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Solid–Liquid Phase Equilibria of (α-Methylnaphthalene + β-Methylnaphthalene) and (Chlorobenzene + Bromobenzene) Systems Under High Pressures

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Solid–liquid phase equilibria of the (α-methylnaphthalene + β-methylnaphthalene) and the (chlorobenzene + bromobenzene) systems have been investigated at temperatures from 278 to 343 K and pressures up to 500 MPa using a high-pressure optical vessel. The uncertainties of the measurements of temperature, pressure, and composition were within ±0.1 K, ±0.5 MPa, and ±0.001 mole fraction, respectively. In both systems, the freezing and melting pressures at a constant composition increase almost linearly with increasing temperatures. In the former system, where the two components can form a solid solution with one another to a limit extent, the eutectic point shifts to a higher temperature and to a α-methylnaphthalene-rich composition with increasing pressures. In the latter system, where the two components are completely soluble in each other in the solid phase, the freezing points of all mixtures lie between those of the pure components at each pressure. It is found that the coexistence curves obtained can be expressed by a quadratic equation in pressure.

KEY WORDS: bromobenzene; chlorobenzene; high pressure; α-methylnaphthalene; β-methylnaphthalene; solid–liquid phase equilibrium; solid solution.

1. INTRODUCTION

Accurate knowledge of high-pressure solid–liquid phase equilibria plays important roles in the design of systems for the new high-pressure crystallization processes. It is essential to study the effect of pressure on the

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various types of solid–liquid phase diagrams. The authors reported the high-pressure solid–liquid equilibria of the benzene + cyclohexane system [1], which is a simple eutectic system with no miscibility in the solid phase, and found that the eutectic point shifts greatly with pressure. Although it is known that the simple eutectic system amounts up to nearly 90% of all organic systems [2], the high-pressure crystallization technique should also be applicable to the solid solution systems [3] in which the solid components are soluble partially or completely within each other. However, solid solution systems have been rarely investigated under high pressures.

In this work, the freezing pressures of the α-methylnaphthalene + β-methylnaphthalene system and the chlorobenzene + bromobenzene system were measured at temperatures from 278 to 343 K and pressures up to 500 MPa. In the former system the solid components are soluble partially, and in the latter system completely. Based on the results, the pressure effect on the phase diagrams of these systems is discussed and coexistence curves are expressed by polynomial equations of pressure.

2. EXPERIMENTAL

Solid–liquid equilibrium measurements were performed by the direct visual observation of phase transition in a high-pressure optical vessel. The apparatus and experimental procedures were almost the same as those used in the previous work [1]. The measurements were carried out in the pressure reduction procedure in order to avoid the superpressing phenomena. At first, the pressure was applied to a sample of a known composition up to a high enough one where the solid phase appeared, and then the pressure was decreased gradually to the freezing pressure on the liquidus where the solid phase completely disappeared. In the case of the chlorobenzene + bromobenzene system, the melting pressure on the solidus, where the liquid phase appeared from the homogeneous solid phase, could also be determined.

The samples used were obtained from commercial sources. The purities of α-methylnaphthalene and β-methylnaphthalene should be better than 98 wt%, and those of chlorobenzene and bromobenzene 99 wt%. The former samples were dried by sodium metal, and the latter by calcium chloride. The uncertainties of measurements of temperature, pressure, and composition are within ±0.1 K, ±0.5 MPa, and ±0.001 mole fraction, respectively.

3. RESULTS AND DISCUSSION

The experimental results are listed in Tables I and II.

