# Correlation of Isoprene-Maleic Anhydride Reaction Rate Constants in Mixed Solvents

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Correlation of the Diels-Alder reaction rate constants of dilute solution for isoprene-maleic anhydride in the pure solvents such as hexane, ethyl acetate, toluene, monochlorobenzene and nitrobenzene, and the binary mixed solvents obtained by the authors are reviewed. For correlating the reaction rate constants in binary mixed solvents an empirical method based on the Arrhenius equation coupled with a Redlich-Kister type excess function introduced to obtain the excess activation energy in the mixed solvents is proposed. It is shown that the present model can correlate the reaction rate constants with a good agreement for the binary mixed solvents. Further, the applicability for the prediction of the excess activation energy for multicomponent mixed solvents by the addition of those for the constituent binary mixed solvents is presented.

***Key Words*** : Reaction rate constant, Diels-Alder reaction, Mixed solvent

## 1 INTRODUCTION

It is pointed out that kinetic solvent effects on reaction rates are enormous. Therefore, for the rational design of a liquid-phase reaction, a method of predicting such effects would provide a very powerful tool. In many cases, a properly chosen mixture of solvents may be better than any individual solvent alone to give a suitable reaction rate. Recently, the enhanced reaction rates were observed near the liquid-liquid or vapor-liquid critical point [1, 2]. Snyder and Eckert [1] reported that the reaction rate of the Diels-Alder reaction of isoprene and maleic anhydride was increased by 30~40% at the critical point of hexane + nitrobenzene mixture. On the other hand, the unusual or anomalous behavior of the Diels-Alder reaction rate near the liquid-liquid critical point reported by Snyder and Eckert [1] was not observed by Nishikawa et al.[2]. However, it has been found that the rate constants of Diels-Alder reaction are strongly depend on the solvent characteristics and compositions, and there have been a few works [1-5] on the reaction rate constants in mixed solvents.

So far, the authors also measured the Diels-Alder reaction rate constants of dilute solution of isoprene and maleic anhydride in the pure solvents such as hexane, ethyl acetate, toluene, monochlorobenzene and nitrobenzene and the binary mixed solvents at 20.8 and 30.0°C [3-5]. In this paper, the experimental results of the reaction rate constants of the Diels-Alder reaction near the liquid-liquid critical point and the correlation methods for the reaction rate constants in the mixed solvents are reviewed based on our previous works [3-5]. An empirical method is proposed to correlate the reaction rate constants in binary mixed solvents based on the Arrhenius equation coupled with a Redlich-Kister type excess function introduced to obtain the excess activation energy in the mixed solvents. It is shown that the present model can correlate the reaction rate constants with a good agreement for the binary mixed solvents. Finally, an extension of the correlation method to the prediction of the excess activation energy for multicomponent mixed solvents by the addition of those for the constituent binary mixed solvents is presented.

## 2 EXPERIMENTAL

### 2.1 Materials

Materials used in this work were isoprene (95.0%) and maleic anhydride (99.5%) as the reactants and hexane (96.0%), ethyl acetate (99.5%), toluene (99.5%), monochlorobenzene (99%) and nitrobenzene (99.5%) as the solvents. These are high-purity reagent grade other than isoprene and all materials were used as received.

### 2.2 Apparatus and Procedures

The Diels-Alder reaction is excellent for fundamental studies because it is a well-characterized reaction system with no significant side reactions. The following Diels-Alder reaction experiments of isoprene and maleic anhydride were carried out at 20.8 and 30.0°C.
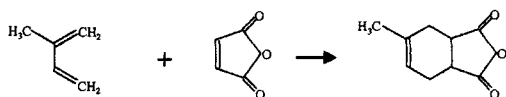
As shown in Figure 1, the temperature 20.8°C is close to the upper critical solution temperature of the hexane + nitrobenzene.

The mixed solvents of given concentration 200 mL in volume was charged into a flask set in a constant temperature bath. Here the reactants in dilute condition of isoprene 1.8 g and maleic anhydride 0.5 g precisely weighed were put into the flask and mixed with a magnetic stirrer. Samples were withdrawn from the flask every given time and analyzed by a gas chromatograph. The gas chromatograph used was a G-L Science GC-353 equipped with an FID detector.

