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# Solid–Liquid Phase Equilibria of Benzene + 2-Methyl-2-Propanol System Under High Pressures

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Solid–liquid phase equilibria of the benzene + 2-methyl-2-propanol system have been investigated at temperatures from 278 to 323 K and pressures up to 300 MPa using a high-pressure optical vessel. 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 pressure at a constant composition increases monotonously with pressure. The eutectic point shifts to a higher temperature and benzene-rich composition with increasing pressure. In order to describe the pressure–temperature–composition relation of high-pressure solid–liquid phase equilibria, a new simple equation has been proposed as follows:

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

where $B$, $C$, and $D$ are the temperature-dependent coefficients and are expressed by the polynomials of reciprocal of temperature. It is found that the solid–liquid coexistence curves of both eutectic systems and solid–solution systems can be correlated satisfactorily by this equation.

**KEY WORDS:** benzene; high pressure; 2-methyl-2-propanol; solid–liquid phase equilibrium.

## 1. INTRODUCTION

The information of solid–liquid phase equilibria plays important roles in the design of crystallization processes. Recently, as the high-pressure crystallization technique has been noticed as a new separation and purification method, accurate knowledge of the high-pressure solid–liquid phase equilibria is now required. In order to investigate the pressure effect on various types of the solid–liquid phase equilibria, the authors

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have measured the benzene + cyclohexane system [1] and the α-methylnaphthalene + β-methylnaphthalene and the chlorobenzene + bromobenzene systems [2]. In this work, solid–liquid phase equilibria of the benzene + 2-methyl-2-propanol (t-butyl alcohol) system, which is a mixture of nonpolar and polar molecules, are measured at temperatures from 278 to 323 K and pressures up to 300 MPa. The effect of pressure on the phase diagram is discussed and coexistence curves are expressed by a proposed new equation.

## 2. EXPERIMENTAL

The measurements were performed in a high-pressure optical vessel. The apparatus and experimental procedure were described in a previous paper [1]. Benzene and 2-methyl-2-propanol were obtained from commercial sources and their purities should be better than 99 wt%. The samples were used after drying by calcium hydride. The uncertainties of the measurements of temperature, pressure, and composition are within ±0.1 K, ±0.5 MPa, and ±0.001 mole fraction, respectively.

## 3. RESULTS

The experimental results are listed in Table I. The freezing pressures of 2-methyl-2-propanol agree well with the literature values [3] and the temperature dependence is expressed by the following equation derived from the Simon equation.

$$P_f = -284.7 + 1.36 \times 10^{-5}\, T^{2.96} \tag{1}$$

where $T$ is in K and $P_f$ in MPa. Equation (1) can reproduce the freezing temperature within ±0.3 K.

A solid–liquid phase diagram at various pressures is shown in Fig. 1. The freezing temperature of each mixture increases monotonously with increasing pressure, and the temperature coefficient of freezing pressure becomes greater as the composition approaches the eutectic mixture. The eutectic temperature and composition are plotted against pressure in Fig. 2. At 0.1 MPa, the eutectic composition of this system $x_1$ (mole fraction of benzene) is 0.53. The eutectic composition of benzene increases with increasing pressure. As a result, from a mixture of $x_1 = 0.55$, benzene crystals were deposited at pressures lower than 100 MPa; on the other hand, 2-methyl-2-propanol crystals were formed at pressures higher than 100 MPa. The eutectic composition was almost constant above 150 MPa. The direction of the shift of eutectic composition could be predicted by the van Laar equation [4], where the eutectic mixture becomes richer in the component whose temperature coefficient of freezing pressure is larger. The direction of the shift of eutectic composition agreed with that predicted by the van Laar equation, as in our previous systems [1, 2]. The eutectic temperature increases monotonously with increasing pressure. The eutectic temperature and composition of the present system are found to be expressed as a function of pressure as follows:

$$T_e = 267 + 0.261 \times P - 2.30 \times 10^{-4} P^2 \qquad (2)$$

$$x_{1e} = 0.525 + 3.85 \times 10^{-4} \ln P - 2.64 \times 10^{-3} \ln P^2 \qquad (3)$$