Table I. Solid–Liquid Equilibrium Data of the [α-Methylnaphthalene (1) + β-Methylnaphthalene (2)] System

x_1 [a]	T (K)	P_f [b] (MPa)	x_1 [a]	T (K)	P_f [b] (MPa)
0	308.2	7.9	0.75	278.2	140.8
	313.2	25.3		283.2	165.2
	323.2	63.9		293.2	216.6
	333.2	99.3		303.2	270.8
	343.2	136.6		313.2	330.6
0.1	303.2	13.4	0.8	278.2	194.6
	313.2	51.9		283.2	224.8
	323.2	88.5		293.2	277.7
	333.2	128.0		303.2	344.4
	343.2	170.8			
			0.82	278.2	261.8
0.25	293.2	15.7		283.2	290.3
	303.2	53.3		293.2	359.0
	313.2	96.9			
	323.2	145.2	0.85	278.2	247.5
	333.2	190.2		283.2	272.9
	343.2	232.6		293.2	329.5
				298.2	362.8
0.4	283.2	14.6			
	293.2	53.2	0.906	278.2	214.4
	303.2	96.2		283.2	242.2
	313.2	137.3		293.2	301.1
	323.2	181.6		303.2	361.8
	333.2	230.7			
	343.2	280.3	0.95	278.2	195.5
				283.2	221.4
0.5	278.2	22.9		293.2	276.5
	283.2	45.2		303.2	335.0
	293.2	88.8			
	303.2	134.0	1.0	278.2	180.3
	313.2	182.3		283.2	201.5
	323.2	230.8		293.2	251.2
	333.2	278.8		303.2	300.9
	343.2	335.6		313.2	351.2
				323.2	405.4
0.6	278.2	52.0			
	283.2	75.1			
	293.2	121.2			
	303.2	166.9			
	313.2	215.1			
	323.2	266.1			
	328.2	292.9			

[a] Mole fraction of α-methylnapthalene.

[b] Freezing pressure.

Table II. Solid–Liquid Equilibrium Data of the [Chlorobenzene (1) + Bromobenzene (2)] System

x_1 [a]	T (K)	P_f [b] (MPa)	P_m [c] (MPa)	x_1 [a]	T (K)	P_f [b] (MPa)	P_m [c] (MPa)
0	278.2	196.0		0.625	278.2	269.7	277.5
	283.2	225.9			283.2	306.1	315.0
	293.2	289.1			293.2	378.5	382.9
	303.2	358.4			298.2	416.5	425.6
	310.2	408.9					
				0.75	278.2	285.4	292.5
0.125	278.2	210.5	213.5		283.2	319.3	326.6
	283.2	243.0	245.9		293.2	390.6	397.8
	293.2	307.9	312.2				
	303.2	376.4	378.8	0.875	278.2	296.5	301.4
	308.2	410.2	415.7		283.2	331.2	341.1
					293.2	406.4	413.4
0.25	278.2	226.0	229.7				
	283.2	257.5	263.5	1.0	278.2	308.5	
	293.2	327.7	332.4		283.2	334.2	
	303.2	395.6	403.2		293.2	418.1	
0.375	278.2	240.9	246.7				
	283.2	273.6	279.7				
	293.2	346.7	349.7				
	300.2	395.9	401.9				
0.5	278.2	256.2	267.3				
	283.2	289.5	303.6				
	293.2	362.6	373.4				
	298.2	400.1	408.0				

[a] Mole fraction of chlorobenzene.

[b] Freezing pressure .

[c] Melting pressure.

3.1. The Pure Components

The freezing pressures of pure chlorobenzene and bromobenzene agreed well with the literature values [4–6]. The freezing pressures of α-methylnaphthalene and β-methylnaphthalene are not reported. The relation of the freezing temperature T_f and pressure P_f of each pure component could be expressed by the following formula, which was derived from the Simon equation:

$$P_f = A + BT^c \tag{1}$$

Table III. Coefficients of Eq. (1)

Substance	A	$10^3 B$	C	Mean dev. (K)	Max. dev. (K)
α-Methylnaphthalene	−453.8	6.81	2.03	0.1	0.3
β-Methylnaphthalene	−544.1	7.66	1.95	0.2	0.3
Chlorobenzene	−545.6	2.18	2.29	0.03	0.1
Bromobenzene	−526.4	1.11	2.38	0.1	0.3

where P_f and T are in MPa and K, respectively. The characteristic parameters A, B, and C are shown in Table III. Equation (1) can reproduce the freezing temperature well within ±0.3 K.

