Studies of Zone Melting. IV. The Equilibrium Distribution Coefficient of the Bibenzyl–Stilbene System†

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Determinations of the equilibrium distribution coefficients of stilbene in bibenzyl by the zone-melting method were performed by using the theory proposed by Burton and his co-workers from the effective distribution coefficients, which were measured at various zone travel rates (0.73, 0.98, 1.16, and 1.47 cm/h) on five samples of bibenzyl containing 0.3, 0.5, 1.0, 2.0, and 4.0 wt % of stilbene. Also, the equilibrium distribution coefficient independent of the concentration was obtained as 5.08 by the extrapolation of the equilibrium distribution coefficient *vs.* the concentration plots to zero concentration. The validity of the obtained results is discussed by a comparison of the values estimated individually by two other methods: the equilibrium distribution coefficient (5.23) determined from the phase diagram of the bibenzyl–stilbene system, and that (5.08) calculated thermodynamically.

It is well known that the distribution of either a solute or an impurity between the solid and liquid phases in the fractional solidification process, in which the zone-melting method is included, is generally not in equilibrium because of the advance of the solid-liquid interface at a considerably rapid rate and the incomplete diffusion of the solute in the molten phase under ordinary experimental conditions.

If the argument is restricted to the binary systems, the distribution of the solute in both phases is represented by the effective distribution coefficient under the non-equilibrium conditions. On the other hand, if an equilibrium is established between the two phases, the distribution of the solute is indicated by the equilibrium distribution coefficient.

For the reasons described above, it is usually difficult for the equilibrium distribution coefficient to be determined directly from a zone-melting experiment. However, it can be estimated with the theory proposed by Burton and his co-workers¹⁾ from the effective distribution coefficients obtained at various zone travel rates.

Determinations of the equilibrium distribution coefficients in this way have been achieved for a variety of binary systems, but the validity of the obtained results has been little discussed in terms of other methods, such as the phase diagram and thermodynamic theory.

In the previous paper,²⁾ the author attempted to estimate the equilibrium distribution coefficient of azobenzene in stilbene, which is less than unity, through the theory given by Burton and his co-workers¹⁾ from zone-melting experiments, and also to compare it with the results obtained from the phase diagram of the system and from the thermodynamic theory of ideal solutions.

It will also be worth-while to study a system in which the distribution coefficient is greater than unity according to the above methods. Therefore, in this paper, similar discussions will be undertaken of the equilibrium distribution coefficient of *trans*-stilbene in bibenzyl, which is greater than unity. The obtained result was somewhat different from that found in the stilbene–azobenzene system.

No zone-melting experiments have previously been reported for the bibenzyl–stilbene system.

Experimental

Materials. The bibenzyl was purified once by recrystallization from ethanol, and the stilbene was zone-refined. The bibenzyl was mixed with stilbene in Pyrex beakers in the concentrations of 0.3, 0.5, 1.0, 2.0, and 4.0 wt %. After a small amount of acetone had been added to these mixtures, they were warmed and stirred gently until all of them were dissoved in acetone, and then the acetone was removed by evaporation in a vacuum desiccator. The samples were powdered in an agate mortar.

The bibenzyl was placed in a length of 27 cm in a Pyrex tube with an internal diameter of 0.7 cm and an outer diameter of 0.9 cm. In addition, the bibenzyl-stilbene mixture prepared by the procedures described above was placed on bibenzyl to a length of 3 cm. Then the tube was sealed off under a dry nitrogen atmosphere of about 0.9 atm.

Apparatus and Procedures. The zone-melting experiments were carried out with the apparatus described in a previous paper.³⁾

The experiments of a single zone pass were carried out under the following conditions: the sample tube was moved upward at the different travel rates of 0.73, 0.98, 1.16, and 1.47 cm/h; the zone length was kept at 3 cm, and the zone temperature was set at 60 °C.

After a single passage of the molten zone, the sample was cut into 3-cm-long divisions. The concentration of stilbene in each portion was determined spectrophotometrically in an ethanol solution by means of a Hitachi 101 spectrophotometer at a wavelength of 295 nm.

