The Reaction Rate in Binary Mixed Solvents

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The rate-determining factors in the reactions in a solution are considered to be (1) the type of reaction, (2) the nature of the chemical species of the reaction, and (3) the nature of the solvent used for the reaction, in addition to (4) such ordinarily-accepted factors as the reaction temperature, the concentration of the solutes and the viscosity of the solution. Studies of these factors up to the present time seem to have been concentrated on (2) and (4). The dependence of the reaction rate on the kind of the solvent, generally referred to as "the solvent effect," includes quite complicated problems, such as "the selectivity of the solvent,"1) the details of which have not yet been solved.

Various attempts have been made to specify the type of effect exerted by solvents on the reaction rate. For example, several reports have been published on the participation of the solvent2) and on the effects of the dielectric constants,3) the *Y*-values4) or the *Z*-values5) of the solvents. However, all these researches relate only to a few special reactions. The

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1) J. B. Hyne, *J. Am. Chem. Soc.*, **82**, 5129 (1960), J. B. Hyne, R. Wills and R. E. Wonka, ibid., **84**, 2944 (1962); J. B. Hyne and R. Wills, ibid., **85**, 3650 (1960).

2) H. E. Zaugg, ibid., **83**, 837 (1961).

3) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, New York (1953), p. 133.

4) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 2700 (1951).

5) E. M. Kosower, ibidi, **80**, 3253 (1958).

determination of the reaction rate can hardly be made for each quantity since each solvent has different selectivities during the course of the reaction.

When two solvents with different selectivities are chosen and mixed, the selectivity is expected to vary with the composition; therefore, the examination of the reaction rate in such mixtures must be profitable for the study of the dependence of the reaction rate on the nature of the solvent. To discuss the reaction rate in a mixed solvent system, the most important problem is whether there exists a general relation between the rate and the composition, a relation which would enable us to construct an empirical formula. Therefore, first an attempt was made to obtain a formula which would generalize the reaction.

The meanings of the parameters which appear in the experimentally-deduced formula will also be discussed.

The Method and the Results

When the relation between the rate constant and the composition of the solvent is discussed, the first problem to be solved is the choice of the measures with which the rate constant, k, and the composition, n, of the solvent are to be expressed. Log k was adopted for the purpose of discussing the reaction rate from the view point of the free energy of activation. Molar fraction was adopted for the expression of the composition of the solvent for the convenience of the discussion of the reaction rate, the rate equation of which is

$$k=\kappa(\boldsymbol{k}T/h)e^{-\Delta F^{\neq}/RT}$$

This equation is based on the absolute rate theory; in it, k is the rate constant, κ is the transmission coefficient, $\boldsymbol{k}$ is the Boltzmann constant, and $\Delta F^{\neq}$ is the free energy of activation.

If there is no selectivity, the plot of log k vs. the composition of the mixed solvent, x, should be linear. Howerer, the relation, as Fig. 1 shows, generally curves upward or downward. This indicates that the rate constant, $\boldsymbol{k}$, in the mixed solvent system would consist of two components, one of which depending on a linear correlation of log k vs. x (the linear plot in Fig. 1) and the other corresponding to the deviation from ideality.

Further treatment enables us to clarify the situation. When the deviation of log k from the linear correlation, Δ log k, taken on the abscissa, the curve shown in Fig. 2 is obtained. The general features of Fig. 2 indicate the following points. (In the figures, the pure solvent which gives the larger rate constant, A, is placed on the right end of the abscissa.