3.2. The α-Methylnaphthalene + β-Methylnaphthalene System

Freezing pressures at each constant composition are given in Table I. It is found that the freezing pressure increases almost linearly with tem-

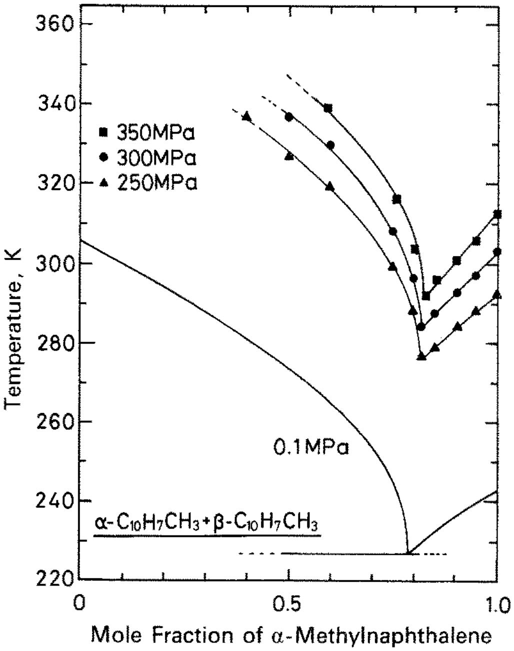

Fig. 1. Solid–liquid phase diagram of the α-methylnaphthalene + β-methylnaphthalene system at constant pressures.

perature and that the temperature coefficient of the freezing pressure, $(\partial P_f/\partial T)_{x_1}$, increases as the composition approaches the eutectic one.

The freezing temperature versus composition diagram is shown in Fig. 1. The coexistence curve shifts to a higher temperature with increasing pressures. At 0.1 MPa, the eutectic composition of this system was known as x_1 (α-methylnaphthalene) $= 0.78$ [7]. With increasing pressures, the eutectic composition shifts to a more α-methylnaphthalene-rich composition up to $x_1 = 0.82$. The change of eutectic composition can be explained by the van Laar equation as already reported [1]:

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

where K is the positive value and subscripts 1, 2, and e denote α-methylnaphthalene, β-methylnaphthalene, and the eutectic mixture, respectively. In this system, as $(\partial P_f/\partial T)_1 - (\partial P_f/\partial T)_2$ is positive, Eq. (2) predicts that the eutectic composition of α-methylnaphthalene increases with increasing pressures.

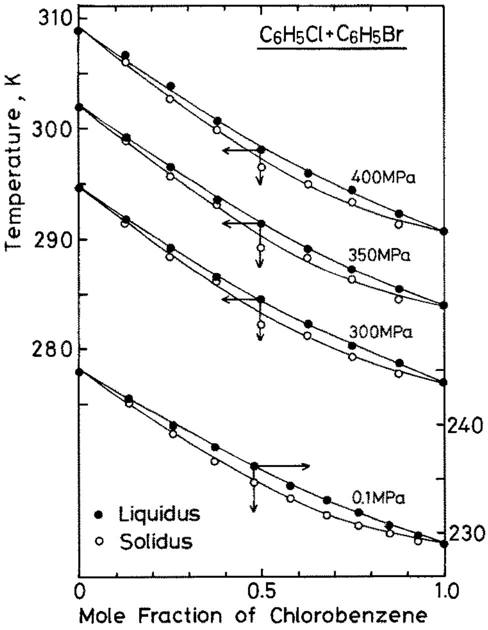

Fig. 2. Solid–liquid phase diagram of the chlorobenzene + bromobenzene system at constant pressures.

