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Effect of Pressure on the Solid–Liquid Phase Equilibria of (Carbon Tetrachloride + *p*-Xylene) and (Carbon Tetrachloride + Benzene) Systems

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Solid–liquid phase equilibria of the carbon tetrachloride + *p*-xylene and the carbon tetrachloride + benzene systems have been investigated at temperatures from 278 to 323 K and pressures up to 500 MPa using a high-pressure optical vessel. The uncertainties in the measurements of temperature, pressure, and composition are within ±0.1 K, ±0.5 MPa, and ±0.001 mole fraction, respectively. In the former system, which has an intermolecular compound with a congruent melting point, the freezing temperature at a constant composition increases monotonously with increasing pressure. The two eutectic points of this system shift to higher temperatures and richer compositions of the compound with increasing pressure. In the latter system, which has two intermolecular compounds with incongruent melting points, the one compound disappears under the present experimental conditions and the incongruent melting point of the other compound changes to the congruent melting point under high pressures. The solid–liquid coexistence curves of these systems can be correlated satisfactorily by the equation previously proposed.

KEY WORDS: benzene; carbon tetrachloride; high pressure; intermolecular compound; *p*-xylene; solid–liquid phase equilibria.

1. INTRODUCTION

The information on solid–liquid phase equilibria at high pressures plays important roles in the design of high-pressure crystallization processes. The authors have reported several solid–liquid phase diagrams under pressures [1–3], where the solid components do not form intermolecular compounds. In the present paper, two typical systems with intermolecular com-

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pounds are selected in order to obtain the basic information on the applicability of the high-pressure crystallization technique [4].

The carbon tetrachloride + p-xylene system forms a solid compound containing equimolecular amounts of the components with a congruent melting point. The carbon tetrachloride + benzene system has two compounds at compositions of 1:1 and 2:1 with incongruent melting points. The pressure effect on the phase diagrams and the behavior of the compounds are discussed based on the experimental results, and the solid–liquid coexistence curves are correlated by the equation previously proposed.

2. EXPERIMENTAL

The measurements were performed in a high-pressure optical vessel, which was described in a previous paper [1]. All the samples were obtained from commercial sources and their purities should be better than 99 wt% for carbon tetrachloride and benzene and 98 wt% for p-xylene. The samples were used after being dried by calcium hydride.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The experimental data are summarized in Tables I and II.

3.1. The Pure Components

The freezing pressures of pure carbon tetrachloride and p-xylene agree well with the literature values [5, 6]. The relation between the freezing temperature and pressure could be expressed by the following equation derived from the Simon equation [2]:

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

where P_f and T are in MPa and K. The coefficients A, B, and C are listed in Table III. Equation (1) can reproduce the freezing temperature within ±0.1 K.

3.2. The Carbon Tetrachloride + p-Xylene System

Carbon tetrachloride and p-xylene form a stable solid compound at a composition ratio of 1:1, and it does not decompose until its melting temperature, which is called a congruent melting point. Figure 1 shows the relation between freezing temperature and composition at various

Table I. Solid–Liquid Equilibrium Data of the [Carbon Tetrachloride (1) + *p*-Xylene (2)] System

