International Journal of Thermophysics, Vol. 8, No. 4, 1987

Solid–Liquid Phase Equilibria of Benzene + Cyclohexane System Under High Pressures

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Received November 24, 1986

Solid–liquid phase equilibria of the benzene + cyclohexane system have been investigated experimentally at temperatures from 278 to 323 K and pressures up to 500 MPa using a newly designed 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 solid–liquid equilibrium pressure at a constant composition increases almost linearly with increasing temperature. The eutectic point shifts to a higher temperature and to a benzene-rich composition with increasing pressure. This trend is found to agree with the direction predicted by the van Laar equation. The solid–liquid coexistence curves can be expressed by the Wilson equation with a mean deviation of 0.007 and a maximum deviation of 0.029 in mole fraction.

KEY WORDS: benzene; cyclohexane; eutectic point; high pressure; solid–liquid phase equilibrium.

1. INTRODUCTION

Recently, the high-pressure crystallization technique [1] has been noticed as a new separation and purification process, because it is superior to other processes, from the viewpoint of the high purity of products and low energy consumption. Accurate knowledge of the solid–liquid phase equilibrium relations at high pressures is essential for the design of this process. However, multicomponent solid–liquid phase equilibria have scarcely been investigated under high pressures, especially for organic liquid systems. Therefore, it is important to study the effect of pressure on various types of phase diagrams of solid–liquid equilibria.

In this work, solid–liquid phase equilibria of the benzene +

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cyclohexane system, in which the liquids are completely soluble in each other and the solid phases are the pure crystalline forms of the two components, were measured at temperatures from 278 to 323 K and pressures up to 500 MPa. The pressure effect on the phase diagram is discussed based on the experimental results and the solid–liquid coexistence curves were correlated by the Wilson equation.

2. EXPERIMENTAL

The measurements were performed in a high-pressure optical vessel designed for visual observation [2]. A schematic diagram of the entire apparatus is shown in Fig. 1. The sample liquid of a known composition was introduced in the equilibrium vessel (A), which was immersed in a water bath (B) thermostatically controlled within ±0.05 K. The pressure was applied to the sample by means of a pressure intensifier (E) and an oil pump (G).

Phase transition can be determined from the appearance of a solid phase by direct visual observation when the pressure of the system is applied step by step at a constant temperature. However, in the case of high-pressure solid–liquid equilibria, the solid phase does not often appear up to pressures considerably higher than the true equilibrium pressure, due to the phenomenon of "superpressing." Therefore, in the present operation, the pressure was applied at first up to a high enough one where the solid phase appeared, and then the pressure was decreased gradually until the solid phase completely disappeared. Such a pressure was recorded as the equilibrium pressure.

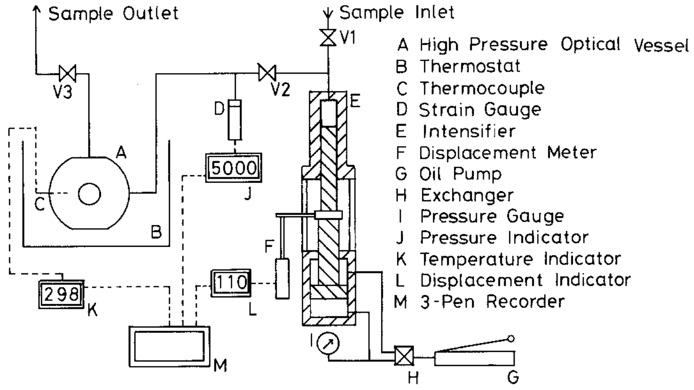

Fig. 1. Schematic diagram of the apparatus.

Pressure was measured with a calibrated digital gauge with a strain sensor (D). Its uncertainty was less than ±0.5 MPa. Temperature was measured with a copper–constantan thermocouple (C) within an error of ±0.05 K. The pressure and temperature of the system were recorded with a pen recorder (M), as well as the displacement of the intensifier piston during the course of measurements.