Phase Diagram of the Bibenzyl–stilbene System. On the phase diagram of this system, several works have been reported.⁴⁻⁶⁾ Kolosov's work,⁶⁾ which is shown in Fig. 1, seems the most accurate among these works. Unfortunately, however, the accuracy in the range of low concentrations of stilbene, which is required for the determination of the equilibrium distribution coefficient from the phase diagram, is as poor in his diagram as in the others. For the purpose of correcting inaccuracies in Kolosov's data, the solidus and liquidus curves at low concentrations of stilbene were determined in detail with a Shimadzu differential scanning calorimeter, SC-20. The obtained results are presented in Fig. 2.

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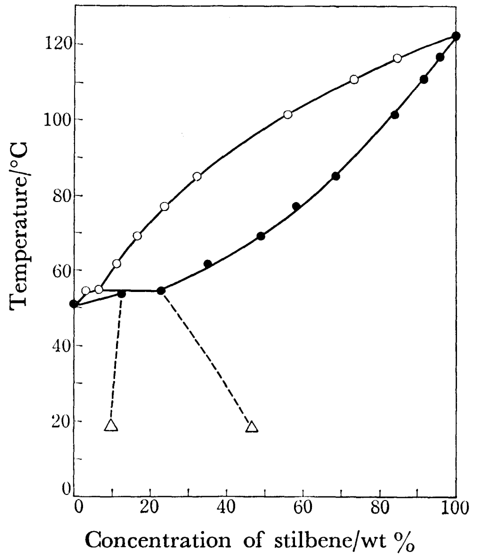

Fig. 1. Phase diagram of bibenzyl–stilbene system (after Kolosov[6]).

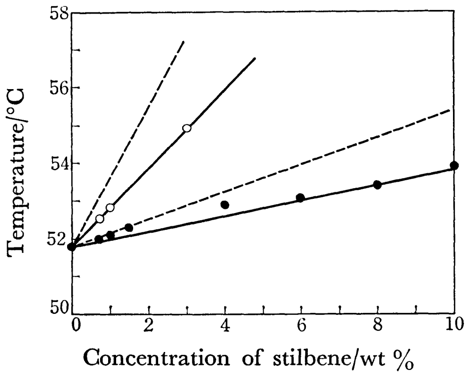

Fig. 2. Phase diagram of bibenzyl–stilbene system in the low concentration of stilbene.

○: Observed liquidus curve, ●: observed solidus curve, ----: ideal solidus and liquidus curves calculated thermodynamically.

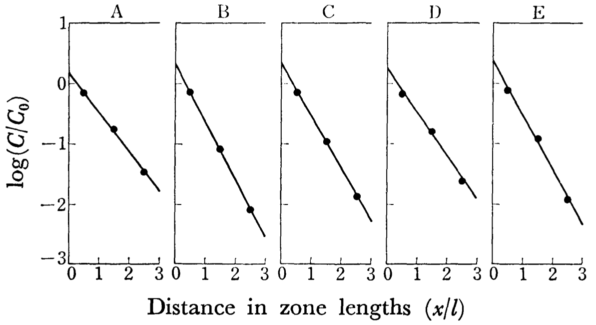

Fig. 3. $\log(C/C_0)$ *vs.* x/l.

A: 0.3% of stilbene; zone travel rate 0.73 cm/h, B: 0.5% of stilbene; zone travel rate 0.73 cm/h, C: 1.0% of stilbene; zone travel rate 0.73 cm/h, D: 2.0% of stilbene; zone travel rate 0.73 cm/h, E: 4.0% of stilbene; zone travel rate 0.73 cm/h.