x_1^a	T(K)	P_f(MPa)[b]	Coexistence crystal[c]
0.00	293.2	20.8	2
	303.2	50.3	2
	313.2	82.2	2
	323.2	113.6	2
0.20	283.2	17.8	2
	293.2	48.9	2
	303.2	81.1	2
	313.2	114.1	2
	323.2	146.5	2
0.30	278.2	17.5	2
	283.2	33.4	2
	293.2	67.1	2
	303.2	99.2	2
	313.2	133.1	2
	323.2	165.7	2
0.35	278.2	24.7	2
	283.2	43.0	2
	293.2	78.8	2
	303.2	113.8	2
	313.2	151.4	2
	323.2	184.3	2
0.38	278.2	31.1	2
	282.3	48.2	2
	293.2	83.3	2
	303.2	121.0	2
	313.2	159.7	2
	323.2	197.7	2
0.40	278.2	33.2	c
	283.2	51.4	c
	288.2	70.9	c
	293.2	87.4	2
	303.2	125.0	2
	313.2	164.1	2
	323.2	204.6	2
0.42	278.2	31.9	c
	283.2	50.7	c
	293.2	87.8	c
	303.2	127.4	c
	313.2	168.3	2
	323.2	209.5	2
0.45	278.2	30.9	c
	283.2	48.5	c
	293.2	86.6	c
	303.2	125.6	c
	313.2	165.7	c
	323.2	210.5	c
0.50	278.2	30.2	c
	283.2	47.2	c
	293.2	85.0	c
	303.2	122.8	c
	313.2	161.8	c
	323.2	205.3	c
x_1	T(K)	P_f(MPa)	Coexistence crystal
0.65	278.2	36.9	*c*
	283.2	53.6	c
	293.2	92.5	c
	303.2	133.2	c
	313.2	173.6	c
	323.2	217.5	c
0.80	278.2	62.6	c
	283.2	82.2	c
	293.2	122.3	c
	303.2	164.3	c
	313.2	211.6	c
	323.2	259.7	c
0.85	278.2	78.6	c
	283.2	100.2	c
	293.2	141.5	c
	303.2	185.7	c
	313.2	235.9	c
	323.2	286.7	c
0.90	278.2	112.7	c
	283.2	137.7	c
	293.2	187.8	c
	303.2	235.8	c
	313.2	280.2	c
	323.2	333.4	c
0.91	278.2	130.0	c
	283.2	157.1	c
	293.2	203.7	c
	298.2	228.3	1
	303.2	251.2	1
	313.2	289.5	1
	323.2	328.7	1
0.925	278.2	136.8	1
	283.2	154.1	1
	293.2	189.7	1
	303.2	225.2	1
	313.2	263.4	1
	323.2	305.4	1
0.95	278.2	113.2	1
	283.2	129.1	1
	293.2	160.7	1
	303.2	197.4	1
	313.2	234.8	1
	323.2	272.7	1
1.0	278.2	75.2	1
	283.2	89.7	1
	293.2	119.4	1
	303.2	149.7	1
	313.2	180.8	1
	323.2	212.6	1

[a] Mole fraction of carbon tetrachloride. [b] Freezing pressure

[c] 1, 2, and c denote carbon tetrachloride, *p*-xylene, and the compound, respectively.

Table II. Solid–Liquid Equilibrium Data of the [Carbon Tetrachloride (1) + Benzene (2)] System

x_1^a	T(K)	P_f(MPa)[b]	Coexistence crystal[c]	x_1	T(K)	P_f(MPa)	Coexistence crystal
0.20	278.2	49.6	2	0.667	278.2	160.1	c
	283.2	72.3	2		283.2	180.1	c
	293.2	117.7	2		293.2	221.2	c
	303.2	165.4	2		303.2	263.8	c
	313.2	215.6	2		313.2	311.5	c
	323.2	265.5	2		323.2	361.3	c
0.40	278.2	118.9	2	0.70	278.2	163.7	c
	283.2	147.3	2		283.2	183.9	c
	293.2	204.2	2		293.2	226.0	c
	303.2	262.6	2		303.2	266.6	c
	313.2	327.2	2		313.2	313.6	c
	323.2	385.6	2		323.2	364.0	c
0.425	278.2	132.9	2	0.75	278.2	170.7	c
	283.2	158.0	2		283.2	192.2	c
	293.2	216.7	2		293.2	233.9	c
	303.2	279.0	2		303.2	278.2	c
	313.2	361.2	2		313.2	324.1	c
	323.2	419.8	c		323.2	371.9	c
0.45	278.2	153.6	2	0.80	278.2	181.9	c
	283.2	184.0	2		283.2	202.4	c
	293.2	258.3	2		293.2	244.8	c
	298.2	285.0	c		303.2	290.2	c
	303.2	313.7	c		313.2	336.1	c
	313.3	364.1	c		323.2	383.1	c
0.475	278.2	173.0	2	0.825	278.2	165.9	1
	283.2	207.2	c		283.2	184.5	1
	293.2	252.3	c		293.2	223.2	1
	303.2	303.4	c		303.2	262.3	1
	313.2	349.7	c		313.2	305.0	1
	323.2	400.0	c		323.2	356.9	1
0.50	278.2	183.7	c	0.85	278.2	144.2	1
	283.2	203.4	c		283.2	161.7	1
	293.2	248.1	c		293.2	199.5	1
	303.2	293.2	c		303.2	239.1	1
	313.2	340.1	c		313.2	284.8	1
	323.2	396.0	c		323.2	328.9	1
0.60	278.2	167.7	c	0.9	278.2	117.0	1
	283.2	187.2	c		283.2	133.3	1
	293.2	228.9	c		293.2	166.4	1
	303.2	271.0	c		303.2	204.7	1
	313.2	317.7	c		313.2	242.8	1
	323.2	371.0	c		323.2	280.7	1

[a] Mole fraction of carbon tetrachloride.