Benzene and cyclohexane were obtained from commercial sources and stored with sodium ribbon to remove the moisture. Their purities should be better than 99.5 wt%. The sample mixtures were prepared by the weighing method, and the uncertainty of the composition is within ±0.001 in mole fraction.

3. RESULTS

The experimental results are summarized in Table I. The freezing pressures of pure benzene and cyclohexane agree well with literature values [3, 4] within the present experimental errors. The relation of the freezing temperature T_f and pressure P_f could be expressed by the Simon equation:

$$P_f = a[(T_f/T_0)^c - 1] + P_0 \tag{1}$$

where T_0 is the freezing temperature at atmospheric pressure P_0. The characteristic parameters a and c are shown in Table II. Equation (1) was found to reproduce the freezing temperature within ±0.4 K at any pressure. The crystalline forms of benzene and cyclohexane under the present experimental conditions are an orthorhombic system [5] and a cubic system [6], respectively.

Solid–liquid coexistence curves of each composition are shown in Fig. 2. Each curve is found to behave almost linearly against temperature, and the temperature coefficient of equilibrium pressure at a constant composition, $(\partial P/\partial T)_{x_1}$, increases as the composition approaches the eutectic mixture. Temperature versus composition plots at various pressures are shown in Fig. 3. At 0.1 MPa, the eutectic composition is $x_1 = 0.26$, the mole fraction of benzene [7]. It is certainly confirmed that the eutectic point shifted to the benzene-rich region with increasing pressure. Accordingly, crystals of cyclohexane were formed from the liquid samples of $x_1 = 0.30$ and $x_1 = 0.33$ under the present experimental conditions. Furthermore, from the samples of $x_1 = 0.35$ and $x_1 = 0.38$, benzene crystals were obtained in the lower pressure region, and on the contrary, cyclohexane crystals were formed in the higher pressure region. The coexistence curves of these compositions (Fig. 2) show inflection points, due to the shift of eutectic

Table I. Solid–Liquid Equilibrium Data of the Benzene + Cyclohexane System

x_1[a]	T (K)	P (MPa)	Coexistence crystal[b]
0.00	283.2	7.6	C
	288.2	16.5	C
	293.2	26.2	C
	298.2	35.4	C
	303.2	45.9	C
	313.2	65.5	C
	323.2	85.1	C
0.10	278.2	37.0	C
	283.2	49.0	C
	293.2	71.3	C
	303.2	96.7	C
	313.2	122.2	C
	323.2	150.9	C
0.20	278.2	92.8	C
	283.2	104.0	C
	293.2	137.2	C
	303.2	166.5	C
	313.2	200.5	C
	323.2	235.4	C
0.30	278.2	183.2	C
	283.2	204.7	C
	293.2	242.7	C
	303.2	282.4	C
	313.2	322.1	C
0.33	278.2	213.5	C
	283.2	234.6	C
	293.2	273.3	C
	303.2	309.3	C
	313.2	349.8	C
	323.2	393.6	C
0.35	278.2	225.7	B
	283.2	256.9	B
	288.2	282.6	C
	293.2	303.3	C
	298.2	327.6	C
	303.2	347.0	C
0.38	278.2	191.2	B
	283.2	226.6	B
	293.2	308.2	B
	298.2	342.2	C
	303.2	380.9	C

Table I. *(Continued)*

x_1[a]	T (K)	P (MPa)	Coexistence crystal[b]
0.40	278.2	178.4	B
	283.2	203.2	B
	293.2	269.6	B
	303.2	347.4	B
0.50	278.2	128.3	B
	283.2	160.6	B
	293.2	221.3	B
	303.2	282.9	B
	313.2	343.4	B
0.60	278.2	98.9	B
	283.2	122.9	B
	293.2	176.0	B
	303.2	230.7	B
	313.2	290.3	B
	323.2	356.8	B
0.70	278.2	69.2	B
	283.2	90.6	B
	293.2	139.5	B
	303.2	188.3	B
	313.2	242.0	B
	323.2	300.5	B
0.80	278.2	43.9	B
	283.2	61.3	B
	293.2	107.8	B
	303.2	152.0	B
	313.2	203.6	B
	323.2	255.6	B
0.90	278.2	16.7	B
	283.2	34.0	B
	293.2	76.8	B
	303.2	118.6	B
	313.2	160.5	B
	323.2	205.4	B
1.00	283.2	15.7	B
	288.2	33.7	B
	293.2	51.8	B
	298.2	70.8	B
	303.2	90.5	B
	313.2	128.6	B
	323.2	173.7	B

[a] Mole fraction of benzene.