3.3. The Chlorobenzene + Bromobenzene System

Both the freezing pressure P_f and the melting pressure P_m at each constant composition were determined as a function of temperature, as given in Table II. Figure 2 shows the relation of the freezing temperature T_f versus composition curve (liquidus) and melting temperature T_m versus composition curve (solidus) at each constant pressure, as well as the literature values at 0.1 MPa [8]. The freezing and melting temperatures change gradually with composition and no definite maximum or minimum was observed throughout the entire range of composition and pressure. The liquidus and solidus move to a higher temperature region with increasing pressures. The difference in the freezing and melting temperatures at any composition is almost independent of the pressure under the present experimental conditions.

3.4. Correlation of Coexistence Curves

Concerning the high-pressure solid–liquid phase equilibria, Baranowski [9] reported recently that there exists a linear relation

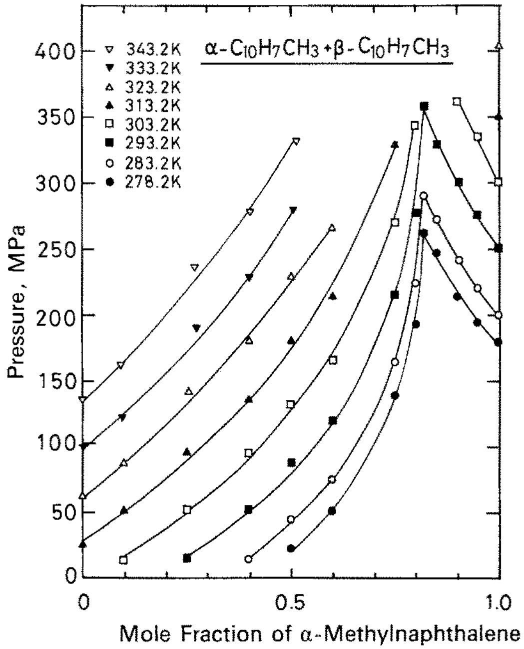

Fig. 3. Freezing pressures of the α-methylnaphthalene + β-methylnaphthalene system at constant temperatures. Points: the experimental data. Curves: the values calculated by Eq. (4).

between the freezing pressure and the logarithm of the mole fraction at a constant temperature in the low concentration region of each component.

$$\ln x_i = b_0 + b_1 P \tag{3}$$

where b_0 and b_1 are the parameters characteristic of the system and temperature and x_i denotes the mole faction of the ith component. Equation (3) was examined using the present results. In the α-methylnaphthalene-rich region ($0.82 \leqslant x_1 \leqslant 1.0$) and the β-methylnaphthalene-rich region

Table IV. Coefficients of Eq. (4)

