

EQUILIBRIUM DISTRIBUTION COEFFICIENT OF STILBENE-AZOBENZENE SYSTEM¹⁾

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The equilibrium distribution coefficients of azobenzene in stilbene were determined through the theory given by Burton and co-workers from the effective distribution coefficients obtained by zone melting experiments with various zone travel rates. These results were compared with the values estimated by other two methods: the phase diagram and the thermodynamic theory.

In zone melting experiments, the measurements were carried out on the five samples of stilbene containing 0.3, 0.5, 0.7, 1.0 and 2.0 wt % of azobenzene with different zone travel rates of 0.73, 0.98, 1.16 and 1.47 cm/hr. The equilibrium distribution coefficients were obtained as 0.31, 0.31, 0.33, 0.35 and 0.37 for the above five samples, respectively. Thus these values were almost independent of the concentration.

From the phase diagram of stilbene-azobenzene system, the equilibrium distribution coefficient was determined to be 0.35 in the concentration of azobenzene, within which both solidus and liquidus curves are regarded as the straight lines.

On the other hand, the equilibrium distribution coefficient was thermodynamically calculated to be 0.34 by assuming the ideality of the system.

These values determined by the above three methods were in good agreement with each other.

Introduction

In the separation of a binary mixture by means of the zone melting method, in the broader sense, the fractional solidification process, the distribution coefficient of the solute or impurity is an important quantity; for it indicates such factors as the degree of separation and the tendency for the solute to be segregated in either solid or liquid phase.

Unless the rate of solidification is negligibly small, no equilibrium is set up between the solid and liquid phases. In this case, the distribution of the solute between two phases is given by the effective distribution coefficient, which depends greatly on the experimental conditions. But when the solid and liquid phases are in equilibrium with each other, the distribution of the solute in both phases is represented by the equilibrium distribution coefficient, which is usually difficult to be determined directly

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1) Some parts of this work were presented at the 32nd Annual Symposium of the Chemical Society of Japan, Tokyo, April (1975) Proceedings, Part I, p. 76

by zone melting owing to the departure from equilibrium in the experimental conditions, but can be estimated with the aid of Burton and co-workers^{2,3)} theory from the effective distribution coefficients obtained at various zone travel rates.

At the present stage of zone melting experiment little is known about the investigation interpreting the equilibrium distribution coefficient determined through Burton and co-workers' theory by the phase diagram of a binary system and also thermodynamic theory.

In this work, the above-mentioned subject is analysed on the equilibrium distribution coefficient of *trans*-azobenzene in *trans*-stilbene.

van Essen and co-workers⁴⁾ reported the separation of stilbene containing 0.5 mol% of azobenzene with a rapid zone refiner, and showed the distribution coefficient of this system to be 0.3.

Experimentals

Materials

The chemicals used in this experiment were stilbene recrystallized one time from ethanol and zone-refined azobenzene. Azobenzene was mixed with stilbene in the concentrations of 0.3, 0.5, 0.7, 1.0 and 2.0 wt%. These mixtures were fused in Pyrex ampoules under dry nitrogen so as to make composition uniform, and then cooled rapidly. The samples were taken out of the ampoules and powdered in an agate mortar.

A Pyrex tube with an internal diameter of 0.7 cm and an outer diameter of 0.9 cm was filled with stilbene to a length of 27 cm, on the top of which stilbene-azobenzene mixture prepared by the procedure described above was placed to a length of 3 cm. Then the tube was sealed off under dry nitrogen of about 0.9 atm.

Apparatus and procedures

Zone melting experiments were carried out with the apparatus described in the previous paper⁵⁾. The sample tubes were moved upward at different zone travel rates of 0.73, 0.98, 1.16 and 1.47 cm/hr. The zone length (l) was kept at 3 cm and the zone temperature was adjusted to 135°C.

After a single passage of molten zone the sample was sliced into 3 cm-long divisions. The concentration of azobenzene in each division was determined spectrophotometrically in ethanol solution with a Shimadzu Baush & Lomb Spectronic 20 spectrophotometer at wavelength of 340 nm.

