decrease in the value of the equilibrium constant, K, and that Eq. (2) is equal to Eq. (1) when the equilibrium constant, K, is equal to zero.

As the denominator of the third term of Eq. (14) increases with the decrease in the value for K, Eq. (14) reduces to Eq. (6) in the limiting case of $K=0$.

The above relations are shown in Figs. 1 and 2, where the calculations have been made for the system in which the ratio of the rate constants, (k_1/k_4), and the difference between the activation energies, $(\Delta E_1{}^{\neq} - \Delta E_4{}^{\neq})$, are equal to one hundred and -4.0 (kcal mol^{-1}) respectively.

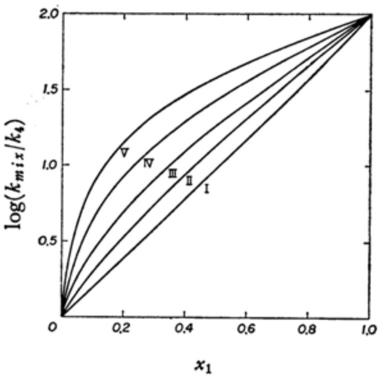

Fig. 1. The calculated values of $\log(k_{mix}/k_4)$ as a function of x_1 for various values of K (x_1= mole fraction of a more polar solvent, 1). $(k_1/k_4)=100$, $\alpha_{14}=0.1$
I: $K=0$, II: $K=5$, III: $K=12$, IV: $K=30$, V: $K=63$

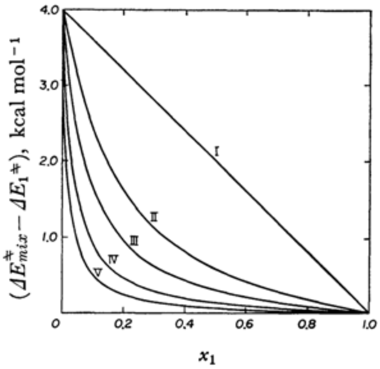

Fig. 2. The calculated values of $(\Delta E^{\neq}_{mix}-\Delta E_1^{\neq})$ as a function of x_1 for various values of K (x_1= mole fraction of a more polar solvent, 1).
$(\Delta E_4^{\neq}-\Delta E_1^{\neq})=4$ kcal mol^{-1}
I: $K=0$, II: $K=5$, III: $K=12$, IV: $K=30$, V: $K=63$

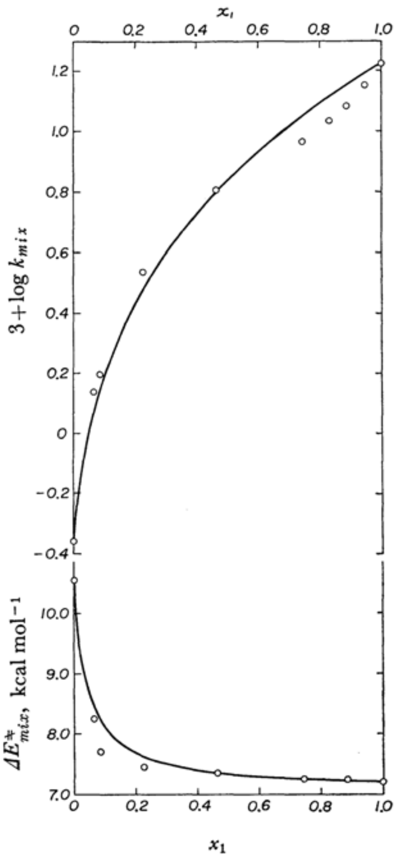

Fig. 3. Dependence of $\log k_{mix}$ and $\Delta E^{\neq}_{mix}$ for the benzoylation of *m*-nitroaniline in benzene-nitrobenzene mixture at 25°C upon mole fraction of nitrobenzene (x_1).
$K=23.5$, $\alpha_{14}=0.10$ (estimated from the equilibrium vapor pressure data)
○ : experimental results in Ref. 2
— : theoretical

Comparison with the Experimental Results

It has been recognized in mixed solvents that when the proportion of the polar solvent is small, the activation parameters as well as the rate constants change rapidly with the composition of the solvent, but when a high proportion of the polar solvent is attained, these changes are slowed down appreciably.[2]

Though this behavior has been attributed to the specific solvation due to a polar solvent,[3] no theoretical treatment has yet succeeded in giving a quantitative explanation of these phenomena in the mixed solvents.

It has been made clear by Figs. 3, 4 and 5,

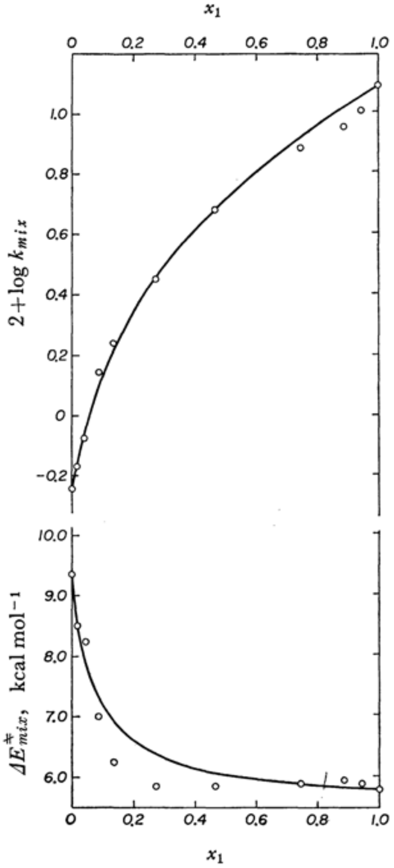

Fig. 4. Dependence of $\log k_{mix}$ and $\Delta E^{\neq}_{mix}$ for the benzoylation of *m*-chloroaniline in benzene-nitrobenzene mixture at 25°C upon mole fraction of nitrobenzene (x_1).
$K=13$, $\alpha_{14}=0.10$ (estimated from the equilibrium vapor pressure data)
○ : experimental results in Ref. 2
— : theoretical

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[2] J. B. Rossell, *J. Chem. Soc.*, **1963**, 5183.