Table 1. The effective distribution coefficient determined by the method of Sue and co-workers

Concentration of stilbene (wt %)	Zone travel rate (cm/h)	K_e from the intercept	K_e from the slope
0.3	0.73	1.57	1.52
	0.98	1.44	1.35
	1.16	1.32	1.25
	1.47	1.39	1.33
0.5	0.73	2.23	2.23
	0.98	2.01	1.89
	1.16	1.97	1.71
	1.47	1.80	1.80
1.0	0.73	2.04	2.00[a]
	0.98	1.85	2.08
	1.16	1.76	1.79
	1.47	1.65	1.76
2.0	0.73	1.72	1.67
	0.98	1.62	1.64
	1.16	1.66	1.68
	1.47	1.42	1.48
4.0	0.73	2.36	2.06
	0.98	2.50	2.16
	1.16	2.18	1.99
	1.47	2.06	1.86

a) The effective distribution coefficient obtained from the slope was adopted to calculate the equilibrium distribution coefficient.

Results and Discussion

Zone-melting Experiments. With the distributions of stilbene along the length of the samples after a single zone pass, the effective distribution coefficients were evaluated by the method of Sue and his co-workers.[7] In this method, the charge of the initial zone length consists of two components, that is, the solute whose distribution coefficient is to be measured and a solvent, while the remainder of the charge consists of a solvent only. The solute concentration, C, after a single zone passage is given at a distance, x, from the top of the sample by

$$\log\frac{C}{C_0} = -0.4343K_e\frac{x}{l} + \log K_e, \qquad (1)$$

where K_e is the effective distribution coefficient; C_0 is the initial concentration of the solute, and l is the zone length. Therefore, a plot of $\log(C/C_0)$ *vs.* x/l yields a straight line, and the slope and intercept of the line give the value of K_e. These relationships are shown in Fig. 3, in which, however, no whole data are represented in order to avoid complication; the values of K_e are shown in Table 1. The slope of Eq. 1 in the systems with distribution coefficients greater than unity is steeper than that in the systems with distribution coefficients less than unity, and the greater the coefficient, the steeper the slope. For this reason, the effective distribution coefficients were unavoidably estimated from only the three plots shown in Fig. 3.

Though the values of K_e estimated from both the slope and intercept in Eq. 1 should coincide with each other, the agreement is poor in the experimental results.[8,9] As one reason for this discrepancy, it may be considered that the assumptions used to derive Eq. 1 are not necessarily rigorously valid; the assumptions used are as follows: a constant distribution coefficient, no diffusion in the solid, a uniform concentration in the liquid, and no change in density on freezing.

The equilibrium distribution coefficient can be obtained from the effective distribution coefficients determined at various zone travel rates and expressed by the following equation by Burton *et al.*:[1)]

$$\log\left(1-\frac{1}{K_e}\right)=\log\left(1-\frac{1}{K_0}\right)-0.4343\frac{\delta V}{D}, \qquad (2)$$

where K_e and K_0 are the effective and equilibrium distribution coefficients respectively; D, the diffusion coefficient of the solute in the melt; δ, the boundary layer thickness, and V, the freezing rate, which may be assumed to be identical with the zone travel rate in the zone-melting experiments. The value of K_0 can be estimated from the plot of $\log(1-1/K_e)$ *vs.* V by Eq. 2. In the estimation of K_0 from Eq. 2, for K_e we employed the values obtained from the intercepts in Fig. 3 except when the value of K_e was taken from the slope: the zone travel rate of 0.73 cm/h for 1.0% of stilbene.

The experimental results are represented in Fig. 4, while Table 2 and Fig. 5 show the relationship between the values of K_0 obtained from the intercepts of the lines in Fig. 4 and the concentrations of stilbene, C. This relationship can be expressed approximately by the following empirical equation:

$$K_0 = 2.50\exp(-3.11C) + 2.58. \qquad (3)$$

Then, the equilibrium distribution coefficient independent of the concentration is evaluated by substituting zero into the C in Eq. 3. Thus the value of 5.08 is obtained.

Here we found that, in contrast to finding for the stilbene–azobenzene system, the concentration dependence of the equilibrium distribution coefficient is fairly great.