[b] Freezing pressure.

[c] 1, 2, and c denote carbon tetrachloride, benzene, and the compound, respectively.

Table III. Coefficients of Eq. (1)

Substance	A	$10^2 B$	C	Mean dev. (K)	Max. dev. (K)
Carbon Tetrachloride	−394.6	3.08	1.71	0.01	0.01
p-Xylene	−446.8	1.13	1.87	0.1	0.1

pressures, as well as that of 0.1 MPa [7]. The freezing pressure increases monotonously with increasing temperature, and the temperature coefficient of the freezing pressure, $(\partial P_f/\partial T)_{xi}$, increases as the composition approaches the eutectic mixture. These trends are similar to the simple eutectic systems already reported [1, 3]. The present system has two eutectic points at $x_1 = 0.94$ and $x_1 = 0.38$ at atmospheric pressure, where x_1

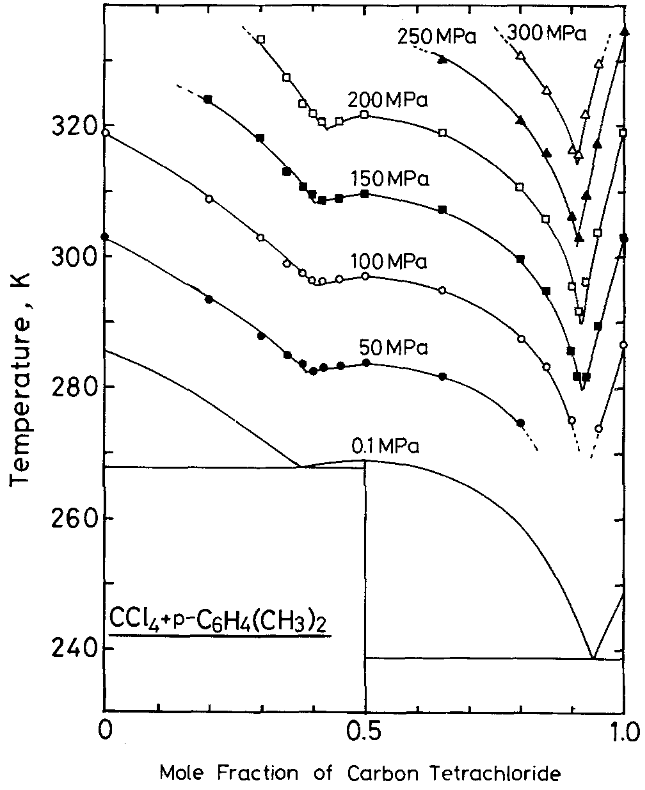

Fig. 1. Solid–liquid phase diagram of the carbon tetrachloride + p-xylene system at various pressures.

denotes the mole fraction of carbon tetrachloride. With increasing pressure, both eutectic points shift not only to higher temperatures, but also to richer compositions of the compound. In the *p*-xylene-rich region, from the mixtures of $x_1 = 0.40$ and 0.42, the crystals of the compound are formed at lower pressures, and on the contrary, the crystals of *p*-xylene appear at higher pressures. The eutectic composition moves to $x_1 = 0.43$ at 200 MPa. In the carbon tetrachloride-rich region, from the mixture of $x_1 = 0.91$, the crystals of the compound are formed at lower pressures and the crystals of the carbon tetrachloride are formed at higher pressures. The shift of the eutectic composition with pressure can be explained from the van Laar equation [8], which suggests that the eutectic point shifts to richer composition of a component whose temperature coefficient of the freezing pressure is larger. In this system, since that coefficient of the compound is larger than those of both pure carbon tetrachloride and *p*-xylene, it is expected that both eutectic mixtures become richer in the compound. The pressure effects on the eutectic temperature and composition (subscript e) can be expressed as a function of pressure by the following equations.

$$T_e = T_{e0} + T_{e1} P + T_{e2} P^2 \tag{2}$$

$$x_{1e} = x_{e0} + x_{e1} P + x_{e2} P^2 \tag{3}$$

The coefficients of Eqs. (2) and (3) are listed in Table IV.