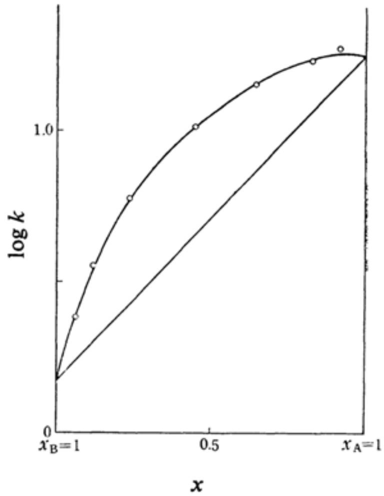

Fig. 1. Correlation between log k vs. the composition of the solvent mixture x.
The Menschutkin reaction in acetone (x_A)-benzene (x_B) mixture, between triethylamine and ethyl iodide.[11] Temp. 40°C

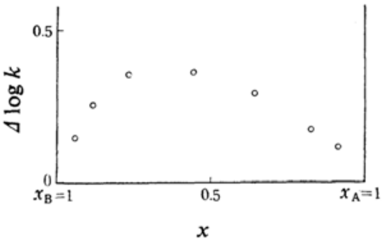

Fig. 2. A relationship between Δ log k vs. x.
The Menschutkin reaction between triethylamine and ethyl iodide.[11]
x_A: Acetone, x_B: Benzene, Temp. 40°C

1) Δ log k is always positive; i.e., Δ log $k>0$.

2) The maximum of Δ log k lies at a molar composition smaller than $x_A=0.5$, where x_A is the molar composition of the solvent A.

Over twenty reactions in various solvent systems were examined to find if the above rules hold true (Table I). These reactions were the most elementary reactions involving (1) the chlorination of aromatic hydrocarbons, (2) the acylation of aromatic bases, and (3) the Menschutkin reactions, the details of which will be described in the following part of this paper.

An empirical equation is derived as follows:

(1) The part of the relation showing the linearity where the additivity rule is rate controlling is:

$$\log k_1=x_A \log k_A+x_B \log k_B \qquad (1)$$

where x_A and x_B are the molar compositions of the components A and B, and k_A and k_B are the rate constants of the same reaction in the pure solvents A and B ($k_A > k_B$), respectively.

(2) The part representing the deviation from linearity may be expressed in correspondence with the theory of non-electrolyte solutions as follows:

$$\varDelta \log k = x_A x_B \{a + b(x_A - x_B) + c(x_A - x_B)^2 + d(x_A - x_B)^3\} \quad (2)$$

Thus, the resultant rate formula must be:

$$\log k \text{ (mixture)} = (1) + (2) = \log k_1 + \varDelta \log k$$
$$= x_A \log k_A + x_B \log k_B + x_A x_B \{a + b(x_A - x_B) + c(x_A - x_B)^2 + d(x_A - x_B)^3\} \quad (4)$$

In view of the significance of the mixed solution, this equation may reasonably be accepted for the purpose of studying the reaction rate in a mixed solution.

The appicabilty of expression 4 depends on the third terms in the equation, where *a*, *b*, *c* and *d* are the parameters indicating the deviation from ideality or the long and short range interactions of the solvents. For the estimation of these parameters, the following method was adopted. The empirically-found $\varDelta \log k$'s were plotted against the molar composition of the solvents. A curve passing through these plots was then drawn. From this curve the values of $\varDelta \log k$'s at some selected points ($x_A = 0.15$, 0.35, 0.65 and 0.85 molar fractions) were obtained and substituted into Eq. 4. A number of the simultaneous equations thus obtained were solved to obtain the values of the respective parameters, *a*, *b*, *c* and *d*.

The curves calculated by the *a*, *b*, *c* and *d* parameters and the experimental plots of $\varDelta \log k$ vs. x_A are compared in Figs. 3 and 4. As is indicated in Table I. The experimental results can be expressed with a good accuracy for various reactions by the appropriate choice of parameters.

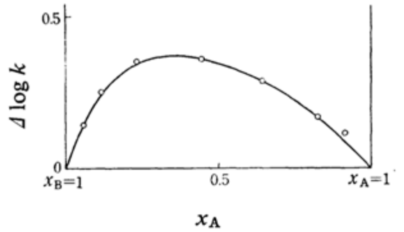

Fig. 3. Plots of $\varDelta \log k$ vs. x_A.
The Menschutkin reaction between triethylamine and ethyl iodide.11)
x_A: Acetone, x_B: Benzene
a, 1.39, *b*, −0.570, *c*, 0.696, *d*, −0.346
○ obtained, —— calcd.