[b] B and C denote benzene and cyclohexane, respectively.

Table II. Coefficients of the Simon Equation (1)

Substance	a (MPa)	c	T_0 (K)	Mean dev. (K)	Max. dev. (K)
Benzene	341	2.76	278.6	0.1	0.4
Cyclohexane	417	1.28	279.6	0.1	0.4

composition with pressure. The shift of the eutectic point could be explained qualitatively by the van Laar equation [8]:

$$\left(\frac{\partial x_1}{\partial P}\right)_e = K\left[\left(\frac{\partial P_f}{\partial T}\right)_1 - \left(\frac{\partial P_f}{\partial T}\right)_2\right] \tag{2}$$

where the subscripts e, 1, and 2 denote the values of the eutectic mixture, pure benzene, and pure cyclohexane, respectively. The quantity K in Eq. (2)

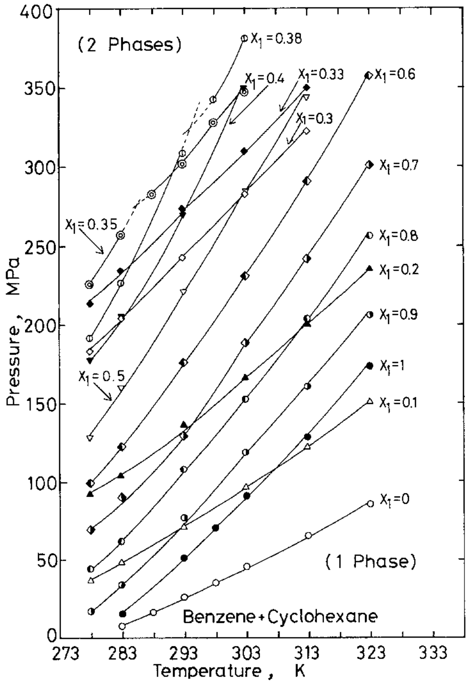

Fig. 2. Solid–liquid equilibria of the benzene + cyclohexane system.

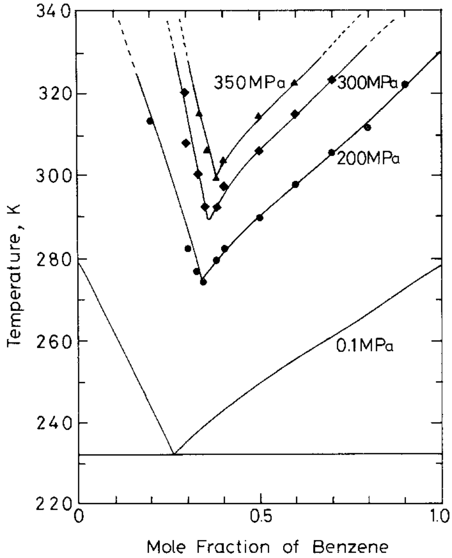

Fig. 3. Solid–liquid phase diagram of the benzene + cyclohexane system at constant pressures.

is a function of temperature, composition, and ΔV_f (volume change of fusion), ΔH_f (latent heat of fusion) of pure components and should be positive in this system. Therefore, the direction of the shift of the eutectic composition depends on the sign of $(\partial P_f/\partial T)_1 - (\partial P_f/\partial T)_2$, which is positive, as may be seen in Fig. 2. Accordingly, Eq. (2) could predict qualitatively the shift of eutectic composition with pressure, which agreed with the present experimental results. The eutectic temperature at 0.1 MPa is about 232 K [7], but it increases monotonically with increasing pressure and amounts to about 300 K at 350 MPa. The shifts of the eutectic composition and temperature found in this work were expressed by the following polynomials:

$$x_{1e} = 0.262 + 4.18 \times 10^{-4} P - 2.64 \times 10^{-7} P^2 \qquad (3)$$

$$T_e = 232 + 0.211 P - 5.66 \times 10^{-5} P^2 \qquad (4)$$

where T_e is in K and P is in MPa.

