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Studies of Zone Melting. VII. Distribution Coefficients of the *p*-Nitrophenol-Naphthalene Eutectic System

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Synopsis. In a zone-melting experiment the effective and equilibrium distribution coefficients of *p*-nitrophenol in naphthalene have been determined by a method based on a determination of the solute concentration in the terminal one zone length after a single zone pass. The effective distribution coefficient (K_e) is determined by

$$K_e = \frac{2}{Z^*+1}\left\{1-\frac{1}{Z^*-1}\left(\frac{C_s^*}{C_0}-1\right)\right\},$$

where C_0 is the initial solute concentration; C_s^* is the solute concentration described above and $Z^*=L/l-1/2$; L and l denote the specimen and zone lengths, respectively. Further, the equilibrium distribution coefficient (K_o) is obtained as

$$K_o = \frac{2(Z^*-B)}{Z^{*2}-1}.$$

The constant (B) is related to the equation $C_s^*/C_0=-AV+B$, where V is the zone travel rate and A is also a constant. The obtained values of K_e and K_o agree with those determined by a method reported previously by the author.

In zone-melting experiments an effective distribution coefficient is generally determined from either the slope or the intercept of a straight line expressing the relationship between the solute concentration and the distance from the starting end of the zone. In many systems, however, a disagreement between the values obtained from the two procedures described above is found for some reason.[1] In addition, for a eutectic system, it is difficult to exactly determine the effective distribution coefficient; it has a comparatively small value compared to that of a mixed crystal system as well as an equilibrium distribution coefficient. In a previous paper[2] the author reported on a method for determining the effective distribution coefficient of a eutectic mixture by a zone-melting process. Even upon using this method, however, disagreement between the two values described above was inevitable.

In the present work the effective distribution coefficient of *p*-nitrophenol in a naphthalene forming eutectic system was determined by a new method. The obtained result agrees with that determined from the slope of the linear equation reported previously.[2] Also, the equilibrium distribution coefficient derived from the above-mentioned result agrees with the value obtained by the previous method.[2]

Theoretical

Determination of the Effective Distribution Coefficient. Consider a rod-shaped specimen with a length L and a constant cross section comprising a uniform eutectic binary mixture;the solute distribution profile after a single zone pass for such a specimen is shown by Fig. 1,[2] from which it is obvious (from the standpoint of material balance) that areas S_1 and S_2 are the same. The line $\overline{C_1C_2}$ is expressed by Eq. 1,[2]

$$C_s = C_0\left(K_e + K_e\frac{x}{l}\right), \tag{1}$$

where C_0 is the initial uniform concentration of the solute; C_s is the solute concentration at a distance x from the top of the specimen after a single zone pass; l is the zone length and K_e is the effective distribution coefficient. Equation 1 is valid for all but the last one zone length. From the conservation of material and refering to Fig. 1,

$$(Z'-1)C_0 - \int_0^{Z'-1} C_0(K_e+K_eZ)\mathrm{d}Z = C_s^* - C_0. \tag{2}$$

In Eq. 2, x/l is replaced by Z, i.e. $Z\equiv x/l$; $Z'\equiv L/l$ and C_s^* is the solute concentration in the terminal one zone length after a single zone pass. The effective distribution coefficient is obtained from Eq. 2 as

$$K_e = \frac{2}{Z^*+1}\left\{1-\frac{1}{Z^*-1}\left(\frac{C_s^*}{C_0}-1\right)\right\}. \tag{3}$$

