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High pressure phase equilibria and critical phenomena of water + *iso*-butane and water + *n*-butane systems to 695 K and 306 MPa

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Abstract

The equilibrium surface (x, p, T, V_m) for water + *iso*-butane was measured and additional equilibrium data for water + *n*-butane are reported. Mole fractions of water for water + *iso*-butane from 0.5 to 0.98, pressures up to 306 MPa and temperatures up to 695 K were studied. Critical curves, represented as the envelope of the isopleths starting at the critical point of water (647 K), went through a temperature minimum and then increased at higher pressures and higher temperatures, giving evidence for (gas + gas) equilibria of the third type. The results are compared with the phase equilibrium of previously measured (water + *n*-alkane) mixtures. The excess molar volumes, V^E, and excess molar Gibbs energies, G^E, for water + *n*-butane on the phase equilibrium surfaces have been calculated for 600 and 620 K from 40 to 200 MPa. All the V^E and G^E values were found to be positive.
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1. Introduction

Physicochemical, theoretical, and experimental investigations of fluid mixtures at high pressure and high temperature have been the focus of research activities many years. The critical curves of binary systems have been studied and discussed [1,2]. Based on the one-fluid van der Waals equation, Scott and van Konynenburg introduced a classification for various types of fluid phase behavior [3,4]. Using the same or similar equations of state, many authors calculated the global phase diagrams [5,6]. A systematic investiga-

tion of the influence of the polarity of one of the two components on the character of the critical curves was made by Gubbins and Twu [7].

An area of particular interest is the combination of nonpolar and highly polar components, such as binary systems containing water as one component. Systems that have been extensively studied are mixtures of water and gases, including $H_2O + N_2$ [8], $H_2O + O_2$, $H_2O + H_2$, $H_2O + CO_2$ [9], and water with noble gases [10,11]. Others systems that have been investigated are water and alkanes [12]. For these systems, the critical curves and some of the phase-equilibrium surfaces have been determined [13,14]. In the water + alkanes (C_4–C_{10}) systems, the critical curves start at the critical point of water go through a temperature minimum and increase to

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higher pressures at higher temperatures. With the exception of the critical curve of water + propane and water + *n*-butane reported by Tsiklis and Ya Michelberger [15], the shape of critical curves for water + *n*-alkane systems change systematically with the number of carbons in the *n*-alkane molecules.

There are many alternative equations of state capable of calculating of fluid-phase equilibria of a diverse range of fluids. Wei and Sadus have reviewed these equations [16]. Neichel and Franck [13] have calculated the critical curves for the six binary systems water + methane to water + hexane and water + dodecane with an equation of state. This equation includes a perturbation type with a repulsion and an attraction term and a square-well potential for intermolecular interaction. The equation contains only three adjustable parameters, which can be interpreted on the basis of molecular models. The experimental data in this work, as well as other works, agree well with the calculated results. In this work, high-pressure phase data and critical curves of water + *iso*-butane and data that complement to our previous work [14] for water + *n*-butane systems are reported.

2. Experimental section

2.1. Materials

The *n*-butane and *iso*-butene (99.5% purity) were supplied by Messer Griesheim (Duesseldorf, Germany) Company and used without further purification. The water was distilled three times and boiled several times before use in order to remove dissolved gases.

2.2. Apparatus

The type of experimental apparatus used in this work has been described by Japas and Franck [8]. The apparatus consists of a horizontally mounted autoclave constructed from a high-strength corrosion-resistant nickel-based superalloy. It has a length of 30 cm, an outer diameter of 8 cm and an inner diameter of 2 cm. On the outside there were three independent heating jackets. Temperature inhomogeneities were minimized by using three Cr–Al thermocouples. Homogenization was achieved by magnetic stirring. A strain gauge precision transducer used to measure pressure

Table 1

Experimental data in the phase equilibrium boundary surface for water + *n*-butane mixture (*x*: mole fraction of water)