**Table I.** Solid–Liquid Equilibrium Data for the [Benzene (1) + 2-Methyl-2-Propanol (2)] System

| $x_1$[a] | $T$ (K) | $P_f$[b] (MPa) | Coexistence crystal[c] |
|---|---|---|---|
| 0 | 303.2 | 16.2 | T |
| | 313.2 | 44.7 | T |
| | 323.2 | 77.9 | T |
| 0.20 | 293.2 | 28.8 | T |
| | 303.2 | 60.1 | T |
| | 313.2 | 98.7 | T |
| | 323.2 | 144.5 | T |
| 0.40 | 278.2 | 16.4 | T |
| | 283.2 | 33.3 | T |
| | 293.2 | 69.4 | T |
| | 303.2 | 112.8 | T |
| | 313.2 | 156.8 | T |
| | 323.2 | 216.8 | T |
| 0.50 | 278.2 | 37.1 | T |
| | 283.2 | 57.1 | T |
| | 293.2 | 99.1 | T |
| | 303.2 | 146.7 | T |
| | 313.2 | 200.8 | T |
| | 323.2 | 267.7 | T |

[a] Mole fraction of benzene.

[b] Freezing pressure.

[c] B and T denote benzene and 2-methyl-2-propanol, respectively.

Table I *(Continued)*

| $x_1$[a] | $T$ (K) | $P_f$[b] (MPa) | Coexistence crystal[c] |
|---|---|---|---|
| 0.525 | 278.2 | 43.0 | T |
| | 283.2 | 63.1 | T |
| | 293.2 | 103.6 | T |
| | 303.2 | 151.3 | T |
| | 313.2 | 208.9 | T |
| | 323.2 | 278.2 | T |
| 0.55 | 278.2 | 41.6 | B |
| | 283.2 | 62.6 | B |
| | 288.2 | 86.3 | B |
| | 293.2 | 112.1 | T |
| | 303.2 | 160.5 | T |
| | 313.2 | 220.6 | T |
| | 323.2 | 287.9 | T |
| 0.575 | 278.2 | 37.3 | B |
| | 283.2 | 59.2 | B |
| | 293.2 | 106.2 | B |
| | 298.2 | 131.2 | B |
| | 303.2 | 155.3 | B |
| | 313.2 | 212.3 | B |
| | 323.2 | 277.6 | B |
| 0.60 | 278.2 | 33.5 | B |
| | 283.2 | 54.0 | B |
| | 293.2 | 99.4 | B |
| | 303.2 | 150.1 | B |
| | 313.2 | 204.1 | B |
| | 323.2 | 270.7 | B |
| 0.70 | 278.2 | 22.0 | B |
| | 283.2 | 41.7 | B |
| | 293.2 | 82.4 | B |
| | 303.2 | 129.2 | B |
| | 313.2 | 180.3 | B |
| | 323.2 | 237.0 | B |
| 0.85 | 278.2 | 10.6 | B |
| | 283.2 | 27.6 | B |
| | 293.2 | 65.7 | B |
| | 303.2 | 108.5 | B |
| | 313.2 | 154.7 | B |
| | 323.2 | 201.1 | B |