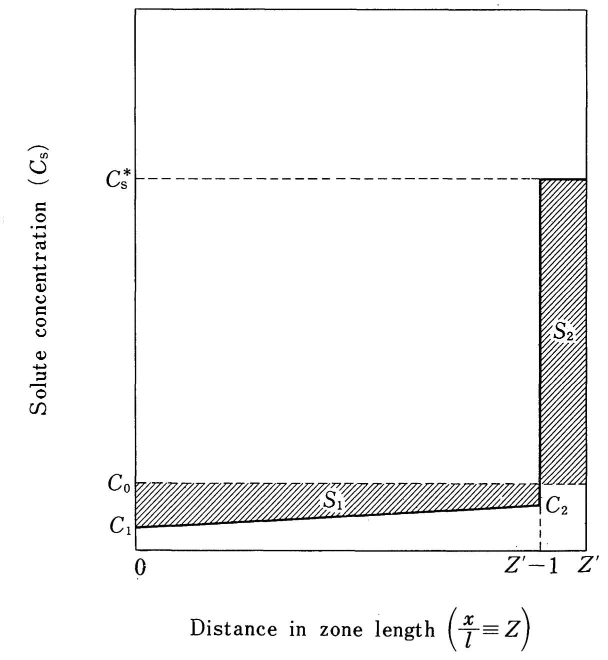

Fig. 1. Schematic diagram representing the material balance after a single zone pass for a eutectic mixture.

Since the solute concentration is determined experimentally as the average value in one zone length, Z' in Eq. 2 can be replaced by $Z^*=L/l-1/2$ in Eq. 3.

Determination of the Equilibrium Distribution Coefficient. In order to find the equilibrium distribution coefficient (K_o) on the basis of Eq. 3, it is necessary for K_e to be expressed as a function of the zone travel rate or freezing rate (V). It is well known for many systems that the relationship among K_e, K_o and V can be expressed by the following Burton–Prim–Slichter's equation:[3)]

$$\ln\left(\frac{1}{K_e}-1\right)=\ln\left(\frac{1}{K_o}-1\right)-\frac{\delta}{D}V, \tag{4}$$

where D and δ are the diffusion coefficient of the solute and the diffusion layer thichness, respectively. Equation 4 is rewritten as

$$\frac{(1-K_o)K_e}{(1-K_e)K_o}=\exp\left(\frac{\delta}{D}V\right). \tag{5}$$

The conditions that $K_o \ll 1$ and $K_e \ll 1$ are valid for a eutectic system.[2)] Equation 5 can thus be rewritten as

$$\frac{K_e}{K_o}=\exp\left(\frac{\delta}{D}V\right), \tag{6}$$

which, if $\delta V \ll D$, reduces to[#]

$$K_e=K_o+aV, \tag{7}$$

where $a \equiv K_o\delta/D$. From Eqs. 3 and 7, the following equation is obtained:

$$\frac{C_s^*}{C_0}=-AV+B, \tag{8}$$

where

$$A=\frac{a(Z^{*2}-1)}{2} \tag{9}$$

and

$$B=-\frac{K_o(Z^{*2}-1)}{2}+Z^*. \tag{10}$$

Constants A and B are the slope and intercept of Eq. 8 respectively, expressing the dependence of C_s^*/C_0 on the zone travel rate (V). The equilibrium distribution coefficient (K_o) can be given from Eq. 10 as

$$K_o=\frac{2(Z^*-B)}{Z^{*2}-1}. \tag{11}$$

Experimental

Materials. Commercial *p*-nitrophenol was purified by zone refining for 50 passes and commercial naphthalene was purified by one recrystallization from a benzene solution. Two naphthalene mixtures containing 0.5 and 1.0 wt% of *p*-nitrophenol were charged in a 30 cm long in Pyrex tubes with an inner diameter of 0.7 cm and outer diameter of 0.9 cm. The tubes were then sealed off under a dry nitrogen atmosphere of about 0.9 atm.

Procedures. The zone-melting experiments were carried out under the following conditions: zone travel rates of 2.47, 2.96, 5.43, 9.21, and 12.80 mm h^{-1}; 1 zone pass; a zone length of 3 cm and a zone temperature of 90±1 °C. The samples after a zone pass were cut into ten fractions, each 3 cm long and equal to the zone length. The samples from each fraction were dissolved in ethanol; color was then developed by adding a small amount of aqueous sodium hydroxide solution. The concentration of *p*-nitrophenol was determined spectrophotometrically by using a Hitachi 100-01 spectrophotometer at a wavelength of 400 nm.