### 2.3 Determination of reaction rate constant

The Diels-Alder reaction of isoprene and maleic anhydride in this work is given by the second order reaction relationship proportional to the each concentration of isoprene and maleic anhydride. Therefore, the reaction rate equation is given as follows.

$$-dC_A/dt = kC_A C_B \qquad (1)$$

The constant $k$ is obtained by integrating the above equation as

$$k = \frac{1}{t(C_{A0}-C_{B0})}\ln\frac{C_A C_{B0}}{C_{A0}C_B} \qquad (2)$$

where

$$C_A = C_{A0} - C_P, \qquad C_B = C_{B0} - C_P \qquad (3)$$

$C_A$, $C_B$ and $C_P$ are the concentrations of isoprene, maleic anhydride and product. $t$ is the reaction time and the subscript 0 denotes the initial concentration. The reaction rate constants were determined from Eq. (2) by measuring the concentration change of the product during the reaction experiments.

## 3 RESULTS

### 3.1 Reaction Rate Constant in Pure Solvent

The reaction rate constant $k$ in general is expressed by the Arrhenius equation as follows.

$$k = A\exp(-E/RT) \qquad (4)$$

If the frequency factor $A$ is dependent on temperature only, $k$ at given temperature is expressed by
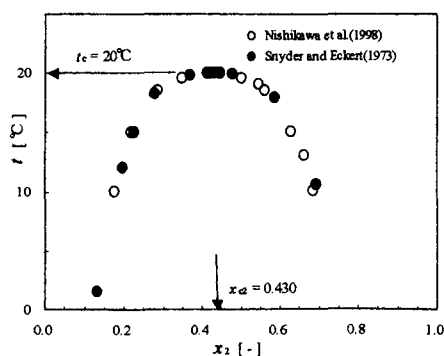
Table 1 Rate constants in pure solvents and cohesive energy densities

| Solvent | $k \times 10^4$ [L·mol$^{-1}$·s$^{-1}$] | | $\delta^2$ (25°C) [J·cm$^{-3}$] |
|---|---|---|---|
| | 20.8 °C | 30 °C | |
| Hexane | 0.30 | 0.50 | 222 |
| Ethyl acetate | 0.55 | 0.81 | 320 |
| Toluene | 0.60 | 1.00 | 350 |
| Monochlorobenzene | 1.44 | 2.30 | 414 |
| Nitrobenzene | 2.66 | 4.79 | 461 |

$$\ln k = a - bE \qquad (5)$$

where $a = \ln A$ and $b = 1/RT$.

In $k$ in Eq. (5) is considered to be linear with the activation energy $E$. Therefore, if $E$ could be related with any characteristic property of solvents, it might have a linear relationship with ln $k$. Here, the cohesive energy density $\delta^2$ given by the solubility parameter squared was selected as the representative property of solvents. The solubility parameters $\delta$ at 25 °C were estimated by the additive method proposed by Fedors [6] and shown in Table 1 and Figure 2. Here $k$ in the solvent of hexane was obtained by extrapolating $k$ in the mixed solvent with nitrobenzene to the pure hexane because of the immiscibility with maleic anhydride. As shown in Figure 2, the relation between ln $k$ and $\delta^2$ seems to be linear. It is concluded that the reaction rate constant in pure solvent can be predicted when the cohesive energy density of solvent $\delta^2$ is available.

### 3.2 Reaction Rate Constant in Binary Mixed Solvent

Figure 3 shows the reaction rate constants of isoprene-maleic anhydride in hexane and nitrobenzene mixed solvent at 20.8°C against the concentration of nitrobenzene $x_2$ compared with the previous works [1, 2]. In this binary mixed solvent, Snyder and Eckert reported the anomalous behavior near the liquid-liquid critical solution point, but it cannot be found in both this work and Nishikawa et al. [2]. The reaction rate constants show S shaped and the strong dependence of the concentration of mixed solvents. The dependences of the solvent concentration on the reaction rate constants are also observed in the other binary solvent systems.



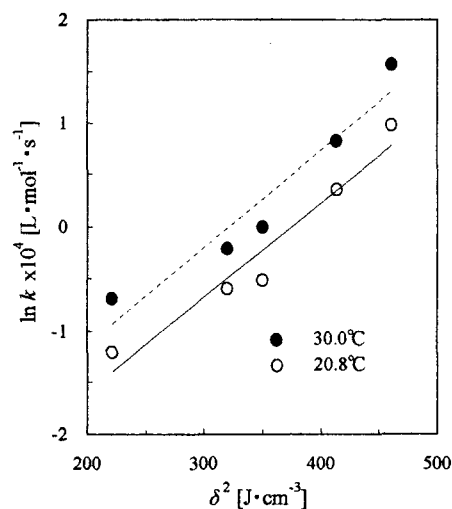Figure 1 Liquid-liquid critical points of hexane(1) + nitrobenzene(2) mixture



Figure 2 Relationship between reaction rate constants and cohesive energy densities in pure solvents

Further, it is found that the difference from the linear relationship between the rate constants and mole fractions of solvents increases with increasing the non-ideality of the mixed solvents [1, 2].