T(K)	Composition range	b_0	b_1	b_2	Deviation[a] Mean	Deviation[a] Max.
		α-Methylnaphthalene + β-methylnaphthalene system				
278.2	$0.82 \leqslant x_1{}^b \leqslant 1.0$	0.4115	-2.336×10^{-3}	—	0.006	0.010
283.2	$0.82 \leqslant x_1 \leqslant 1.0$	0.4416	-2.214×10^{-3}	—	0.003	0.004
293.2	$0.82 \leqslant x_1 \leqslant 1.0$	0.4705	-1.887×10^{-3}	—	0.004	0.010
303.2	$0.906 \leqslant x_1 \leqslant 1.0$	0.4873	-1.616×10^{-3}	—	0.002	0.003
278.2	$0.18 \leqslant x_2{}^c \leqslant 0.5$	−0.5145	-8.291×10^{-3}	1.410×10^{-5}	0.003	0.004
283.2	$0.18 \leqslant x_2 \leqslant 0.6$	−0.3765	-8.080×10^{-3}	1.186×10^{-5}	0.005	0.012
293.2	$0.18 \leqslant x_2 \leqslant 0.75$	−0.1376	-7.562×10^{-3}	8.636×10^{-6}	0.010	0.026
303.2	$0.2 \leqslant x_2 \leqslant 0.9$	6.424×10^{-4}	-5.867×10^{-3}	3.269×10^{-6}	0.013	0.026
313.2	$0.25 \leqslant x_2 \leqslant 1.0$	0.1382	-4.746×10^{-3}	3.091×10^{-7}	0.011	0.024
323.2	$0.4 \leqslant x_2 \leqslant 1.0$	0.2867	-4.404×10^{-3}	—	0.008	0.018
333.2	$0.5 \leqslant x_2 \leqslant 1.0$	0.3880	-3.883×10^{-3}	—	0.002	0.003
343.2	$0.5 \leqslant x_2 \leqslant 1.0$	0.4886	-3.535×10^{-3}	—	0.005	0.009
		Chlorobenzene + bromobenzene system (liquidus)				
278.2	$0.375 \leqslant x_1{}^d \leqslant 1.0$	−9.541	5.215×10^{-2}	-6.888×10^{-5}	0.006	0.016
283.2	$0.375 \leqslant x_1 \leqslant 1.0$	−9.767	4.670×10^{-2}	-5.323×10^{-5}	0.004	0.008
293.2	$0.375 \leqslant x_1 \leqslant 1.0$	−15.42	6.495×10^{-2}	-6.716×10^{-5}	0.007	0.013
298.2	$0.375 \leqslant x_1 \leqslant 1.0$	−12.95	4.656×10^{-2}	-3.983×10^{-5}	0.001	0.002
278.2	$0.375 \leqslant x_2{}^e \leqslant 1.0$	−2.338	2.993×10^{-2}	-9.210×10^{-5}	0.008	0.012
283.2	$0.375 \leqslant x_2 \leqslant 1.0$	−2.086	2.500×10^{-2}	-6.983×10^{-5}	0.003	0.007
293.2	$0.375 \leqslant x_2 \leqslant 1.0$	−5.267	4.019×10^{-2}	-7.616×10^{-5}	0.011	0.018
298.2	$0.375 \leqslant x_2 \leqslant 1.0$	−5.100	3.588×10^{-2}	-6.230×10^{-5}	0.011	0.015

[a] In mole fraction.

[b] Mole fraction of α-methylnaphthalene.

[c] Mole fraction of β-methylnaphthalene.

[d] Mole fraction of chlorobenzene.

[e] Mole fraction of bromobenzene.

($0 \leqslant x_1 \leqslant 0.5$), Eq. (3) is found to represent the data satisfactorily. But in the intermediate composition range of $0.5 \leqslant x_1 \leqslant 0.82$ of the α-methylnaphthalene + β-methylnaphthalene system and in all compositions of the chlorobenzene + bromobenzene system, Eq. (3) cannot reproduce the present results. Therefore, in order to express the entire range of coexistence curves, Eq. (3) was revised as follows:

$$\ln x_i = b_0 + b_1 P + b_2 P^2 \tag{4}$$

The parameters b_0, b_1, and b_2 are listed in Table IV for each system and temperature. As an example, the relations between the freezing pressure and the composition for the α-methylnaphthalene + β-methylnaphthalene system at various constant temperatures are shown in Fig. 3, where the points are the experimental data and the curves are the values calculated by Eq. (4). As seen in Table IV, Eq. (4) reproduces each liquidus satisfactorily within a mean deviation of 0.008 and a maximum deviation of 0.026 in mole fraction.

4. CONCLUSION

Solid–liquid phase equilibria of the α-methylnaphthalene + β-methylnaphthalene system and the chlorobenzene + bromobenzene system were investigated under high pressures. The freezing and melting temperatures at a constant composition increase almost linearly with increasing pressures for both systems. The eutectic point of the former system shifts to a higher temperature and to a more α-methylnaphthalene-rich region with pressure. The freezing and melting temperatures of the latter system at each constant pressure change almost linearly with composition. It is found that the coexistence curves can be expressed by a quadratic equation in pressure.

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