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

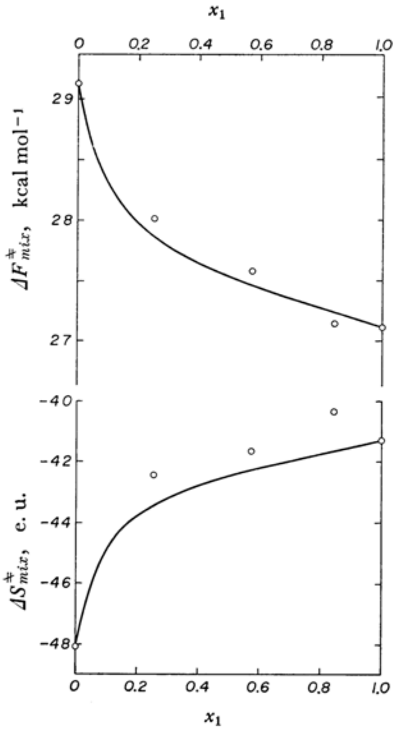

Fig. 5. Dependence of $\Delta F^{\neq}_{mix}$ and $\Delta S^{\neq}_{mix}$ for the Menschutkin reaction between triethylamine and ethylbromide in benzene-acetone mixture at 100°C upon mole fraction of acetone. $K=24.5$, $\alpha_{14}=0.664$ (refered to the value for toluene-acetone mixture[8]).

○ : experimental results in Ref. 7

— : theoretical

that not only the behavior of the rate constants, but also the behavior of the activation parameters in mixed solvents, can be explained semiquantitatively by the model offered by the authors.

In spite of the assumptions contained in the second model drawn from the results shown in Figs. 3, 4 and 5, the second model would be useful for the study of the effects of solvents on the reaction rates.

In Part I of this series, the authours have shown that the reaction rates in a binary mixed solvent may be expressed with good accuracy by the formula:[4]

$$\log k_{mix} = x_1 \log k_1 + x_4 \log k_4 + x_1x_4 \times \{a + b(x_1 - x_4) + c(x_1 - x_4)^2 + d(x_1 - x_4)^3\} \tag{16}$$

Both the theoretical equations derived on the basis of the first model and the second model consist of two components, one of which depends on a linear correlation of log k *vs.* x, while the other corresponds to the deviation from linearity.

From a comparison of Eq. (1) with Eq. (16), the parameter, a, should be expressed by:

$$2.303a = (-\alpha_{14}) \tag{17}$$

In regular solutions the value for α has been shown to be generally positive and relatively small (*ca.* 0.1—2.0);[5,6] on the other hand, the value for a calculated from the experimental results is positive and relatively large (*ca.* 0.8—3.1).[4] Therefore, the relation would not generally be present.

The above conclusion is equivalent to the fact that the first model failed to represent the behavior of the reaction rates in binary mixed solvents.[1]

In Part II of this series[1] and in this paper it has been decided that the second model is suitable for the representation of the pictures of the reaction in a solution.

As the parameter, a, can be calculated from the value for $\log k_{mix}$ at $x_1=x_4=0.5$, the relation is given from Eqs. (2) and (16):

$$2.303 \times a = 4\left\{\ln\{(K/2)+1\} - \frac{1}{2}\ln(K+1) - \left(\frac{\alpha_{M^{\neq}4}}{4}\right)\right\} \tag{18}$$

The large positive deviation from linearity, so that the large positive value for a corresponds to the large value for K, and the fact that $\Delta \log k_{mix}$ is always positive in binary mixed solvents, show that there exists a significant specific solvation of an activated complex due to a more polar solvent.

The value for $\Delta \log k_{mix}$ has a maximum value at the position where:

$$\frac{\mathrm{d}(\Delta \log k_{mix})}{\mathrm{d}x_1} = 0 = \frac{K}{(x_1K+1)} - \ln(K+1) \tag{19}$$

(for simplicity the term containing the coefficient, α, is omitted.)
From Eq. (19),
when:

$$K \geqq 1,\ x_{1,\,max} \leqq 0.44 \tag{20}$$

where $x_{1,mix}$ stands for the mole fraction of a solvent, 1, at which $\Delta \log k_{mix}$ has a maximum value.

It has been found that the maximum of $\Delta \log k_{mix}$ lies at a mole fraction smaller than $x_1=0.5$, where x_1 stands for the mole fraction of the solvent, 1 in which the reaction proceeds more

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

[5] 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).

[6] J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliff, N. J. (1962).

[7] W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 492 (1935).

[8] R. V. Drye and J. M. Prausnitz, *Trans. Faraday Soc.*, **61**, 1338 (1965).

rapidly.⁴⁾ Judging from the relation (Eq. (20)), the above phenomenon ought to be observed in systems where the equilibrium constant, K, has a large value, as is shown in Figs. 3, 4, and 5.

Though the various properties of the parameter a, have been confirmed,⁴⁾ this model seems to be insufficient for a further discussion of the properties of the parameter, a.