Comparing the pressure effect on the eutectic compositions for both eutectic points, that in the *p*-xylene-rich region is nearly two times of that in the carbon tetrachloride-rich region. Therefore, it is expected that the eutectic composition in the *p*-xylene-rich region would approach $x_1 = 0.5$ in higher-pressure regions, and the congruent melting point should change to the incongruent melting point, where the compound decomposes at a temperature lower than its melting temperature.

3.3. The Carbon Tetrachloride + Benzene System

At 0.1 MPa, the carbon tetrachloride + benzene system has two intermolecular compounds at the composition ratios of 1:1 (compound **I**) and 2:1 (compound **II**), and both of them decompose at a temperature below their melting points, which is called an incongruent melting point. A eutectic point exists at $x_1 = 0.78$ between pure carbon tetrachloride and compound **II** at atmospheric pressure [9]. Figure 2 shows the relation between freezing temperature and composition at various pressures. The shape of the phase diagram is found to change extensively at high pressures; that is, the incongruent melting point of compound **II** turns to the congruent melting point, and compound **I** disappears. As a result, this system has two eutectic points under high pressures. The eutectic composition in the carbon tetrachloride-rich region is almost constant near $x_1 = 0.81$. On the other hand, another eutectic point in the benzene-rich region shifts to the benzene-rich composition with increasing pressure. From the mixtures of $x_1 = 0.425$, 0.45, and 0.475, the crystals of the benzene are formed at lower pressures, and the solid compound **II** deposits at higher pressures. The eutectic temperature and composition of each eutectic point are expressed as a function of pressure by Eqs. (2) and (3). The coefficients in these equations are listed in Table IV.

3.4. The Correlation of Solid–Liquid Coexistence Curves

The solid–liquid coexistence curves of these systems are correlated by the equation previously proposed [3]:

$$\ln x_i = -1/RT\{C(T)[P - B(T)] + D(T)[P^2 - B(T)^2]\} \qquad (4)$$

Table IV. Coefficients of Eqs. (2) and (3).

	Pressure range (MPa)	T_{e0}	T_{e1}	T_{e2}
	Carbon tetrachloride (1) + *p*-xylene (2) system			
Carbon tetrachloride-rich region	$0 \leqslant P \leqslant 300$	239	0.285	-9.62×10^{-5}
p-Xylene-rich region	$0 \leqslant P \leqslant 200$	268	0.302	-2.00×10^{-4}
	Carbon tetrachloride (1) + benzene (2) system			
Carbon tetrachloride-rich region	$180 \leqslant P \leqslant 390$	232	0.268	-8.07×10^{-5}
Benzene-rich region	$180 \leqslant P \leqslant 420$	235	0.252	-9.74×10^{-5}
	Pressure range (MPa)	x_{e0}	x_{e1}	x_{e2}
	Carbon tetrachloride (1) + *p*-xylene (2) system			
Carbon tetrachloride-rich region	$0 \leqslant P \leqslant 300$	0.943	-2.01×10^{-4}	2.55×10^{-7}
p-Xylene-rich region	$0 \leqslant P \leqslant 200$	0.382	2.95×10^{-4}	-3.12×10^{-7}
	Carbon tetrachloride (1) + benzene (2) system			
Benzene-rich region	$180 \leqslant P \leqslant 420$	0.558	-4.82×10^{-4}	4.08×10^{-7}

The temperature dependences of the coefficients B, C, and D could be expressed by the polynomials of the reciprocal of temperature.

$$B(T) = B_0 + B_1/T + B_2/T^2 \tag{5}$$

$$C(T) = C_0 + C_1/T + C_2/T^2 \tag{6}$$

$$D(T) = D_0 + D_1/T + D_2/T^2 \tag{7}$$

Table V. Coefficients of Eqs. (5)–(7)