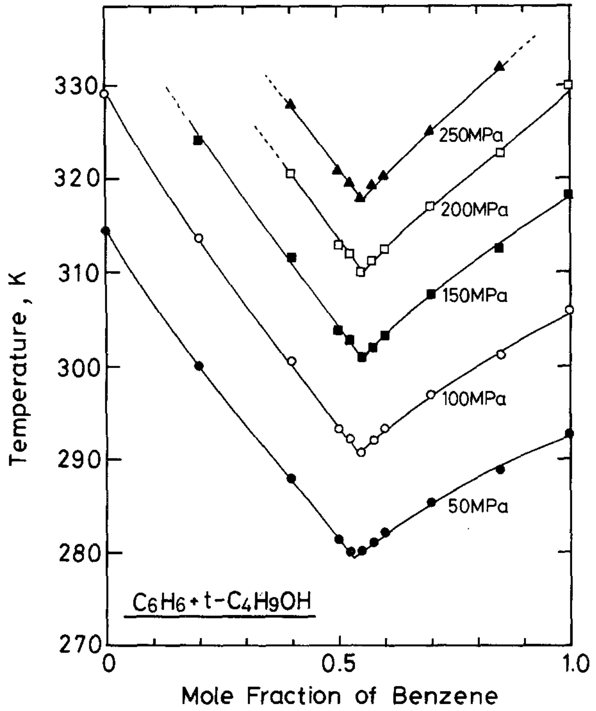

**Fig. 1.** Solid–liquid phase diagram of the benzene + 2-methyl-2-propanol system at constant pressures.

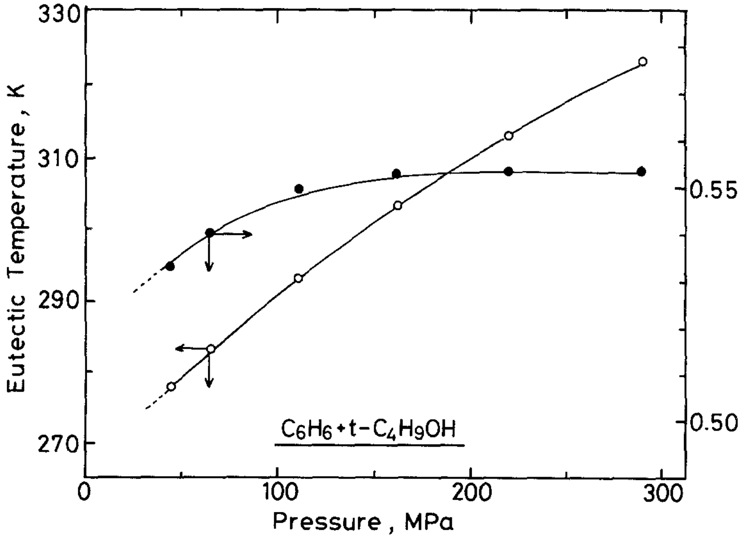

**Fig. 2.** Pressure dependence of eutectic temperature and composition of the benzene + 2-methyl-2-propanol system.

## 4. DISCUSSION

### 4.1. Relation Between Equilibrium Pressure and Logarithm of Composition

At a constant temperature, the relation of the equilibrium pressure and the composition of simple eutectic systems with no mutual miscibility in the solid phase was expressed by Baranowski [5] as follows:

$$\ln \gamma_i x_i = -\frac{1}{RT}\int_{P_{fi}}^{P} \Delta v_{ls}\, dP \tag{4}$$

where $\gamma_i$ denotes the activity coefficient of the $i$th component in the liquid phase, $P_{fi}$ is the freezing pressure, and $\Delta v_{ls}$ is the molar volume difference between the liquid and the solid phases. Assuming that the liquid phase is the ideal solution ($\gamma_i = 1$) and that $\Delta v_{ls}$ is constant and equal to the volume change of fusion $\Delta v_{fi}$, the following relation was derived:

$$\ln x_i = -\frac{\Delta v_{fi}}{RT}(P - P_{fi}) \tag{5}$$

Equation (5) means that there exists a linear relation between equilibrium pressure and logarithm of composition. In spite of the above approximation, Baranowski reported that the linear relation holds not only in the dilute solution region but also in the highly concentrated region in the benzene + chloroform system [5], the benzene + thiophene system [6], the benzene + toluene system [7], and the benzene + methanol system [8].

Therefore, the relation of equilibrium pressure and logarithm of composition is investigated in the present system. Figure 3 shows the relation in the benzene-rich region ($x_{1e} \leqslant x_1 \leqslant 1.0$). As seen in Fig. 3, the linear relation of Eq. (5) cannot hold strictly for each isotherm. In the concentrated range of $0.7 \leqslant x_1 \leqslant 1.0$, each isotherm was fitted to Eq. (5), and from the gradient of the straight line, $\Delta v_{fi}$ was calculated at each temperature. However, $\Delta v_{fi}$ calculated by Eq. (5) is found to differ greatly from the experimental value. For example, $\Delta v_{fi}$ from Eq. (5) at 283.2 K is 30.9 $\text{cm}^3 \cdot \text{mol}^{-1}$; on the contrary, $\Delta v_{fi}$ from experiments is 9.1 $\text{cm}^3 \cdot \text{mol}^{-1}$ [9]. This discrepancy could come from the assumption that the term of activity coefficient was neglected in Eq. (5). This can be supported by the following fact. In the benzene + cyclohexane system, the relation of equilibrium pressure and logarithm of composition was investigated at $0.5 \leqslant x_1 \leqslant 1.0$, where the linear relation holds, and the coefficient $\Delta v_{fi}$ was calculated. At 283.2 K, $\Delta v_{fi}$ is 11.3 $\text{cm}^3 \cdot \text{mol}^{-1}$, which does not agree with either the experimental value or the calculated value of the benzene + 2-methyl-2-propanol system. Comparing the two systems, the activity coefficient of each mixture is

