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Effect of Pressure on the Solid–Liquid Phase Equilibria of Binary Organic Systems[1]

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Solid–liquid phase equilibria of the binary mixtures of the organic liquids have been investigated at temperatures from 278 to 343 K and pressures up to 500 MPa using a high-pressure optical vessel. The systems investigated are as follows: (1) simple eutectic systems—benzene + cyclohexane system and benzene + 2-methyl-2-propanol system; (2) eutectic systems with formation of intermolecular compounds—carbon tetrachloride + p-xylene system and carbon tetrachloride + benzene system; (3) partial solid solution system—α-methylnaphthalene + β-methylnaphthalene system; and (4) complete solid solution system—chlorobenzene + bromobenzene system. The uncertainties of the measurements of temperature, pressure and composition are within ± 0.1 K, ± 0.5 MPa, and ± 0.001 mole fraction, respectively. The freezing and melting temperatures at a constant composition increase monotonously with pressure. The eutectic mixture becomes richer in the component whose temperature coefficient of the freezing pressure is larger and the eutectic temperature rises monotonously with increasing pressure in the eutectic systems. The pressure–temperature–composition relation of the solid–liquid phase equilibria can be expressed satisfactorily by an equation newly proposed.

KEY WORDS high pressure; mixtures; organic liquid; phase equilibrium.

1. INTRODUCTION

Recently, the high-pressure crystallization technique has been realized as an advanced separation and purification method from the viewpoint of the high purity of the products and low energy consumption [1, 2]. However,

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the knowledge of multicomponent high-pressure solid–liquid phase equilibria, which is essential for the design of this process, has been scarcely investigated, especially for the organic systems. Therefore, it is essential to investigate the pressure effect on various types of phase diagrams and to establish the correlation method of high-pressure solid–liquid phase equilibria.

In this work, solid–liquid phase equilibria of six systems of binary mixtures of organic liquids have been investigated by the direct visual observation of the phase transition. The pressure effect on the various phase diagrams is reviewed inclusively based on the experimental results and the solid–liquid coexistence curves are correlated by a newly proposed equation.

2. EXPERIMENTAL

The measurements were performed in a high-pressure optical vessel, which was described elsewhere [3]. All the samples were obtained from commercial sources and they were used after being dried by calcium hydride.

3. RESULTS AND DISCUSSION

3.1. The Simple Eutectic Systems

The benzene + cyclohexane [3] and benzene + 2-methyl-2-propanol [4] systems are the simple eutectic systems with no miscibility in the solid phase. Figure 1 shows the pressure–temperature–composition relation of the benzene + cyclohexane system. The freezing temperature at a constant composition increases monotonously with increasing pressure, and the pressure effect on the freezing temperature $(\partial T_f/\partial P)_{xi}$ decreases as the composition approaches the eutectic mixture. The eutectic point of this system shifts to higher temperatures and benzene-richer compositions with increasing pressure. At 0.1 MPa, the eutectic composition of the benzene + cyclohexane system is x_1 (mole fraction of benzene) $=0.26$ [5]. On the other hand, under high pressures it shifts to $x_1=0.35$ at 250 MPa and 0.38 at 340 MPa. The pressure effect on the eutectic composition could be explained by the van Laar equation [6] as follows:

$$(\partial x_1/\partial P)_e = K[(\partial P_f/\partial T)_1 - (\partial P_f/\partial T)_2] \qquad (1)$$

where subscript e denotes the values of the eutectic mixture. As the quantity K is positive in this system and the sign of $(\partial P_f/\partial T)_1-(\partial P_f/\partial T)_2$ is also