Results and Discussion

Determination of the Effective Distribution Coefficient. As an example, the distribution of *p*-nitrophenol along a sample initially containing 1.0 wt% of this compound after a single zone pass at 2.96 mm h^{-1} is shown in Fig. 2; it represents the same profile as in Fig. 1, except that the ordinate is indicated by C_s/C_0 instead of C_s. The effective distribution coefficient was obtained by substituting the observed value of C_s^*/C_0 into Eq. 3. The relationship between the effective distribution coefficient and zone travel rate is shown in Fig. 3, together with the values obtained by a previously reported method,[2)] i.e. values from the slope of Eq. 1. The values obtained by these two methods agreed with

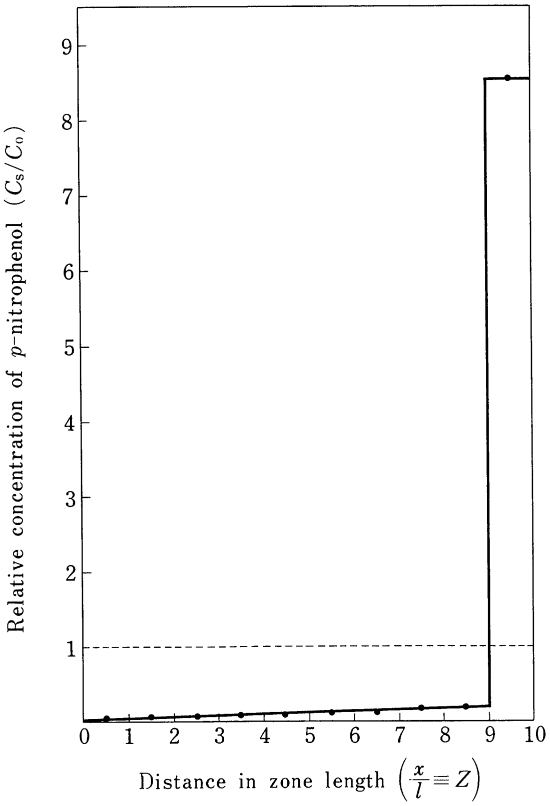

Fig. 2. Distribution of *p*-nitrophenol after a single zone pass at 2.96 mm h^{-1}; 1.0 wt% of *p*-nitrophenol.

[#] $\exp(x)=1+x+\frac{x^2}{2!}+\cdots$, $x \equiv \delta V/D$ and the squares and higher power of x can be neglected for the present case.

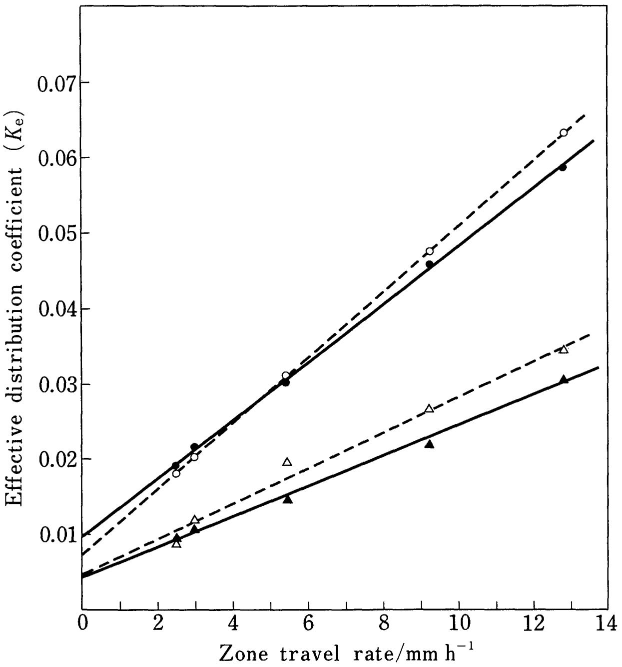

Fig. 3. Relationship between the effective distribution coefficient and the zone travel rate. ●: values for 1.0 wt% of *p*-nitrophenol determined by Eq. 3. ○: values for 1.0 wt% of *p*-nitrophenol determined from the slope of Eq. 1. ▲: values for 0.5 wt% of *p*-nitrophenol determined by Eq. 3. △: values for 0.5 wt% of *p*-nitrophenol determined from the slope of Eq. 1.