4. DISCUSSION

For the simple eutectic system with no miscibility in the solid phase, solid–liquid coexistence curves should be calculated as follows [9]:

$$x_1 = \frac{1}{\gamma_1} \exp\left(\frac{\Delta H_{f1}}{RT_{f1}} \frac{T - T_{f1}}{T}\right) \tag{5}$$

$$x_2 = \frac{1}{\gamma_2} \exp\left(\frac{\Delta H_{f2}}{RT_{f2}} \frac{T - T_{f2}}{T}\right) \tag{6}$$

where T_{f1}, T_{f2} and ΔH_{f1}, ΔH_{f2} are the freezing temperatures and the latent heats of fusion of pure benzene and cyclohexane; R is the gas constant. Equation (5) expresses the coexistence curve from $x_1 = 1$ to $x_1 = x_{1e}$ (eutectic composition), and Eq. (6) from $x_2 = 1$ ($x_1 = 0$) to $x_2 = x_{2e}$. The activity coefficients in the liquid phase, γ_1 and γ_2, have been calculated by the Wilson equation [10]:

$$\ln \gamma_1 = -\ln(x_1 + A_{12}x_2) + x_2\left(\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right) \tag{7}$$

$$\ln \gamma_2 = -\ln(A_{21}x_1 + x_2) - x_1\left(\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right) \tag{8}$$

where A_{12} and A_{21} are the Wilson parameters, which are functions of temperature and pressure. In this work, the Wilson parameters were expressed as follows:

$$A_{12} = a_{10} + a_{11}/T + a_{12}/P \tag{9}$$

$$A_{21} = a_{20} + a_{21}/T + a_{22}/P \tag{10}$$

Table III. Coefficients of Eqs. (9) and (10)

	Benzene side	Cyclohexane side
a_{10}	0.6356	1.728
a_{11} (K)	−284.8	−438.3
a_{12} (MPa)	45.14	−7.257
a_{20}	1.303	−1.369
a_{21} (K)	−81.26	536.2
a_{22} (MPa)	−9.244	−4.443
Mean dev.[a]	0.007	0.007
Max. dev.[a]	0.028	0.029

[a] In mole fraction.

The six coefficients in these equations were determined using the experimental results and are shown in Table III. The values of ΔH_f and T_f in Eqs. (5) and (6) were obtained from the literature [3, 4, 11]. For cyclohexane, the values of T_f and ΔH_f exist only in the pressure range up to 300 MPa, therefore the extrapolated values were used in higher pressure ranges. The calculated results are shown by solid curves in Fig. 3. Equations (5)–(10) are found to reproduce the experimental data satisfactorily, with a mean deviation of 0.007 in mole fraction and a maximum deviation of 0.029.

5. CONCLUSIONS

Solid–liquid phase equilibria of the benzene + cyclohexane system under high pressure were investigated in a newly designed high-pressure optical vessel. It was found that solid–liquid equilibrium pressure at a constant composition increases almost linearly with temperature. The eutectic point shifts to a higher temperature and to a more benzene-rich region with increasing pressure. The solid–liquid coexistence curves were expressed satisfactorily by the Wilson equation as a function of temperature and pressure.

As the next step, it is considered important to investigate the solid–liquid equilibria of systems in which two components form solid solutions with one another partially or completely. The authors are now carrying out measurements on such systems.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Mr. M. Moritoki and Mr. N. Nishiguchi of Kobe Steel, Ltd., for their advice on the design of the present apparatus and stimulating discussions throughout the course of this work.

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