T (K)	p (MPa)	V_m (cm^3/mol)	T (K)	P (MPa)	V_m (cm^3/mol)	T (K)	P (MPa)	V_m (cm^3/mol)
$x = 0.65$								
600	24.6	151.0	633	87.2	68.6	689	244.8	54.4
608	39.1	84.4	647	123.7	63.1	698	276.4	53.7
$x = 0.75$								
616	34.9	79.0	664	145.0	51.2	700	264.8	45.1
628	59.2	64.5	673	173.4	49.0			
$x = 0.85$								
602	20.1	113.1	623	37.7	63.0	653	126.7	38.0
622	33.4	67.5	647	116.3	39.9			
$x = 0.95$								
628	19.3	39.6	622	37.1	31.1	625	109.6	29.0
632	21.4	38.8	620	43.4	30.6	631	134.7	28.9
637	24.8	37.4	617	61.9	29.9	640	180.1	28.6
634	28.2	36.2	621	80.3	29.4	644	189.8	28.0
628	32.7	34.2						
$x = 0.98$								
635	20.5	37.5	627	29.4	29.3	609	99.7	23.8
639	23.5	35.1	623	30.7	28.4	617	150.1	22.4
642	24.0	34.2	620	31.4	27.9	626	183.1	21.9
636	26.9	32.8	615	33.8	26.7	628	198.2	21.7
631	28.6	30.9						

was maintained at a constant temperature of 25 °C during the runs.

The autoclave volume, V, was calibrated by means of weighing water and was determined to have a volume of 60.13 cm^3 at 25 °C and 100 MPa. The pressure–volume dependence, $(\mathrm{d}V/\mathrm{d}p)_T(1/V)$, was 2.060×10^{-5} MPa^{-1}. The temperature–volume dependence, $(\mathrm{d}V/\mathrm{d}T)_p(1/V)$, was 4.050×10^{-5} K^{-1}. The small volume between the pressure transducer and the autoclave, also called the dead volume, was less than 0.15 cm^3. The uncertainties in temperature and pressure were ±0.5 K and ±0.1 MPa, respectively. Each end of the autoclave contained a sapphire window so that the contents of the autoclave could be observed with a light beam mirror.

2.3. Procedure

The synthetic method was used to determine the phase boundaries. A weighed quantity of n-butane or iso-butane was introduced into the evacuated autoclave. According to the desired mole fraction, the needed quantity of water was injected with a screw press. Then, the temperature was slowly increased (1.5–2 K/min) and the samples were stirred continuously. The pressure of the system was raised under

Table 2

Experimental data for the phase equilibrium boundary surface for water + iso-butane (x: mole fraction of water)

T (K)	P (MPa)	V_m (cm^3/mol)	T (K)	P (MPa)	V_m (cm^3/mol)	T (K)	P (MPa)	V_m (cm^3/mol)
$x = 0.50$								
547	13.5	260.3	575	29.1	124.4	595	59.8	88.1
567	27.1	137.9	580	38.2	111.4	651	188.8	71.1
$x = 0.60$								
566	16.7	208.4	602	42.5	98.7	695	305.6	57.1
589	29.5	126.6	624	85.7	75.6			
597	40.4	99.7	648	141.4	66.5			
$x = 0.70$								
588	20.7	116.1	621	57.1	78.7	658	149.3	56.8
607	35.7	104.4	634	81.7	50.0	693	264.0	50.1
$x = 0.80$								
605	22.6	116.1	628	37.8	78.7	649	111.3	49.5
614	26.8	104.4	647	108.9	50.0	674	191.0	44.8
$x = 0.90$								
608	18.9	99.3	627	33.5	58.1	639	110.3	38.1
613	19.9	89.6	623	39.6	52.2	643	129.9	32.4
627	26.7	80.7	622	44.6	46.1	653	170.7	30.1
630	28.9	77.4	625	59.8		658	190.1	27.2
631	29.2	77.3	630	89.9	40.1			
$x = 0.925$								
620	18.1	72.3	627	32.2	47.2	635	109.7	36.1
627	20.4	69.1	624	35.2	41.6	640	129.8	33.2
632	22.7	66.7	620	38.8	40.2	646	150.0	30.1
637	25.3	62.1	619	48.9		651	169.1	27.6
634	28.1	53.9	622	61.8	38.9	657	197.2	25.3
631	29.9	50.2	630	90.4	37.7			
$x = 0.98$								
620	16.7	57.8	636	25.9	41.3	621	33.7	30.2
625	18.6	53.4	631	26.4	38.8	633	165.9	26.3
631	20.3	50.0	627	27.8	37.2	649	215.2	22.6
637	21.9	49.3	623	28.8				
641	24.3	47.2	618	30.5	34.7			

isochoric conditions. The pressure increasing with temperature was simultaneously recorded. The resulting p–T curves showed a break point in the transition from two phases to single phase regions. The observations of the break points were also an indication of the appearance of a second phase. The agreement of the break point determined from the disappearance of the second phase and that determined from the appearance of the second phase agreed within ± 1 K and $\pm 0.3\%$ of the total pressure. Each break point was noted as a point on the pTx-phase boundary surface.