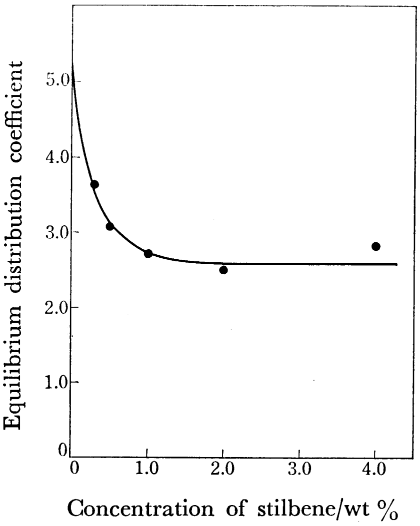

Fig. 5. The relation between equilibrium distribution coefficient and concentration of stilbene.
●: Observed values, ——: calculated curve by Eq. 3.

TABLE 2. THE RELATION BETWEEN THE CONCENTRAION OF STILBENE AND THE EQUILIBRIUM DISTRIBUTION COEFFICIENT

Concentration of stilbene (wt %)	Equilibrium distribution coefficient	
	Obsd	Calcd from Eq. 3
0.3	3.64	3.56
0.5	3.06	3.11
1.0	2.71	2.69
2.0	2.50	2.58
4.0	2.82	2.58

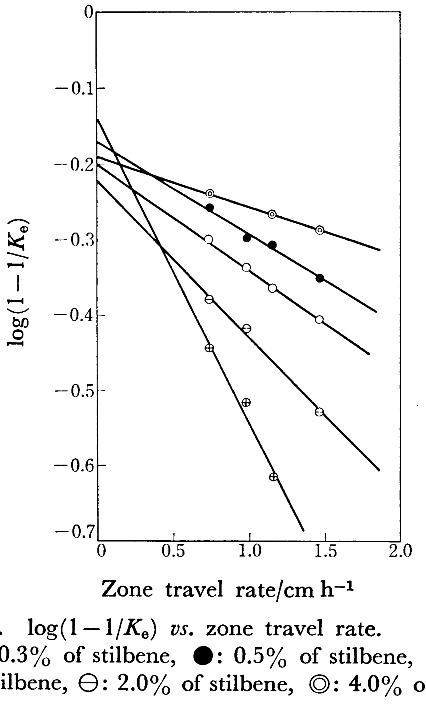

Fig. 4. $\log(1-1/K_e)$ *vs.* zone travel rate.
⊕: 0.3% of stilbene, ●: 0.5% of stilbene, ○: 1.0% of stilbene, ⊖: 2.0% of stilbene, ◎: 4.0% of stilbene.

Stilbene and azobenzene have the same crystal structure and almost the same molecular size, and form a complete series of solid solutions. On the other hand, the similarities of the crystal structure and molecular size of bibenzyl and stilbene are less than those of stilbene and azobenzene;[10)] hence, bibenzyl and stilbene form a peritectic system.

As one reason for such a difference between the concentration dependence of the equilibrium distribution coefficients found in the two systems, the fact described above may be considered.

In Fig. 4 straight lines for 0.5, 1.0, and 2.0% of stilbene are arranged in order of concentration. On the deviations from these arrangements of straight lines found in 0.3 and 4.0% of stilbene, it is considered that the effective distribution coefficient of 0.3% of stilbene might be smaller than the others because of the variation in the value of either D or δ for some reason. However the regularity, as shown in Table 2 and Fig. 5, might be restored in the equilibrium distribution coefficient, for it is independent of the above two factors. In the case of 4.0% of stilbene, the effective distribution coefficient becomes greater than those of 0.5—2.0% of stilbene. This result may be due to the transition at the peritectic point, at which a discontinuous change occurs in the distribution coefficient; this phenomenon is the so-called peritectic jump reported by Schildknecht.[11)]

Determination by Phase Diagram. The solidus and liquidus curves shown in Fig. 2 are approximately straight lines; their empirical equations are as follows:

$$t_s = 0.199C_s + 51.8, \tag{4}$$

$$t_l = 1.04C_l + 51.8, \tag{5}$$

where t_s and t_l are the solidus and liquidus temperatures in degrees of centigrade, and where C_s and C_l are the concentrations of stilbene in the solid and liquid phases respectively.