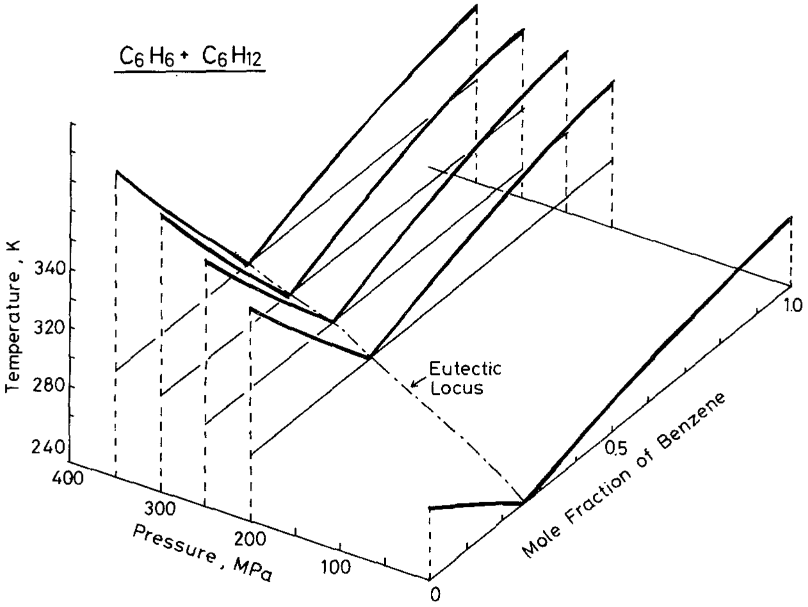

Fig. 1. Pressure–temperature–composition relation of the benzene + cyclohexane system.

positive, Eq. (1) suggests that the eutectic mixture becomes richer in the first component (benzene). The tendency is found to agree with the present experimental results. The similar trend is obtained for the benzene + 2-methyl-2-propanol system, where the eutectic composition of this system changes from $x_1 = 0.53$ at 0.1 MPa to $x_1 = 0.55$ at 150 MPa.

3.2. The Eutectic Systems with Formation of Intermolecular Compounds

The carbon tetrachloride + *p*-xylene system [7] has an intermolecular compound at the composition ratio of 1:1, and it does not decompose until its melting temperature, which is called a congruent melting point. Figure 2A shows the solid–liquid phase diagram at various pressures. This system has two eutectic points at $x_1 = 0.94$ and $x_1 = 0.38$ (x_1 mole fraction of carbon tetrachloride) at atmospheric pressure [8]. The freezing curve shifts to a higher temperature monotonously with increasing pressure. Both eutectic points shift to richer compositions of the compound. In the carbon tetrachloride-rich region, the eutectic composition becomes $x_1 = 0.91$ at 300 MPa, and in the *p*-xylene-rich region it becomes $x_1 = 0.43$ at 200 MPa. The pressure effect on the eutectic composition is greater in the *p*-xylene-rich region. Therefore, it is supposed that in higher-pressure regions, the

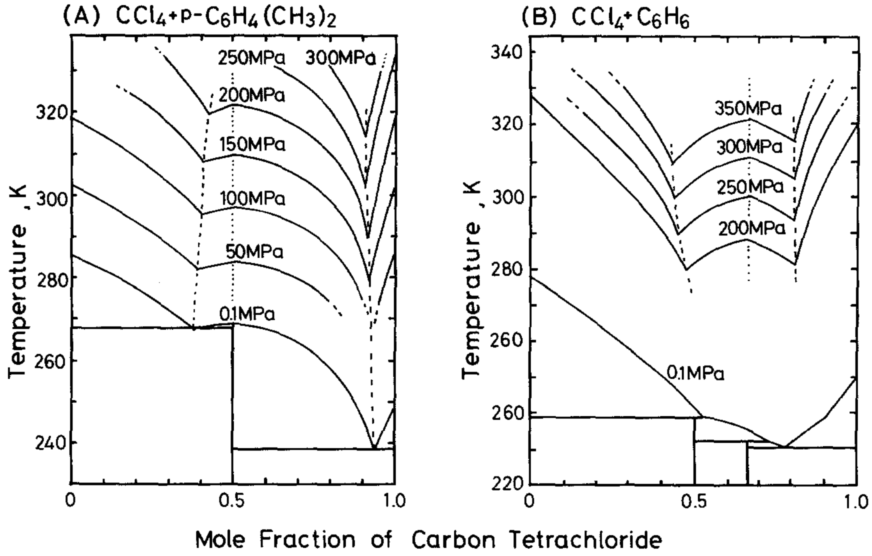

Fig. 2. Solid–liquid phase diagrams of the eutectic systems with formation of intermolecular compounds at various pressures: (A) the carbon tetrachloride + *p*-xylene system; (B) the carbon tetrachloride + benzene system.

eutectic point in the *p*-xylene rich-region would approach 0.5, and the congruent melting point should change to the incongruent melting point, where the compound decomposes until its melting temperature.