## 4 CORRELATION AND DISCUSSION

### 4.1 Correlation Method in Binary Mixed Solvent

In the binary mixed solvent systems, the rate constant $k$ in each pure solvent is given by the Arrhenius equation as aforementioned.

$$k_1 = A \exp(-E_1/RT), \quad k_2 = A \exp(-E_2/RT) \tag{6}$$

Here, the rate constant in mixed solvent $k_m$ is assumed to be expressed as same as pure solvent.

$$k_m = A \exp(-E_m/RT) \tag{7}$$

The activation energy in mixed solvent $E_m$ is required to estimate $k_m$. In this work, we propose the following equation for predicting $E_m$ :

$$E_m = x_1 E_1 + x_2 E_2 + \Delta E_{12} \tag{8}$$

where $x$ is the mole fraction of solvent and $\Delta E_{12}$ the excess quantity of activation energy. When $\Delta E_{12}$ is assumed to be zero, namely in ideal or reference state the rate constant in mixed solvents $k_m^\circ$ is given by Eqs. (6) − (8) with the rate constants in pure solvents as follows.

$$\ln k_m^\circ = x_1 \ln k_1 + x_2 \ln k_2 \tag{9}$$

In the real mixed solvents ($\Delta E_{12} \neq 0$), the following equation is derived by the above equations.

$$\ln k_m = \ln k_m^\circ - \Delta E_{12}/RT \tag{10}$$

Further, introducing a Redlich-Kister type excess function for $\Delta E_{12}$, the following equation is given as:

$$\Delta E_{12}/RT = \{E_m - (x_1 E_1 + x_2 E_2)\}/RT$$
$$= x_1 x_2 \{a_{12} + b_{12}(x_1 - x_2)\} \tag{11}$$

where the parameters $a_{12}$ and $b_{12}$ have to be evaluated experimentally. The rate constants in mixed solvents $k_m$ can be estimated by Eq. (10) with $k_1$ and $k_2$ in the pure solvents when the parameters $a_{12}$ and $b_{12}$ are given.

### 4.2 Correlation Results

Figures 4 and 5 show the dependency of the concentration of nitrobenzene on the reaction rate constants of isoprene and maleic anhydride in the mixed solvent of hexane + nitrobenzene and ethyl acetate + nitrobenzene. The values of $k_m$ show the positive deviation from those obtained by Eq. (9) for $k_m^\circ$. The correlation based on Eq. (11) was performed with the excess activation energy $\Delta E_{12}$ obtained by Eq. (10). The values of parameters $a_{12}$ and $b_{12}$ adjusted with the experimental data, which are assumed to be independent of temperature, are shown in Table 2. The deviations between the experimental and calculated results are also shown in Table 2. The solid lines in Figures 4 and 5 represent the rate constants in mixed solvents calculated with $\Delta E_{12}$ by Eq. (11). The correlation performance is fairly good as shown in Table 2 and Figures 4 and 5.

### 4.3 Excess Activation and Excess Gibbs energies

It is considered that the excess activation energy is dependent on the behavior of non-ideality in the mixed solvents. Therefore we
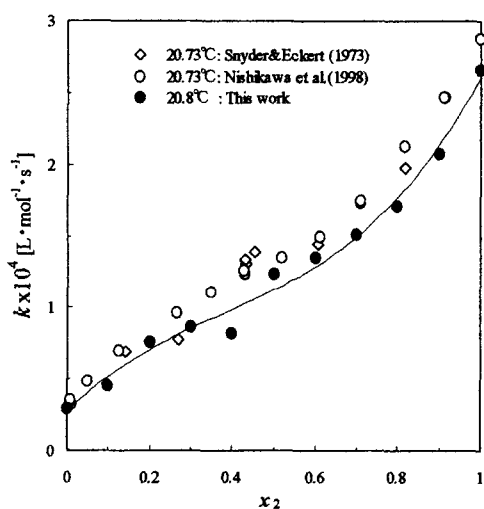