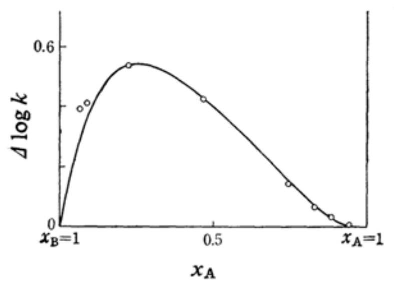

Fig. 4. Plots of $\varDelta \log k$ vs. x_A.

Benzoylation of *m*-nitroaniline.7)
x_A: Nitrobenzene, x_B: Benzene
a, 1.60, *b*, −1.70, *c*, 1.02, *d*, −1.51,
Temp., 25°C
○ obtained, —— calcd.

Discussion

The Theoretical Derivation of Expression 4.—When the solvent effect of a reaction in a solution is discussed, it is necessary to take the effect of solvation into consideration. Taking the state in a vacuum as the standard, the relationship of the free energies with the reaction process is considered. In Fig. 5 the free energies of activation in a vacuum and in a solution are compared.

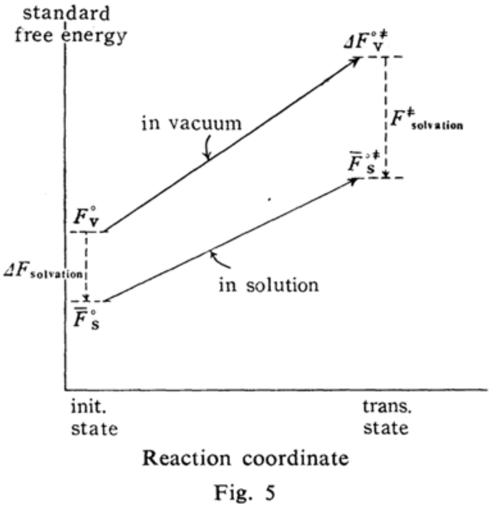

Fig. 5

The free energies of activation are indicated as:
Free energy of activation in a vacuum:

$$\varDelta F_v^{\circ\neq} = \varDelta F_v^{\circ\neq} - F_v^{\circ}$$

Free energy of activation in a solution:

$$\varDelta \bar{F}_s^{\circ\neq} = \varDelta \bar{F}_s^{\circ\neq} - \bar{F}_s^{\circ}$$

$$\bar{F}_s^{\circ} = F_v^{\circ} + \varDelta F_{\text{solvation}}$$

and

$$\bar{F}_s^{\circ\neq} = F_v^{\circ\neq} + \varDelta F^{\neq}_{\text{solvation}}$$

where F_v°, $F_v^{\circ\neq}$, $\bar{F}_s^{\circ}$ and $\bar{F}_s^{\circ\neq}$ are the free energies of the initial and the transition states in