The carbon tetrachloride + benzene system [7] has two intermolecular compounds at 0.1 MPa. One is at the composition ratio of 1 : 1 (compound I) and the other is at the composition ratio of 2 : 1 (compound II). Both compounds have incongruent melting points where the compounds decompose until their melting temperatures [9]. Figure 2B shows the solid–liquid phase diagram at various pressures. However, the shape of the phase diagram changes extensively at high pressures. Compound I disappears under this experimental condition. The incongruent melting point of compound II turns to the congruent melting point. As a result, this system has two eutectic points under high pressures. The eutectic point in the benzene-rich region shifts to the benzene-richer composition and in the carbon tetrachloride-rich region the eutectic composition is almost constant at $x_1 = 0.81$.

3.3. The Partial Solid Solution System

The α-methylnaphthalene + β-methylnaphthalene system [10] is a partial solid solution system, in which the solid components can be soluble

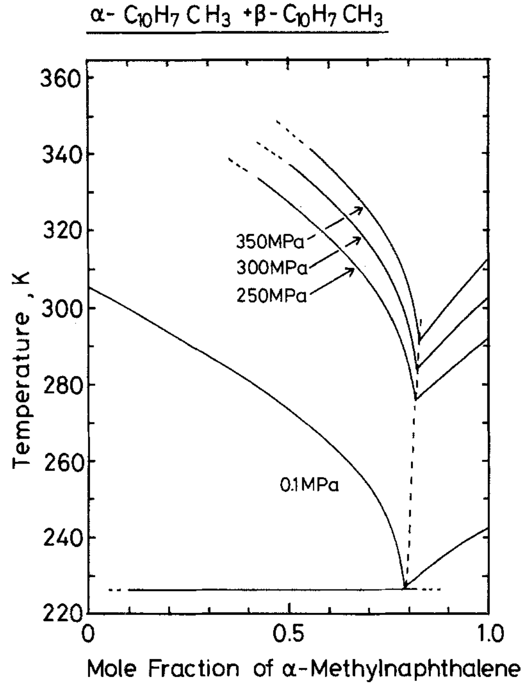

Fig. 3. Solid–liquid phase diagram of the α-methylnaphthalene + β-methylnaphthalene system at various pressures.

with each other to a limited extent. In this work, the freezing curves of this system were measured. Figure 3 shows the relation between the freezing temperature and the composition at various pressures. The freezing curve shifts to a higher temperature monotonously with increasing pressure. The eutectic composition of this system is $x_1 = 0.78$ (x_1: mole fraction of α-methylnaphthalene) at 0.1 MPa [11]. With increasing pressure, the eutectic composition shifts to $x_1 = 0.82$. Applying the van Laar equation as simple eutectic systems, since the temperature coefficient of the freezing pressure of α-methylnaphthalene is larger than that of β-methylnaphthalene, it is expected that the eutectic mixture becomes richer in α-methylnaphthalene, in accord with the experimental results.