Composition range	B_0	B_1	B_2	C_0	C_1	C_2	D_0	D_1	D_2	Deviation[d]	
										Mean	Max.
Carbon tetrachloride (1) + p-xylene (2) system											
$0.5 \leqslant x_1 \leqslant x_{1\mathrm{e}}$[a]	3.263×10^3	-1.540×10^6	1.783×10^8	-876.2	5.168×10^5	-7.236×10^7	-1.413	1.031×10^3	-1.874×10^5	0.003	0.015
$x_{1\mathrm{e}}$[a] $\leqslant x_1 \leqslant 1.0$	2.301×10^3	-1.020×10^6	1.115×10^8	8.466	-5.118×10^3	1.002×10^6	—	—	—	0.002	0.006
$0.5 \leqslant x_2 \leqslant x_{2\mathrm{e}}$[b]	3.263×10^3	-1.540×10^6	1.783×10^8	681.1	-4.459×10^5	7.366×10^7	—	—	—	0.007	0.020
$x_{2\mathrm{e}}$[b] $\leqslant x_2 \leqslant 1.0$	2.767×10^3	-1.367×10^6	1.647×10^8	1.234×10^3	-7.027×10^5	1.017×10^8	-0.4977	171.9	-9.597×10^3	0.004	0.013
Carbon tetrachloride (1) + benzene (2) system											
$0.667 \leqslant x_1 \leqslant 0.81$	4.273×10^3	-2.009×10^6	2.405×10^8	-1.673×10^3	6.059×10^5	-5.097×10^7	0.6849	-315.9	7.319×10^4	0.003	0.012
$0.81 \leqslant x_1 \leqslant 1.0$	2.301×10^3	-1.020×10^6	1.115×10^8	-31.73	1.878×10^4	-2.369×10^6	—	—	—	0.005	0.012
$0.333 \leqslant x_2 \leqslant x_{2\mathrm{e}}$[c]	4.273×10^3	-2.009×10^6	2.405×10^8	297.7	-1.646×10^5	1.985×10^7	2.241	-1.511×10^3	2.594×10^5	0.006	0.023
$x_{2\mathrm{e}}$[c] $\leqslant x_2 \leqslant 1.0$	3.548×10^3	-1.732×10^6	2.072×10^8	-197.6	1.147×10^5	-1.570×10^7	3.078×10^{-2}	10.47	-6.720×10^3	0.007	0.018

[a] $x_{1\mathrm{e}} = 0.943 - 2.01 \times 10^{-4} P + 2.55 \times 10^{-7} P^2$ (P: MPa). $x_{2\mathrm{e}} = 1 - x_{1\mathrm{e}}$.

[b] $x_{1\mathrm{e}} = 0.382 + 2.95 \times 10^{-4} P - 3.12 \times 10^{-7} P^2$ (P: MPa). $x_{2\mathrm{e}} = 1 - x_{1\mathrm{e}}$.

[c] $x_{1\mathrm{e}} = 0.558 - 4.82 \times 10^{-4} P + 4.08 \times 10^{-7} P^2$ (P: MPa). $x_{2\mathrm{e}} = 1 - x_{1\mathrm{e}}$.

[d] In mole fraction.

The coexistence curves where the pure crystals of the components are formed (in the composition range of $x_{ie} \leqslant x_i \leqslant 1.0$) could be correlated directly by Eqs. (4)–(7). The right side of Fig. 3 shows the relation of freezing pressure to the logarithm of composition at $x_{1e} \leqslant x_1 \leqslant 1.0$ of the carbon tetrachloride + *p*-xylene system. The parameters in Eqs. (5)–(7) are listed in Table V.

On the other hand, the coexistence curves where the crystals of the compounds are formed (in the composition range of $x_{ic} \leqslant x_i \leqslant x_{ie}$, x_{ic}: the composition of the compound) could be correlated by a modified equation for the compound formation. When the compound is formed at a composition ratio of *m*: *n*, Eq. (4) is rewritten as follows:

$$\begin{aligned} &\ln x_i^m(1-x_i)^n - \ln x_{ic}^m(1-x_{ic})^n \\ &\quad = -1/RT\{C(T)[P-B(T)] + D(T)[P^2-B(T)^2]\} \end{aligned} \tag{8}$$