Table I. Results of calculation of the parameters, a, b, c and d in Eq. 4

No.	Reaction	Solvent system	Reactants	Temp. of reaction, C°	Parameter				Ref.
					a	b	c	d	
1	Chlorination	CH_3CN-nitromethane	Toluene+Cl_2	25	−0.3	—	—	—	6)
2			2-Chloronaphthalene+Cl_2	25	0	0	0	0	6)
3	Acylation	Benzene-nitrobenzene	*i*-Butyryl Cl+*m*-Nitroaniline	25	1.28	−1.42	−0.0917	−1.25	7)
4			Benzoyl Cl+*m*-Nitroaniline	25	1.60	−1.70	1.02	−1.51	7)
5			Benzoyl Cl+*m*-Chloroaniline	25	1.16	−0.853	0.424	−1.10	7)
6		Benzene-phenylcyanide	Benzoyl Cl+*m*-Nitroaniline	25	3.12	−1.70	1.52	−1.41	7)
7	The Menschutkin reaction	Benzene-nitrobenzene	Triethylamine+MeI	100	1.94	−0.610	0.740	−1.370	8)
8			Triethylamine+*i*-PrI	100	2.20	−1.73	0.485	0.454	8)
9			Pyridine+MeI	100	2.10	−1.06	0.290	0.420	9)
10			Pyridine+*i*-PrI	100	1.96	−1.07	0.936	−0.710	8)
11		*i*-Pr-ether-nitrobenzene	Pyridine+MeI*	100	1.460	1.925	0.863	−6.833	9)
12		Benzene-EtOH	Pyridine+MeI	100	0.84	−0.80	0.963	−0.10	9)
13		Acetone-nitrobenzene	Pyridine+MeI	100	0.80	0	0	0	9)
14		Diphenylether-propylenecarbonate	4-Picoline+*n*-BuBr	100	1.56	−1.20	0.92	−0.055	10)
15		Benzene-acetone	Triethylamine+EtI**	100	1.070	−0.138	0.639	−0.426	11)
16			Pyridine-MeI	100	1.400	−0.510	0.686	−0.420	9)
17		Benzene-nitrobenzene	Triethylamine+MeI	40	1.80	−1.10	1.03	−0.764	8)
18			Pyridine+Benzyl Br	45	2.00	−0.948	0.868	−1.27	12)
19			Triethylamine+Benzyl Br	45	1.60	−0.980	1.370	−1.330	12)
20		Benzene-EtOH	Pyridine+Benzyl Br	45	1.780	−1.53	1.340	−0.870	12)
21			Triethylamine+Benzyl Br	45	1.740	−1.260	1.200	−0.614	12)
22		Dioxane-acetone	Triethylamine+EtI	40	1.14	−0.489	0.349	−0.318	11)

* The reaction was too complex to be expressed with four parameters.

** The results are not clear because the numbers of the data are scarce.

a vacuum and in a solution respectively, and where $\Delta F_{\mathrm{v}}^{\circ\ddagger}$ and $\Delta\bar{F}_{\mathrm{s}}^{\circ\ddagger}$ are the free energies of activation in a vacuum and in a solution respectively.

Therefore,

$$\Delta\bar{F}_{\mathrm{s}}^{\circ\ddagger}=\Delta F_{\mathrm{v}}^{\circ\ddagger}+(\Delta F_{\mathrm{solvation}}^{\ddagger}-\Delta F_{\mathrm{solvation}}) \quad (5)$$

The reason why the solvent effect appears in the reaction in a solution must be due mostly to the difference in $(\Delta F_{\mathrm{solvation}}^{\ddagger}-\Delta F_{\mathrm{solvation}})$ for various solvents. What is most important in the discussion of the solvent effect is $\bar{F}_{\mathrm{s}}^{\circ}$ and $\bar{F}_{\mathrm{s}}^{\circ\ddagger}$, namely, the standard free energies of the initial and the transition states in the solution.

The free energies of the standard state of a solute in solvents 1 and 2 are expressed by $\bar{F}_1^{\circ}$ and $\bar{F}_2^{\circ}$, and the free energy of the solute in the standard state in a mixture of 1 and 2, by $\bar{F}_{12}^{\circ}$; x_1 and x_2 are the molar fractions of solvents 1 and 2 in the mixture. The next relation is assumed to hold when the free energy of the solute in the mixed solvent affected by component 1 is $F^{\circ}_{1x_1x_2}$:

$$\begin{aligned}\bar{F}^{\circ}_{1x_1x_2}=\bar{F}_1^{\circ}&+\boldsymbol{RT}\cdot a_{12}x_2^2+\boldsymbol{RT}b_1x_2^2(x_1-x_2)\\&+\boldsymbol{RT}\cdot c_{12}\cdot x_2^2(x_1-x_2)^2\\&+\boldsymbol{RT}\cdot d_{12}\cdot x_2^2(x_1-x_2)^3 \qquad (6)\end{aligned}$$