3.4. The Complete Solid Solution System

The chlorobenzene + bromobenzene system [10] is a complete solid solution system in which solid components are soluble in each other at any

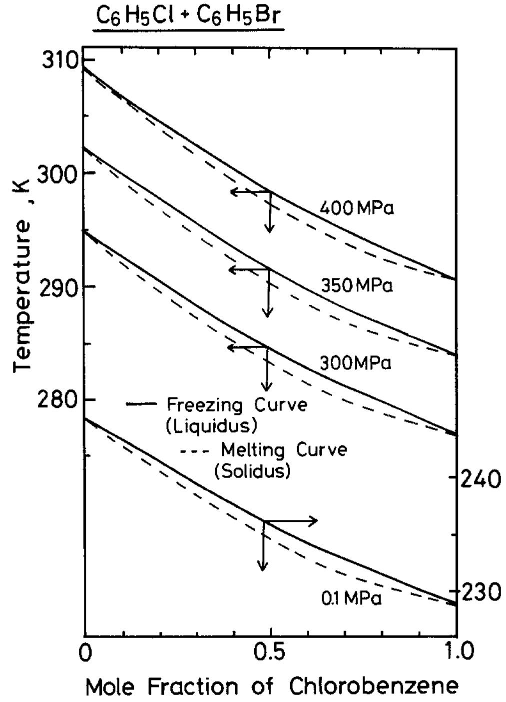

Fig. 4. Solid–liquid phase diagram of the chlorobenzene + bromobenzene system at various pressures.

composition. Figure 4 shows the relation of freezing temperature versus composition curve (liquidus) and the melting temperature versus composition curve (solidus) at various pressures with those at 0.1 MPa [12]. The freezing and melting temperatures change monotonously with composition and no definite maximum or minimum is observed throughout the entire range of composition and pressure. Both freezing and melting temperatures rise monotonously with increasing pressure. The difference between freezing and melting temperature at any composition is almost independent of pressure under these experimental conditions.

3.5. Correlation of Solid–Liquid Coexistence Curves

At a constant temperature, the relation of freezing pressure and composition can be expressed as follows [10]:

$$\ln x_i = b_0 + b_1 P + b_2 P^2 \tag{2}$$

where b_0, b_1, and b_2 are the coefficients characteristic of the system and temperature. To express the temperature dependence of these coefficients, the relation of temperature–pressure–composition of solid–liquid equilibria can be described. The authors have proposed a new equation as follows:

$$\ln x_i(P, T) = -1/RT\{C(T)[P - B(T)] + D(T)[P^2 - B(T)^2]\} \qquad (3)$$

The temperature dependences of the coefficients B, C, and D are expressed by the polynomials of the reciprocal of the temperature, respectively. Equation (3) is found to express the liquidus of both eutectic systems and solid solution systems satisfactorily.

For the coexistence curves of the systems forming intermolecular compounds at the composition ratio of $m{:}n$, Eq. (3) could be expanded as follows:

$$\begin{aligned}\ln x_i^m(1 - x_i)^n - \ln x_{\mathrm{ic}}^m(1 - x_{\mathrm{ic}})^n \\ = -1/RT\{C(T)[P - B(T)] + D(T)[P^2 - B(T)^2]\} \qquad (4)\end{aligned}$$

where x_{ic} denotes the mole fraction of an intermolecular compound. Equation (4) can reproduce the experimental results satisfactorily for the compound systems.

4. CONCLUSIONS

Solid–liquid phase equilibria of six systems of binary organic mixtures have been investigated under high pressure. The phase diagrams change with increasing pressure as follows.

(1) The freezing curves shift to higher temperatures monotonously, except for the carbon tetrachloride + benzene system.

(2) In the eutectic systems, the eutectic mixture becomes richer in the component whose temperature coefficient of freezing pressure is larger. This trend agrees with the direction predicted by the van Laar equation.

(3) In the carbon tetrachloride + *p*-xylene system, two eutectic points shift to the compound-rich compositions. In higher-pressure regions, it is expected that the eutectic composition in the *p*-xylene-rich region approaches 0.5, and the congruent melting point turns to the incongruent melting point.

(4) On the contrary, in the carbon tetrachloride + benzene system, one compound disappears and the incongruent melting point of another compound changes to the congruent melting point.

(5) In the chlorobenzene + bromobenzene system, the freezing and melting temperatures change monotonously with composition at constant pressure.

The solid–liquid coexistence curves can be correlated satisfactorily by an equation newly proposed for all systems. In order to investigate the behavior of the phase diagram with pressure, the authors are carrying out the measurements for other systems.

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