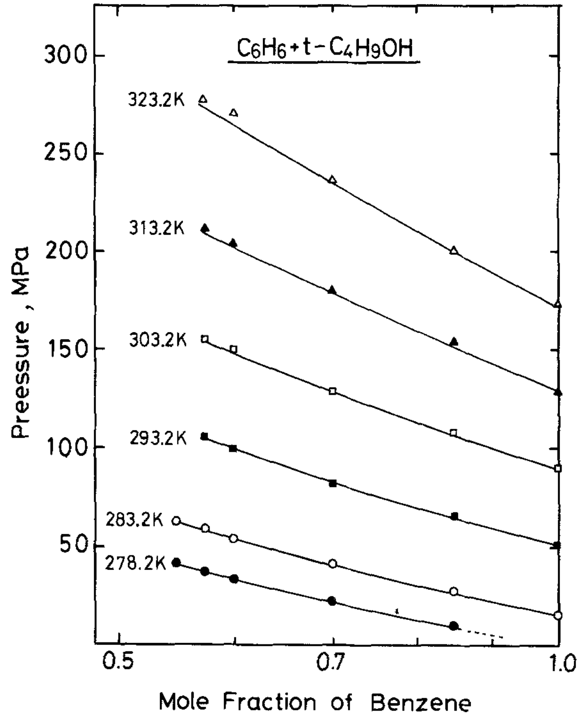

Fig. 3. Pressure versus logarithm of composition diagram of the benzene + 2-methyl-2-propanol system ($x_{1e} \leqslant x_1 \leqslant 10$).

larger in the benzene + 2-methyl-2-propanol system, which is the mixture of nonpolar and polar materials. This fact suggests that the activity coefficient of these systems can be expressed by the linear function of pressure, and as a result Eq. (5) is available. Therefore, determining $\Delta v_{fi}$ from the solid–liquid equilibrium data, Eq. (5) can be available as the correlation equation. For the next step, based on Eq. (5), a new equation was established.

## 4.2. A New Equation

Equation (5) can be applied only in a limited range of composition. In order to express the entire range of composition, the following quadratic equation in pressure [2] is needed:

$$\ln x_i = b_0 + b_1 P + b_2 P^2 \tag{6}$$

The relation between Eq. (4) and Eq. (6) was explained by Baranowski [5] as follows. It is assumed that $\Delta v_{\mathrm{ls}}$ in Eq. (4) is not constant but is a linear function of pressure as follows:

$$\Delta v_{\mathrm{ls}} = \Delta v_{\mathrm{ls0}}(1 - \beta P) \tag{7}$$

Substituting Eq. (7) into Eq. (4), the following relation was obtained:

$$\ln \gamma_i x_i = -\frac{1}{RT}\left[\Delta v_{\mathrm{ls0}}(P - P_{\mathrm{f}i}) - \frac{1}{2}\Delta v_{\mathrm{ls0}}\,\beta(P^2 - P_{\mathrm{f}i}^2)\right] \tag{8}$$

In the same way of Eq. (5), if the term of the activity coefficient can be included in the terms of $\Delta v_{\mathrm{ls0}}$ and $\Delta v_{\mathrm{ls0}}\,\beta$, solid–liquid coexistence curves can be expressed by the similar form of Eq. (8). Finally, the authors present a new equation based on Eq. (8) as follows:

$$\ln x_i(P, T) = -\frac{1}{RT}\{C(T)[P - B(T)] + D(T)[P^2 - B(T)^2]\} \tag{9}$$

The three parameters $B$, $C$, and $D$ in Eq. (9) correspond to the terms of $P_{\mathrm{f}i}$, $\Delta v_{\mathrm{ls0}}$, and $\Delta v_{\mathrm{ls0}}\,\beta$, respectively. $B$ is equal to the freezing pressure of the pure $i$th component where the temperature is higher than the freezing temperature at 0.1 MPa, but it becomes negative under the freezing temperature. The various types of solid–liquid phase diagrams were correlated by Eq. (9).