Phase diagram of stilbene-azobenzene system

For lack of the reliabilities of phase diagram of stilbene-azobenzene system reported formerly by

2) J. A. Burton, R. C. Prim and W. P. Slichter, *J. Chem. Phys.*, **21**, 1987 (1953)

3) J. A. Burton, E. D. Kolb, W. P. Slichter and J. D. Struthers, *ibid.*, **21**, 1991 (1953)

4) M. J. van Essen, P. F. J. van der Most and W. M. Smit, "Purification of Inorganic and Organic Materials", p. 201, ed. by M. Zief, Marcel Dekker, Inc., New York, N. Y. (1969)

5) H. Nojima, *Nippon Kagaku Zasshi*, **91**, 810 (1970)

other workers, the authors re-created the phase diagram of the system with Shimadzu Thermal Analyser DT-20B. The obtained result is shown in Fig. 1. In order to determine the equilibrium distribution coefficient from the phase diagram, it is necessary to obtain more accurate phase diagram at a low concentration range of azobenzene. For this purpose the solidus and liquidus curves of the system were determined carefully up to 10 wt % of azobenzene. The determined curves are represented in Fig. 2.

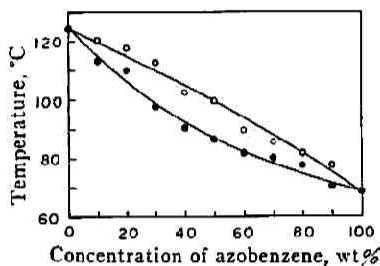


Fig. 1 Phase diagram of stilbene-azobenzene system
○: liquidus curve
●: solidus curve

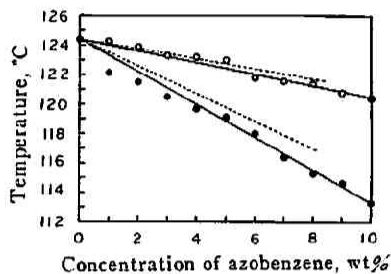


Fig. 2 Phase diagram of stilbene-azobenzene system up to 10% of azobenzene
○: observed liquidus curve
●: observed solidus curve
... ideal liquidus and solidus curves calculated thermodynamically

Results and Discussions

Zone melting experiments

From the distribution of azobenzene along the length of the sample after a single zone pass determined by the method described above, the effective distribution coefficient was evaluated by Sue and co-workers⁶⁾ method: binary mixture containing a solute, whose distribution coefficient is to be measured, is placed on the top of the sample tube filled with a pure solvent. A single zone passage was carried out through the specimen. After a zone passage the solute concentration C at a distance x from the top of the sample is expressed by Eq. (1).

$$\log\left(\frac{C}{C_0}\right) = -0.4343 \frac{K_e x}{l} + \log K_e \quad (1)$$

where K_e is the effective distribution coefficient and C_0 is the initial concentration of the solute, and 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 .

The equilibrium distribution coefficient can be obtained from the effective distribution coefficients through the theory which is expressed by Burton and co-workers^{2,3)} in the following equation:

6) P. Sue, J. Pauly and A. Nouaille, *Bull. Soc. Chim. France*, 5, 593 (1958)

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

where K_e and K_0 are the effective and equilibrium distribution coefficients, respectively. D is the solute diffusion coefficient in the melt, δ is the boundary layer thickness, and V is the freezing rate, which, in the present case, is assumed to be equal to the zone travel rate.

The equilibrium distribution coefficient K_0 can be estimated from the plot of $\log(1/K_e-1)$ vs. V by Eq. (2). The experimental results are represented in Fig. 3 and Table 1.