The equilibrium distribution coefficient independent of the concentration is given by Eq. 6 from the definition of distribution coefficient and Eqs. 4 and 5:

$$K_0 = \frac{C_s}{C_l} = \frac{1.04}{0.199} = 5.23. \tag{6}$$

Despite the fact that both solidus and liquidus curves are approximately straight, as shown in Fig. 2, the concentration dependence of the equilibrium distribution coefficient is fairly great in the results of the zone-melting experiments. This suggests that the equilibrium distribution coefficient estimated by the theory of Burton and his co-workers is the so-called interfacial distribution coefficient,[12] which seems to be not necessarily the same as the equilibrium distribution coefficient obtained by the phase diagram.

Determination by Thermodynamic Theory. In the binary systems, the relationship for the solid-liquid phase equilibrium is thermodynamically expressed by Eq. 7 at a constant pressure:

$$\ln\frac{a_s}{a_l} = \frac{\Delta H_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta C_p}{R}\left(1 - \frac{T_0}{T} + \ln\frac{T_0}{T}\right), \tag{7}$$

where a_s and a_l are the activities of the solute in the solid and liquid phases respectively. ΔH_0 and T_0 are the heat of fusion and the melting point of the solute; T is the temperature at which the solid and liquid phases are in equilibrium with each other; ΔC_p is the difference between the heat capacities of the liquid and the solid solute at the melting point; R is the gas constant. The definition of the activity prescribes that, as the concentration of the solute tends to zero, the activity tends to be equal to the concentration. Therefore, for a dilute solution, the equilibrium distribution coefficient may be written as follows:

$$K_0 = \frac{a_s}{a_l} = \frac{C_s}{C_l}. \tag{8}$$

That is, the left-hand side of Eq. 7 can be rewritten as $\ln K_0$.

Since the tendency of the solute concentration to tend to zero is, in other words, for the composition to tend to that of a pure solvent, substituting the melting point of the solvent for T in Eq. 7 may yield an equilibrium distribution coefficient independent of the concentration.

In Fig. 2, the smaller the concentration of stilbene, the closer the gap between the observed lines, represented by the full lines, and those calculated by the thermodynamic theory of the ideal solution, represented by the dotted lines. Therefore, the equilibrium distribution coefficient independent of the concentration can be calculated by means of Eqs. 7 and 8. To calculate the value of K_0, the numerical values substituted in Eq. 7 are as fusion:

ΔH_0 is the heat of fusion of stilbene: 25800 J/mol,*
T_0 is the melting point of stilbene: 397.6 K,*
T is the melting point of bibenzyl: 325.0 K,*
ΔC_p is the difference between the heat capacities of liquid and solid stilbene at the melting point: 45.3 J/mol.**

Thus, the value of 5.08 was obtained.

Though the similarities in the crystal structure and in molecular size between stilbene and bibenzyl are less than those of stilbene and azobenzene, as has already been described, the assumption of an ideal solution also, in this system, holds in low concentrations of stilbene. Moreover, the equilibrium distribution coefficient calculated thermodynamically agrees with those obtained from the zone-melting experiments and phase diagram, as shown in Table 3.

TABLE 3. THE EQUILIBRIUM DISTRIBUTION COEFFICIENTS DETERMINED BY THE THREE METHODS

Method employed for the determination of the equilibrium distribution coefficient	Equilibrium distribution coefficient
Zone melting	5.08
Phase diagram	5.23
Thermodynamic theory	5.08

Conclusion

In the zone-melting experiments, the equilibrium distribution coefficient extrapolated to zero concentration of stilbene agreed ultimately with the values determined from the phase diagram and thermodynamic theory. This fact differs considerably from that found in the stilbene–azobenzene system with regard to the concentration dependence of the equilibrium distribution coefficient. However, the determination of the equilibrium distribution coefficient through the theory of Burton and his co-workers, which is based on a dynamic process consisting of a heterogeneous reaction, was related to the methods taking account of the equilibrium conditions, that is, the phase diagram and the thermodynamic theory.

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* Measured on zone-refined specimens with a Shimadzu differential scanning calorimeter, SC-20.

** Estimated from the data cited in Timmermans' book.[13]

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