Figure 3   Rate constants for isoprene + maleic anhydride reaction near critical solution temperature of hexane(1) + nitrobenzene(2) mixture
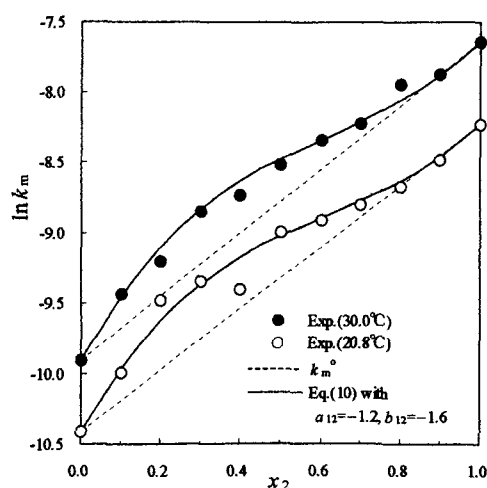


Figure 4   Rate constants for isoprene + maleic anhydride reaction at 20.8 and 30℃ in hexane(1) + nitrobenzene(2) mixture



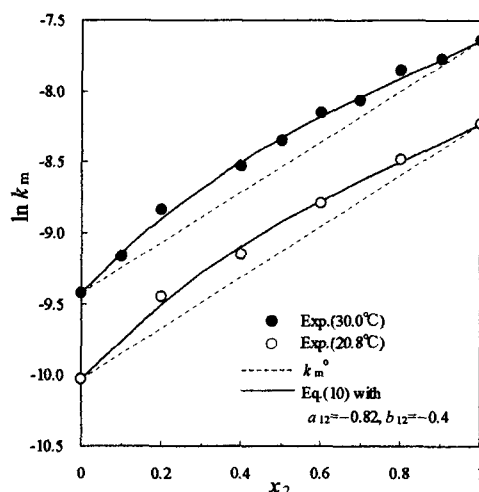Figure 5   Rate constants for isoprene + maleic anhydride reaction at 20.8 and 30℃ in ethyl acetate(1) + nitrobenzene(2) mixture

Table 2   Correlation performance for rate constants of isoprene + maleic anhydride reaction in mixed solvents containing nitrobenzene (2)

| Component (1) | $t$ [℃] | $a_{12}$ | $b_{12}$ | $N$ | Error [%] |
|---|---|---|---|---|---|
| Hexane | 20.8 | -1.2 | -1.6 | 9 | 6.5 |
|  | 30.0 |  |  | 9 | 4.5 |
| Ethyl acetate | 20.8 | -0.82 | -0.4 | 4 | 3.6 |
|  | 30.0 |  |  | 8 | 3.1 |
| Toluene | 20.8 | -0.72 | 0 | 9 | 10.5 |
|  | 30.0 |  |  | 9 | 6.0 |
| Monochlorobenzene | 30.0 | -0.45 | 0 | 9 | 2.3 |

Error [%] = $100/N$ $\Sigma$ | $k_{m,i}^{calc} - k_{m,i}^{exp}$ | / $k_{m,i}^{exp}$
$N$=number of data points

Table 3   Excess activation and Gibbs energies

| Mixed solvent | Max. point | | Max. point | |
|---|---|---|---|---|
| (1)  +  (2) | $x_2$ | $-\Delta E_{12}/RT$ | $x_2$ | $G^E/RT$ |
| Hexane + Nitrobenzene | 0.31 | 0.39 | 0.52 | 0.51 |
| Ethyl acetate + Nitrobenzene | 0.38 | 0.22 | 0.50 | 0.13 |
| Toluene + Nitrobenzene | 0.50 | 0.18 | 0.50 | 0.08 |
| Monochlorobenzene + Nitrobenzene | 0.50 | 0.11 | 0.50 | 0.01 |

examined the relation between the excess activation energy $\Delta E_{12}$ and excess Gibbs energy $G^E$. Here the excess Gibbs energy $G^E$ was evaluated by the following Eq. (12) with the activity coefficients $\gamma$ based on the regular solution theory as given by Eq. (13) [7].