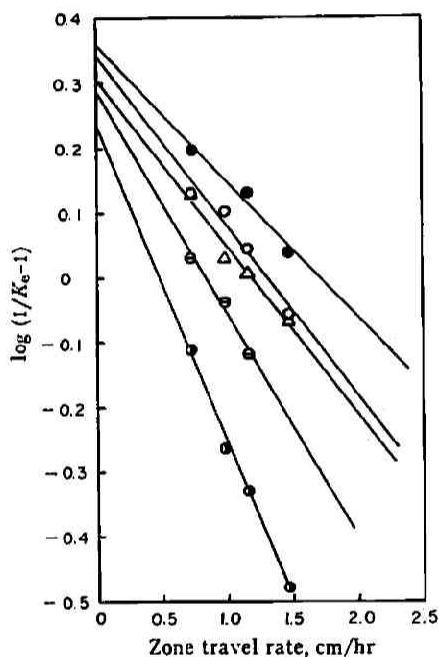


Fig. 3 $\log(1/K_e-1)$ vs. zone travel rate

- : 0.3% of azobenzene
- : 0.5% of azobenzene
- △: 0.7% of azobenzene
- : 1.0% of azobenzene
- : 2.0% of azobenzene

Table 1 The equilibrium distribution coefficients determined by the three methods

Method employed for determination of the equilibrium distribution coefficient	Equilibrium distribution coefficient	
Zone melting	0.3% of azobenzene	0.31
	0.5% of azobenzene	0.31
	0.7% of azobenzene	0.33
	1.0% of azobenzene	0.35
	2.0% of azobenzene	0.37
Phase diagram	0.35	
Thermodynamic calculation	0.34	

Strictly speaking, the equilibrium distribution coefficient estimated by Burton and co-workers' theory is the so-called interfacial distribution coefficient⁷⁾, which seems to be not necessarily the same

7) J. S. Shah, "Crystal Growth", p. 104, ed. by B. P. Pamplin, Pergamon Press, Oxford (1975)

as the equilibrium distribution coefficients obtained by the phase diagram and the thermodynamic theory. However, in the present case, the obtained results are in fairly good agreement with each other as described below.

A slight concentration dependence of the equilibrium distribution coefficient was observed, which seems to indicate that both solidus and liquidus curves are approximately straight lines as shown in Fig. 2, and therefore, the equilibrium distribution coefficient may be nearly taken as a constant under the experimental concentrations.

Determination by phase diagram

The observed solidus and liquidus curves shown in Fig. 2, represented by the full lines, can be expressed by the following empirical formulae:

$$T_s = -1.1076 C_s + 124.4 \quad (3)$$

$$T_l = -0.3922 C_l + 124.4 \quad (4)$$

where T_s and T_l are the solidus and liquidus temperatures, and C_s and C_l are the concentrations of azobenzene in the solid and liquid phases, respectively.

From Eqs. (3) and (4) and the definition of the distribution coefficient, the following value was obtained:

$$K_0 = C_s/C_l = 0.3922/1.1076 = 0.35 \quad (5)$$

namely: the equilibrium distribution coefficient independent of the concentration is expressed as the ratio of the slope of the liquidus curve to that of the solidus curve provided that these are straight lines.

Determination by thermodynamic calculation

From Fig. 2, in which the solidus and liquidus curves calculated thermodynamically by assuming the ideality of the system are shown as well as the observed curves, it is reasonable for the system to be assumed as an ideal solution, particularly in a low concentration of azobenzene. Also this assumption would be supported by the fact that azobenzene and stilbene have the same crystal structure and almost identical molecular size⁸⁾. Consequently, the equilibrium distribution coefficient can be expressed thermodynamically by Eq. (6)

$$\ln K_0 = \frac{\Delta H_0}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (6)$$

where ΔH_0 and T_0 are the heat of fusion and the melting point of azobenzene, which are 21700 J/mol and 341.0 K, respectively. R is the gas constant. By substituting a value in the vicinity of the melting point of stilbene, which is 397.6 K, into T in Eq. (6), the equilibrium distribution coefficient independent of the concentration was evaluated to be 0.34.

8) A. I. Kitaigorodsky, "Organic Chemical Crystallography", p. 372, Consultants Bureau Enterprises, Inc., New York, N. Y. (1961)

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In this work, it was proved that the equilibrium distribution coefficients estimated by the three methods based on rather different assumptions agreed with each other, and the relation among these three methods has become apparent to some extent.

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