### 4.3. Correlation of Solid–Liquid Phase Equilibria

The benzene + 2-methyl-2-propanol system was correlated by Eq. (9). The coexistence curve was divided at the eutectic point and the coefficients of Eq. (9) were determined for each side and temperature. These coefficients in the benzene-rich region are shown in Fig. 4 as a function of temperature. The coefficients are found to be expressed satisfactorily by the following polynomials in the reciprocal of temperature:

$$B(T) = B_0 + B_1/T + B_2/T^2 \tag{10}$$

$$C(T) = C_0 + C_1/T + C_2/T^2 \tag{11}$$

$$D(T) = D_0 + D_1/T + D_2/T^2 \tag{12}$$

The parameters of Eqs. (10)–(12) are listed in Table II. The present equation can reproduce the experimental results with a mean deviation of 0.005 and a maximum deviation of 0.016 in mole fraction. The solid curves in Figs. 1 and 3 are the values calculated by Eqs. (9)–(12).

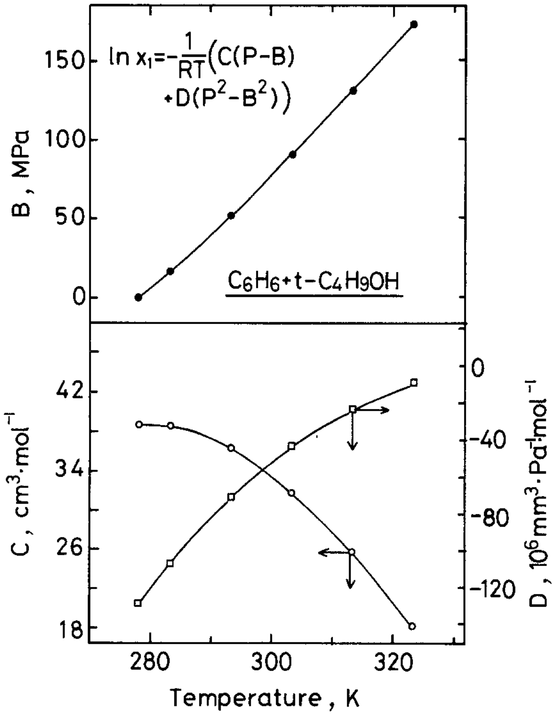

**Fig. 4.** Temperature dependence of the coefficients in Eq. (9) of the benzene + 2-methyl-2-propanol system $(x_{1e} \leqslant x_1 \leqslant 1.0)$.

Moreover, the systems already reported were correlated by this equation in the same way. The parameters obtained for Eqs. (10)–(12) are also listed in Table II. For example, the benzene + cyclohexane system can be correlated with a mean deviation of 0.006 and a maximum deviation of 0.021, which is superior to the correlation using the Schröder–van Laar equation and Wilson equation [1]. Equation (9) can be available essentially only for the simple eutectic system, but the liquidus of the α-methylnaphthalene + β-methylnaphthalene and chlorobenzene + bromobenzene systems, in which two solids are soluble partially or completely in each other, can be also expressed satisfactorily by this equation with a mean deviation within 0.009 in mole fraction. However, the deviation between the experimental and the calculated values of the solidus of the chlorobenzene + bromobenzene system became two or three times that of the liquidus. Since the precision of the measurements of the solidus is lower than that of the liquidus, this result does not mean that the present equation cannot be available for the correlation of the solidus.