Similarly, the free energy of the solute affected by component 2, $\bar{F}^{\circ}_{2x_1x_2}$, is as follows:

$$\begin{aligned}\bar{F}^{\circ}_{2x_1x_2}=\bar{F}_2^{\circ}&+\boldsymbol{RT}\cdot x_1{}^2\{a_{21}+b_{21}\cdot(x_2-x_1)\\&+c_{21}\cdot(x_2-x_1)^2+d_{21}(x_2-x_1)^2\} \qquad (7)\end{aligned}$$

and in a 1—2 system:

$$a_{12}=a_{21},\ b_{12}=-b_{21},\ c_{12}=c_{21}\ \text{and}\ d_{12}=-d_{21}$$

When n_1 mole of the solute in solvent 1 is mixed with n_2 mole of the solute in solvent 2, the total free energy of the solute in the solvent is $(n_1+n_2)\bar{F}_{12}^{\circ}$; therefore,

$$\begin{aligned}(n_1+n_2)\bar{F}_{12}^{\circ}=n_1\bar{F}_1^{\circ}&+n_1\bar{F}_2^{\circ}+n_1\boldsymbol{RT}x_2^2\{a_{12}\\&+b_{12}(x_1-x_2)+c_{12}(x_1-x_2)^2+d_{12}(x_1-x_2)^3\}\\&+n_2\boldsymbol{RT}x_2^2\{a_{21}+b_{21}(x_2-x_1)+c_{21}(x_1-x_1)^2\\&+d_{21}(x_2-x_1)^3\}=n_1\bar{F}_1^{\circ}+n_2\bar{F}_2^{\circ}+(n_1\boldsymbol{RT}x_2^2\\&+n_2\boldsymbol{RT}x_1^2)\{a_{12}+b_{12}(x_1-x_2)^2+c_{12}(x_1-x_2)^2\\&+d_{12}(x_1-x_2)^3\} \qquad (8)\end{aligned}$$

Since $n_1/(n_1+n_2)=x_1$ and $n_2/(n_1+n_2)=x_2$

$$\begin{aligned}\bar{F}_{12}^{\circ}=x_1\bar{F}_1^{\circ}+x_2\bar{F}_2^{\circ}&+\boldsymbol{RT}x_1x_2\{a_{12}+b_{12}(x_1-x_2)\\&c_{12}(x_1-x_2)^2+d_{12}(x_1-x_2)^3\} \qquad (9)\end{aligned}$$

A similar relation holds for $\bar{F}_{12}^{\circ\ddagger}$. Therefore, the free energy of the activation in the mixture is:

$$\begin{aligned}\Delta\bar{F}_{12}^{\circ\ddagger}=\bar{F}_{12}^{\circ\ddagger}-\bar{F}_{12}^{\circ}&=x_1\Delta\bar{F}_1^{\circ\ddagger}+x_2\Delta\bar{F}_2^{\circ\ddagger}\\&+\boldsymbol{RT}x_1x_2\{a'_{12}+b'_{12}(x_1-x_2)\\&+c'_{12}(x_1-x_2)^2+d'_{12}(x_1-x_2)^3\} \qquad (10)\end{aligned}$$

where a'_{12}, b'_{12}, c'_{12} and d'_{12} are the arithmetic sums of the initial and the transition states respectively.