$$G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{12}$$

$$\ln \gamma_1 = \nu_1/RT(\delta_1 - \delta_2)^2 \phi_2 ,$$

$$\ln \gamma_2 = \nu_2/RT(\delta_1 - \delta_2)^2 \phi_1 \tag{13}$$

Where the solubility parameters $\delta$ and the molar volumes of solvents $\nu$ at 25 ℃ can be estimated by the additive model proposed by Fedors [6] as mentioned earlier (see Table 1 for $\delta$). $\phi$ is the volume fraction and calculated as follows.

$$\phi_1 = x_1 \nu_1/(x_1 \nu_1 + x_2 \nu_2), \quad \phi_2 = 1 - \phi_1 \tag{14}$$

The comparison between the excess activation and excess Gibbs energies is shown in Table 3. Though the concentrations of solvents at the maximal points of excess energies and these excess energies are not the same, the tendency giving the maximum of these excess energies for the mixed solvents is qualitatively similar. Namely, it is found that the value of $-\Delta E_{12}/RT$ increases with increasing $G^E/RT$ or the extent of non-ideality in the mixed solvents.

### 4.4   Extension to Multicomponent Mixed Solvents

The correlation method proposed for the binary mixed solvents in this study might be extend to the multicomponent mixed solvents when the additivity of excess activation energy is accepted. So the rate constants in multicomponent mixed solvents more than ternary systems can be predicted using those in the pure and the constituent binary mixed solvents. Based on the discussion aforementioned in the binary mixed solvents the reaction rate constants of dilution solution in the multicomponent mixed solvents can be given as follows:

$$\ln k_m = \sum_i x_i \ln k_i - \sum_{j>i} \Delta E_{ij}/RT \tag{15}$$

where

$$\Delta E_{ij}/RT = x_i x_j \{a_{ij} + b_{ij} (x_i - x_j)\} \tag{16}$$

In Eq. (15), $k_i$ denotes the rate constant in the pure solvent $i$ and $\Delta E_{ij}$ means the excess activation energy for the binary mixture of solvents $i$ and $j$ which is defined by

$$- \Delta E_{ij}/RT = \ln k_m - (x_i \ln k_i + x_j \ln k_j) \tag{17}$$

Here, it is assumed that the excess activation energy for the multicomponent mixture of solvents can be approximated by the addition of that for each binary mixture, for example $\Delta E_{123} = \sum \Delta E_{ij} = \Delta E_{12} + \Delta E_{13} + \Delta E_{23}$ for a ternary mixed solvent.

However, the reaction rate constants in the ternary mixed solvents are not available. Therefore, the present correlation method should be evaluated when many data can be available in the future.

## 5   CONCLUSION

Diels-Alder reaction rate constants of dilute solution for isoprene-maleic anhydride in the pure solvents such as hexane, ethyl acetate, toluene, monochlorobenzene and nitrobenzene and in the binary mixed solvents were described. An empirical method proposed for correlating the reaction rate constants in binary mixed solvents based on the Arrhenius equation in which a Redlich-Kister type excess function is introduced to obtain the excess activation energy in the mixed solvents was reviewed. It was shown that the present model can correlate the reaction rate constants with a good agreement for the binary mixed solvents.

Further, it is suggested that the present correlation method is useful for predicting the rate constants in multicomponent mixed solvents. The applicability to the multicomponent mixed solvents should be examined by the experimental results in the future works.

### Nomenclature

| | | |
|---|---|---|
| $A$ | =frequency factor | [ - ] |
| $a_{ij}, b_{ij}$ | =constants | [ - ] |
| $C$ | =concentration | [mol・L$^{-1}$] |
| $E$ | =activation energy | [J・mol$^{-1}$] |
| $G^E$ | =excess Gibbs energy | [J・mol$^{-1}$] |
| $k$ | =reaction rate constant | [L・mol$^{-1}$・s$^{-1}$] |
| $R$ | =gas constant | [J・mol$^{-1}$・K$^{-1}$] |
| $t$ | =temperature | [℃] |
| $\nu$ | =molar volume | [cm$^3$・mol$^{-1}$] |
| $x$ | =mole fraction | [ - ] |
| $\Delta E$ | =excess activation energy | [J・mol$^{-1}$] |
| $\delta$ | =solubility parameter | [(J・cm$^{-3}$)$^{1/2}$] |
| $\gamma$ | =activity coefficient of liquid phase | [ - ] |
| $\phi$ | =volume fraction | [ - ] |

<Subscript>

| 1, 2, 3 | =components |
|---|---|
| m | =mixture |

<Superscript>

| o | =ideal |
|---|---|

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