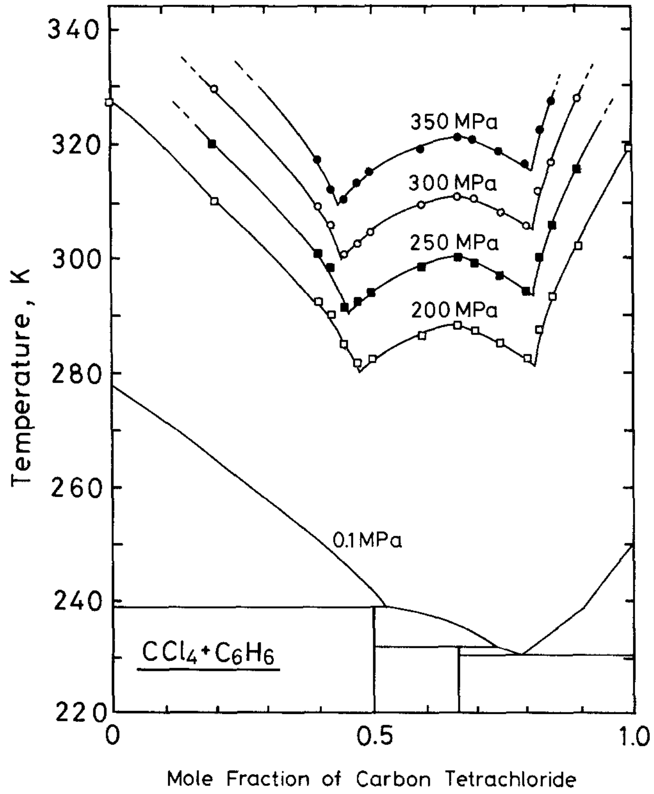

Fig. 2. Solid–liquid phase diagram of the carbon tetrachloride + benzene system at various pressures.

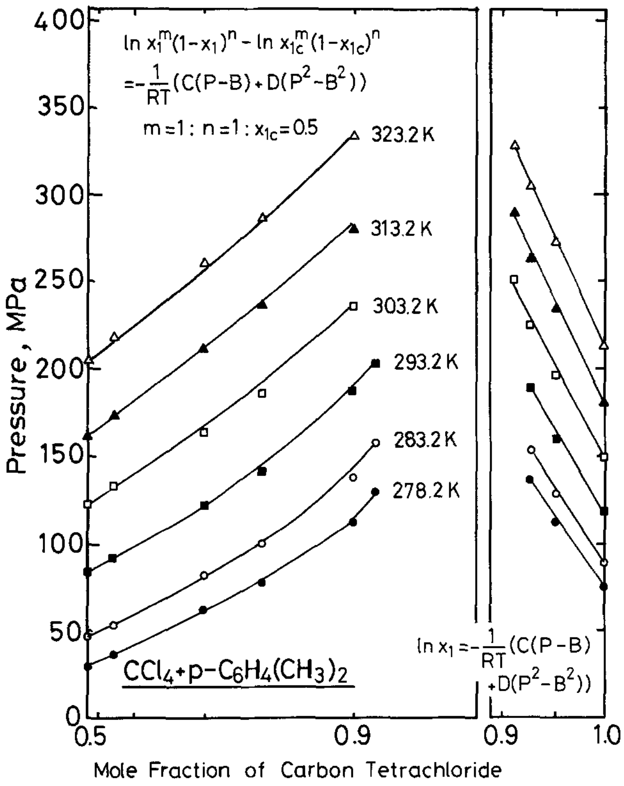

Fig. 3. Freezing pressure versus logarithm of composition diagram of the carbon tetrachloride + *p*-xylene system in the composition range of $0.5 \leqslant x_1 \leqslant x_{1e}$ and $x_{1e} \leqslant x_1 \leqslant 1.0$.

Equation (8) was derived from the Schröder–van Laar equation modified for the compound systems [10]. The left side of Fig. 3 shows the relation between the freezing pressure and the left-hand side of Eq. (8) at $0.5 \leqslant x_1 \leqslant x_{1e}$ of the carbon tetrachloride + *p*-xylene system. The linear relation can be held in a range of $0.5 \leqslant x_1 \leqslant 0.85$. The coexistence curves of the compound system can be correlated satisfactorily by Eq. (8) and Eqs. (5)–(7) except for the composition range near the compound. The parameters of Eqs. (5)–(7) are also listed in Table V.

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