According to the absolute reaction rate theory cited above,

$$\boldsymbol{RT}\ln k=\mathrm{const}\ -\Delta F^{\ddagger}$$

Consequently, it is clear that the following relation holds so long as Eqs. 6 and 7 are valid;

$$\begin{aligned}\log k_{12}=x_1\log k_1&+x_2\log k_2+x_1x_2\\&\times\{a+b(x_1-x_2)+c(x_1-x_2)^2+d(x_1-x_2)^3\} \qquad (11)\end{aligned}$$

In the above discussion, the free energies of standard state in pure solvents are $\bar{F}_1^{\circ}$ and $\bar{F}_2^{\circ}$. When two solvents are mixed together, the free energy of the mixture is sufficiently expressed by $(x_1\bar{F}_1^{\circ}+x_2\bar{F}_2^{\circ})$ if the change is ideal. Actually, however, various interactions occur; therefore, a series of terms must be added as corrections. The parameters of the solution, then enable us to determine the interaction in the real mixtures.

A Discussion of the Calculated Parameter: The Nature of *a*.—The important factors which determine the rate constant of the reaction are; (1) the type of reaction (or the charge type), (2) the nature and the structure of the reaction species, and (3) the nature of the solvent used, as has been mentioned above. The four parameters in Eq. 11, *a*, *b*, *c* and *d*, are the quantities that relate to the rate constant. Therefore, it is quite reasonable to suppose that *a*, *b*, *c* and *d* are affected by the three factors described above as is the rate constant.

It is sure from the nature of the proposed formula 11 that *a* is the most important parameter of the four. The value of *a* may easily be calculated, since it is $\log k/x_1x_2$ at an equimolar mixture of solvents 1 and 2. When the mixed solution consists of equal or nearly equal molar amounts of the components (1 and 2), Eq. 11 reduces to:

$$\log k_{12}=x_1\log k_1+x_2\log k_2+x_1x_2a \quad (12)$$

Moreover, in discussing the deviation from

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6) R. H. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **84**, 3635 (1962).

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11) E. Tomila and P. Kauranen, *Acta Chem. Scand.*, **8**, 1152 (1954).

12) G. Michin, R. Ginsburg and Ch. Moissejewa, *J. Chim. de l'Ukraine, L. Wissenschaft Teil*, **136**; *Chem. Zentralb.*, **1926**, **II**, 2376.

ideality, the parameter *a* is convenient for the mixed solution, while the ideal mixture exhibits the following relation;

$$\log k_{12} = x_1 \log k_1 + x_2 \log k_2 \qquad (13)$$

The three kinds of reaction shown in Table I will now be considered. Although the magnitude of *a* can not be determined from the type of reaction only, it keeps an almost constant value even when the reactants vary over a wide range as long as the solvent system is the same during reactions of the same type (for example, Nos. 1 and 2, Nos. 3, 4 and 5, Nos. 7, 8, 9 and 10, Nos. 15 and 16, Nos. 17, 18 and 19, and Nos. 20 and 21 in Table I). However, it changes greatly if the solvent system is different, even when both the reaction and the reactants are the same (for example, Nos. 4 and 6, and Nos. 9, 11, 12, 13 and 16 in Table I). From the characteristics of *a*'s described above, it can be concluded that *a* is sensitive to the type of reaction and the solvent system, but that it is not affected by the nature of the reactant as long as the solvent system and the type of reaction are the same.

The Theoretical Derivation of The Additivity of the Parameter *a*.—The following formulae will hold when a two-component system changes ideally for three kinds of solvent, the components being 1, 2 and 3 respectively:

$$\varDelta\overline{F}^{\circ\ddagger}_{12} = x_1\varDelta\overline{F}^{\circ\ddagger}_{1} + x_2\varDelta\overline{F}^{\circ\ddagger}_{2} \qquad x_1 + x_2 = 1 \qquad (14)$$

$$\varDelta\overline{F}^{\circ\ddagger}_{23} = x_2\varDelta\overline{F}^{\circ\ddagger}_{2} + x_3\varDelta\overline{F}^{\circ\ddagger}_{3} \qquad x_2 + x_3 = 1 \qquad (15)$$

$$\varDelta\overline{F}^{\circ\ddagger}_{13} = x_1\varDelta\overline{F}^{\circ\ddagger}_{1} + x_3\varDelta\overline{F}^{\circ\ddagger}_{3} \qquad x_1 + x_3 = 1 \qquad (16)$$