Table 1. Equilibrium Distribution Coefficients Determined by Three Methods

Methods employed	Equilibrium distribution coefficient, 0.5 wt% of *p*-nitrophenol	Equilibrium distribution coefficient, 1.0 wt% of *p*-nitrophenol
From Eqs. 8 and 11	4.26×10^{-3}	7.39×10^{-3}
From the intercepts of solid lines in Fig 3	4.23×10^{-3}	9.73×10^{-3}
From the intercepts of dotted lines in Fig. 3	4.51×10^{-3}	7.46×10^{-3}

each other, as is shown in Fig. 3; it is thus obvious that Eq. 7 is valid for this experiment.

Determination of the Equilibrium Distribution Coefficient. It is evident that Eq. 8 is valid for this experiment, as is shown in Fig. 4. By substituting the values of the intercepts of the straight lines in Fig. 4 into Eq. 11, the equilibrium distribution coefficients were evaluated. The obtained values are shown in Table 1 together with those obtained from the intercepts of the straight lines in Fig. 3, as described in a previous paper;[2] these values agree with each other.

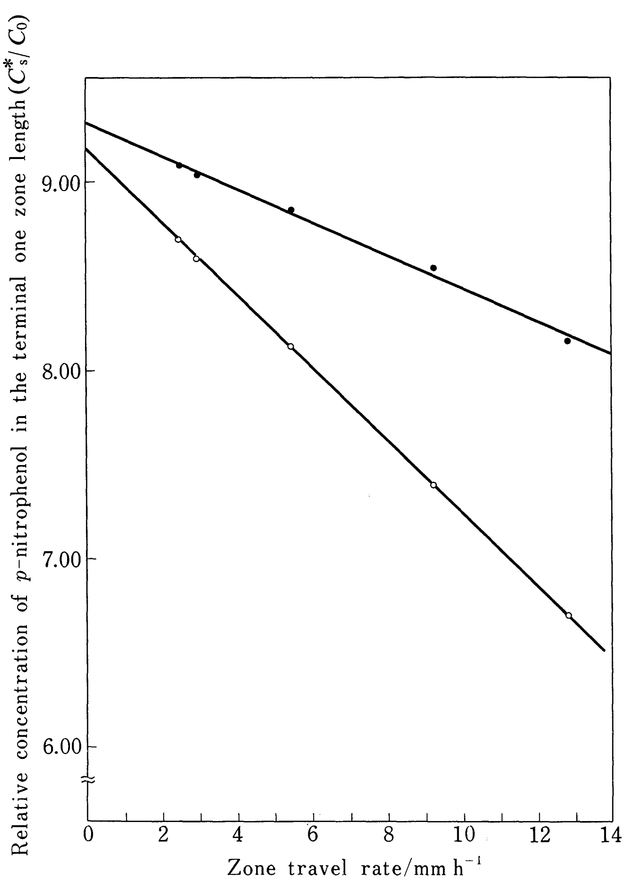

Fig. 4. Relationship between the relative concentration of *p*-nitrophenol in the terminal one zone length and the zone travel rate. ○: 1.0 wt% of *p*-nitrophenol. ●: 0.5 wt% of *p*-nitrophenol.

Conclusion

The effective distribution coefficient of *p*-nitrophenol in naphthalene could be determined by the present method, which agrees with that determined from the slope of Eq. 1. Also, the equilibrium distribution coefficient agrees with the value obtained by a previously reported method.[2] In the present method, both the effective and equilibrium distribution coefficients are determined from the solute concentration in the terminal one zone length, in which the enrichment of the solute is so large that the concentration can be accurately determined even for a specimen with a low solute concentration, in contrast with conventional methods.

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