**Table II.** Coefficients of Equations (10)–(12)

| Composition range | $10^{-3} B_0$ | $10^{-6} B_1$ | $10^{-8} B_2$ | $C_0$ | $10^{-3} C_1$ | $10^{-6} C_2$ | $10^3 D_0$ | $D_1$ | $10^{-3} D_2$ | Deviation[c] Mean | Deviation[c] Max |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Benzene (1) + 2-methyl-2-propanol (2) system | | | | | | | | | | | |
| $x_{1e}{}^a \leqslant x_1 \leqslant 1.0$ | 3.462 | −1.680 | 1.995 | −1156 | 674.6 | −95.18 | −1963 | 1390 | −245.5 | 0.005 | 0.016 |
| $x_{2e}{}^a \leqslant x_2 \leqslant 1.0$ | 2.718 | −1.384 | 1.715 | −2.008 | −14.84 | −5.848 | −474.0 | 291.6 | −44.16 | 0.004 | 0.012 |
| Benzene (1) + cyclohexane (2) system | | | | | | | | | | | |
| $x_{1e}{}^b \leqslant x_1 \leqslant 1.0$ | 3.276 | −1.572 | 1.838 | −72.79 | 35.85 | −3.306 | −262.9 | 179.9 | −30.48 | 0.007 | 0.012 |
| $x_{2e}{}^b \leqslant x_2 \leqslant 1.0$ | 1.089 | −0.4474 | 0.3969 | −11.72 | 8.614 | −1.048 | −118.0 | 76.39 | −12.69 | 0.005 | 0.013 |
| α-Methylnaphthalene (1) + β-methylnaphthalene (2) system | | | | | | | | | | | |
| $0.82 \leqslant x_1 \leqslant 1.0$ | 4.121 | −1.848 | 2.090 | −14.26 | −5.566 | — | — | — | — | 0.004 | 0.012 |
| $0.18 \leqslant x_2 \leqslant 1.0$ | 3.492 | −1.835 | 2.349 | 108.3 | −69.20 | 12.21 | −921.2 | 602.6 | −98.38 | 0.009 | 0.033 |
| Chlorobenzene (1) + bromobenzene (2) system (liquidus) | | | | | | | | | | | |
| $0.375 \leqslant x_1 \leqslant 1.0$ | 5.849 | −2.538 | 2.772 | −4376 | 2350 | −324.0 | 5499 | −3182 | 471.0 | 0.005 | 0.016 |
| $0.375 \leqslant x_2 \leqslant 1.0$ | 6.414 | −3.019 | 3.586 | −2942 | 1556 | −210.0 | 7322 | −4321 | 650.9 | 0.008 | 0.019 |
| Chlorobenzene (1) + bromobenzene (2) system (solidus) | | | | | | | | | | | |
| $0.375 \leqslant x_1 \leqslant 1.0$ | 5.849 | −2.538 | 2.772 | 5383 | −3112 | 449.6 | −9654 | 5660 | −833.3 | 0.014 | 0.074 |
| $0.375 \leqslant x_2 \leqslant 1.0$ | 6.414 | −3.019 | 3.586 | 2949 | −1799 | 268.2 | −2287 | 1214 | −147.8 | 0.012 | 0.038 |

[a] $x_{1e} = 0.525 + 3.85 \times 10^{-4} \ln P - 2.64 \times 10^{-3} \ln P^2$ ($P$ in MPa), $x_{2e} = 1 - x_{1e}$.
[b] $x_{1e} = 0.262 + 4.18 \times 10^{-4} P - 2.64 \times 10^{-7} P^2$ ($P$ in MPa), $x_{2e} = 1 - x_{1e}$.
[c] In mole fraction.

## 5. CONCLUSION

Solid–liquid phase equilibria of the benzene + 2-methyl-2-propanol system were investigated under high pressure using an optical vessel. The freezing pressure of each mixture increases monotonously with increasing pressure. The eutectic point shifts to a higher temperature and benzene-rich region with increasing pressure. This trend agrees with the direction predicted by the van Laar equation, as well as the case of the benzene + cyclohexane and $\alpha$-methylnaphthalene + $\beta$-methylnaphthalene systems already reported.

A new simple equation, Eq. (9), has been developed for the correlation of high-pressure solid–liquid phase equilibria. This equation can express the coexistence curves of both simple eutectic systems and solid-solution systems.

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