Let us now discuss the relation among $\varDelta\overline{F}^{\circ\ddagger}_{12}$, $\varDelta\overline{F}^{\circ\ddagger}_{23}$ and $\varDelta\overline{F}^{\circ\ddagger}_{13}$. When a 1—2 solvent system and a 2−3 solvent system are mixed,

$$\begin{aligned}\varDelta\overline{F}^{\circ\ddagger}_{12} + \varDelta\overline{F}^{\circ\ddagger}_{23} &= x_1\varDelta\overline{F}^{\circ\ddagger}_{1}\\ &+ x'_2\varDelta\overline{F}^{\circ\ddagger}_{2} + x'_2\varDelta\overline{F}^{\circ\ddagger}_{2} + x'_3\varDelta\overline{F}^{\circ\ddagger}_{3} \qquad (17)\end{aligned}$$

where (x_1 and x_2) are the molar fractions in the 1—2 system and (x'_2 and x'_3) are those in the 2—3 solvent system, (x_1 and x_2) being independent of (x'_2 and x'_3). If the condition $x_1 + x'_3 = 1$ is satisfied, the sum for each independent system comes to show the behavior of the 1—3 system. Thus, the activation free energy of the 1—3 system can be calculated from the sum of the 1—2 and 2—3 mixed component systems:

$$\begin{aligned}\varDelta\overline{F}^{\circ\ddagger}_{12} + \varDelta\overline{F}^{\circ\ddagger}_{23} &= x_1\varDelta\overline{F}^{\circ\ddagger}_{1}\\ &+ (1-x_1)\varDelta\overline{F}^{\circ\ddagger}_{1} + (1-x_3')\varDelta\overline{F}^{\circ\ddagger}_{2} + x_3'\varDelta\overline{F}^{\circ\ddagger}_{3} \qquad (17')\end{aligned}$$

Since $x_1 + x_3' = 1$,

$$\varDelta\overline{F}^{\circ}_{12} + \varDelta\overline{F}^{\circ\ddagger}_{23} = \varDelta\overline{F}^{\circ\ddagger}_{2} + x_1\varDelta\overline{F}^{\circ\ddagger}_{1} + x_2'\varDelta\overline{F}^{\circ\ddagger}_{3} \qquad (18)$$

If $(x_1 + x_3' = 1)$ is rewritten as $(x_1 + x_3 = 1)$,

$$\varDelta\overline{F}^{\circ\ddagger}_{12} + \varDelta\overline{F}^{\circ\ddagger}_{23} = \varDelta\overline{F}^{\circ\ddagger}_{2} + \varDelta\overline{F}^{\circ\ddagger}_{12} \qquad (19)$$

The above consideration may be continued further and applied to the system which has the term *a* the deviation from an ideal system:

$$\begin{aligned}&\varDelta\overline{F}^{\circ\ddagger}_{12} = x_1\varDelta\overline{F}^{\circ\ddagger}_{1} + x_2\varDelta\overline{F}^{\circ\ddagger}_{2} + \boldsymbol{RT}x_1x_2a_{12},\\ &\qquad x_1 + x_2 = 1 \qquad (20)\end{aligned}$$

$$\begin{aligned}&\varDelta\overline{F}^{\circ\ddagger}_{23} = x_2\varDelta\overline{F}^{\circ\ddagger}_{2} + x_3\varDelta\overline{F}^{\circ\ddagger}_{3} + \boldsymbol{RT}x_2x_3a_{23},\\ &\qquad x_2 + x_3 = 1 \qquad (21)\end{aligned}$$

$$\begin{aligned}&\varDelta\overline{F}^{\circ\ddagger}_{13} = x_1\varDelta\overline{F}^{\circ\ddagger}_{1} + x_3\varDelta\overline{F}^{\circ\ddagger}_{3} + \boldsymbol{RT}x_1x_3a_{13},\\ &\qquad x_1 + x_3 = 1 \qquad (22)\end{aligned}$$