3. Results and discussion

3.1. Phase equilibrium and critical curves

Tables 1 and 2 give the experimental data for water $+$ n-butane and water $+$ iso-butane systems, respectively. Since the main purpose of this work was

to determine the accurate shapes of the critical curves for these two aqueous C_4 alkanes systems, measurements were made for compositions from $x(H_2O) = 0.5$ to $x(H_2O) = 0.98$ for water $+$ iso-butene, while the new compositions for water $+$ n-butane from $x(H_2O) = 0.65$ to $x(H_2O) = 0.98$.

Some of the isopleths $p(T)$, cross-sections for constant mole fraction, are shown in Figs. 1 and 2. These isopleths are the borderlines between the two-phase region and the single-phase region. The two-phase region is always on the left side of the isopleths. In the high-pressure-region all isopleths show a steep ascent, but in the low-pressure-region the forms of the isopleths are complex. At high concentrations of water ($x(H_2O) > 0.90$) and low pressures, the isopleths exhibited a temperature minimum. The minimum became less pronounced with decreasing $x(H_2O)$. Isothermal p–x curves obtained from the isopleths are shown in Figs. 3 and 4. These isotherms were obtained by interpolating the data graphically. In Figs. 3
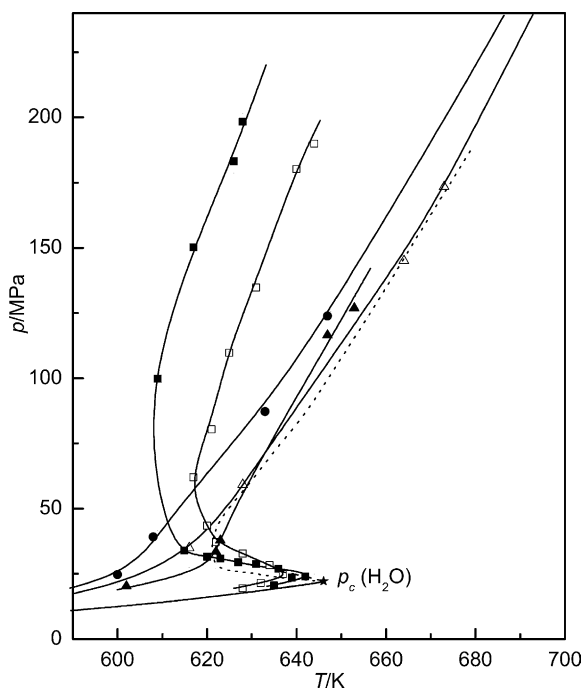