As before, when $x_1 + x_3 = 1$,

$$\begin{aligned}\varDelta\overline{F}^{\circ}_{12} + \varDelta\overline{F}^{\circ}_{23} &= x_1\varDelta\overline{F}^{\circ\ddagger}_{1} + (1-x_1)\varDelta\overline{F}^{\circ\ddagger}_{2}\\ &\quad + \boldsymbol{RT}x_1(1-x_1)a_{12} + x_3\varDelta\overline{F}^{\circ\ddagger}_{\infty}\\ &\quad + (1-x_3)\varDelta\overline{F}^{\circ\ddagger}_{2}\boldsymbol{RT}x_3(1-x_3)a_{23}\\ &= \varDelta\overline{F}^{\circ\ddagger}_{2} + x_1\varDelta\overline{F}^{\circ\ddagger}_{1} + x_3\varDelta\overline{F}^{\circ\ddagger}_{3}\\ &\quad + \boldsymbol{RT}x_1x_3(a_{12} + a_{23}) \qquad (23)\end{aligned}$$

If the relation of Eq. 19 holds as in the ideal change, the relation

$$a_{12} + a_{22} = a_{13} \qquad (24)$$

must also hold.

The Additivity of the Parameter *a* in the Menschutkin Reaction.—Relation 24, obtained above, may be applied to the case of the Menschutkin reaction.

When benzene, acetone and nitrobenzene are taken as the solvent components 1, 2 and 3 respectively, the relation among them is described in Table II and in Fig. 6. While $a_{12} + a_{23} = 2.03$ from the sum of the average values of a_{12} and a_{23} as listed in Table II, the average value of a_{13} experimentally obtained

TABLE II. THE PARAMETER *a*'S IN THE MENSCHUTKIN REACTION AT 100°C, IN BENZENE (1), ACETONE (2) AND NITROBENZENE (3) SYSTEMS

Benzene-acetone		Acetone-nitrobenzene		Benzene-nitrobenzene	
a_{12}		a_{23}		a_{13}	
Triethylamine+EtI	1.07[11]	Pyridine+MeI	0.80[9]	Triethylamine+MeI	1.94[8]
Pyridine+MeI	1.40[9]			Triethylamine+*i*-PropI	2.20[8]
				Pyridine+MeI	2.10[9]
				Pyridine+*i*-PropI	1.96[8]
Average	1.28			Average	2.05

is 2.05. Therefore, it was found that the additivity rule 24 holds among these three a's if the deviation from ideal is taken into account up to the first term, as in Eq. 12.

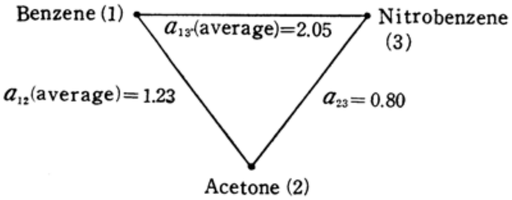

Fig. 6.

Summary

The reaction rate in binary mixed solvents have been discussed and following facts confirmed:

1) A linear relation does not hold between $\log k$ and the molar fraction of the components in most cases.

2) The deviation from linearity is usually positive, and the maximum deviation is found at $x_A \leq 0.5$, x_A is the molar fraction of a component in which the rate is faster than in another component.

3) The experimental results may be expressed with good accuracy by the formula:

$$\log k = x_A \log k_A + x_B \log k_B + x_A x_B a + b(x_A - x_B) + c(x_A - x_B)^2 + d(x_A - x_B)^3$$

4) The parameter a depends upon the type of reaction and the solvent system, but it does not depend on the nature of the reactants.

5) The additivity of has been proved theoretically and confirmed a for the Menschutkin reaction in various solvent mixtures.

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