Fig. 1. (Gas $+$ gas) equilibria for $\{(1-x)n$-butane $+ x$H$_2$O$\}$: $p(T)$ sections for constant mole fraction x (($\bullet$) $x = 0.65$; ($\square$) $x = 0.75$; ($\blacktriangle$) $x = 0.85$; ($\square$) $x = 0.95$; ($\blacksquare$) $x = 0.98$. ($\bigstar$) The broken line is the critical curve of the mixture; the solid line is the saturation pressure curve of water.
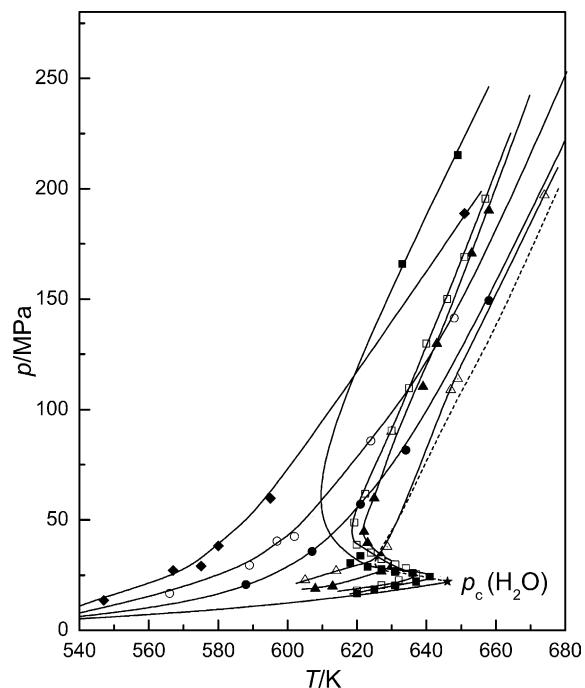
Fig. 2. (Gas $+$ gas) equilibria for $\{(1-x)iso$-butane $+ x$H$_2$O$\}$: $p(T)$ sections for constant mole fraction x (($\square$) $x = 0.50$; ($\bigcirc$) $x = 0.60$; ($\bullet$) $x = 0.70$; ($\square$) $x = 0.80$; ($\blacktriangle$) $x = 0.90$; ($\square$) $x = 0.925$; ($\blacksquare$) $x = 0.98$. ($\bigstar$) The broken line is the critical curve of the mixture; the solid line is the saturation pressure curve of water.
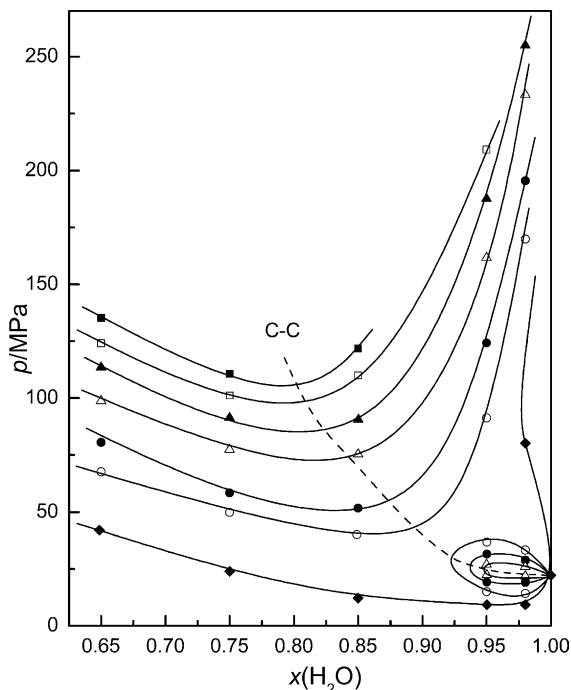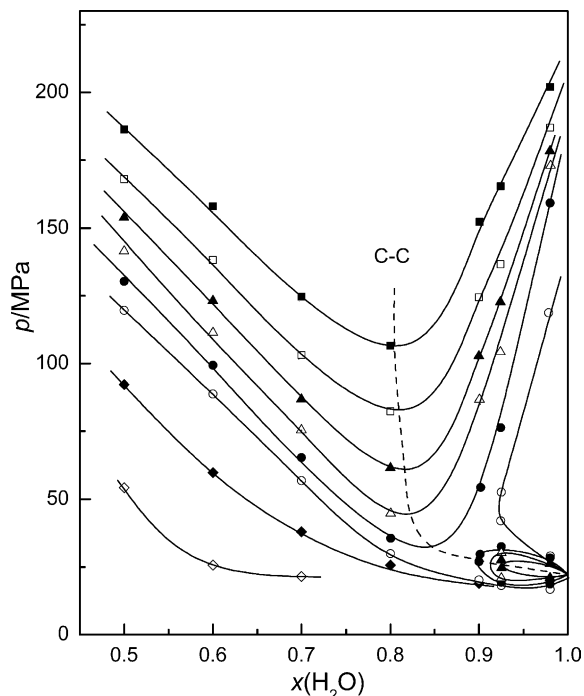
Fig. 3. (Gas + gas) equilibria for $\{(1-x)n\text{-butane} + x\text{H}_2\text{O}\}$: isothermal $p(x)$ diagrams ((□) 609 K; (○) 622 K; (●) 628 K; (□) 636 K; (▲) 642 K; (□) 646 K; (■) 650 K). (★) The broken line is the critical curve of the mixture.

Fig. 4. (Gas + gas) equilibria for $\{(1-x)iso\text{-butane} + x\text{H}_2\text{O}\}$: isothermal $p(x)$ diagrams ((□) 590 K; (□) 608 K; (○) 620 K; (●) 625 K; (□) 630 K; (▲) 635 K; (□) 641 K; (■) 649 K). (★) The broken line is the critical curve of the mixture.

and 4, the critical curves of the two systems, cc, (broken line) were estimated more accurately from the experimental results.

Table 3 gives the critical values for the water + n-butane and water + iso-butane systems. In Fig. 5 the critical curves obtained in this work are compared with the critical curves of other water+n-alkane systems. The latter were taken from the literatures [13–15,17–19]. In the low pressure region, there is a fair agreement between the phase data and critical curves of water+n-butane in this work with the literature data [17,19], except Tsiklis and Ya Michelberger's [15].

With the exception of the critical curve of the water + n-butane system (the broken line) reported by Tsiklis, the critical curves of the water + n-alkane systems change systematically with the number of carbons in the n-alkane molecule. From Fig. 5 it was found that all critical curves of water + n-alkane systems were discontinuous. According to the type III of the classification from van Konynenburg and

Table 3
Critical temperature, T_c, and critical pressure, p_c, values for the water + n-butane and water + iso-butane systems

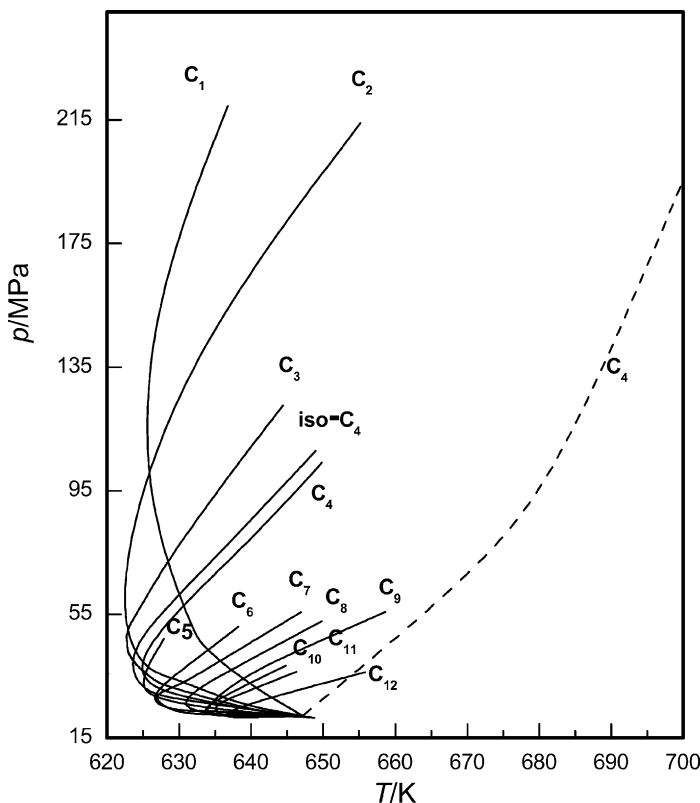| T_c (K)	p_c (MPa)	x_c
Water + n-butane		
650	106.0	0.80
646	97.2	0.81
642	84.2	0.83
636	71.1	0.85
628	56.9	0.87
622	43.0	0.89
622	29.0	0.92
628	26.5	0.94
636	23.2	0.96
Water + iso-butane		
649	106.6	0.80
641	81.0	0.81
635	61.1	0.82
630	44.6	0.82
625	32.5	0.85
625	28.1	0.90
630	26.1	0.91
635	25.7	0.93

Fig. 5. (Gas + gas) equilibria for $\{(1-x)n\text{-butane} + x\text{H}_2\text{O}\}$: $p(T)$ projections of the critical curves. The n-alkanes are indicated with the symbol C_n; iso-C_4 indicates iso-butane. (★) The broken line is the critical curve of the water + n-butane system reported by Tsiklis.

Scott [4], an upper branch begins at the critical point of water and the critical pressure first increases slightly as the temperature decreases. The curve goes through a temperature minimum and then the critical pressure increases as temperature increases. In Table 4, the corresponding temperature minima of the critical curves are given. The temperature minima decreased from C_1 to C_3, but slightly increased again from C_3 to C_{12}. The critical pressure decreased with the numbers of carbon in the n-alkane molecule. Fig. 6 illustrates this effect. From Table 4 and Fig. 6, we can predict that the corresponding temperature minima should not be less than 625 K, and that the critical pressures at these temperature minimums should be less than 29 MPa and the mole fraction should be greater than 0.89 for water + n-alkane with more than eight carbon atoms systems.

Table 4
Critical pressure, p_c, values at the temperature minimum of the critical curves for the water + n-alkane systems

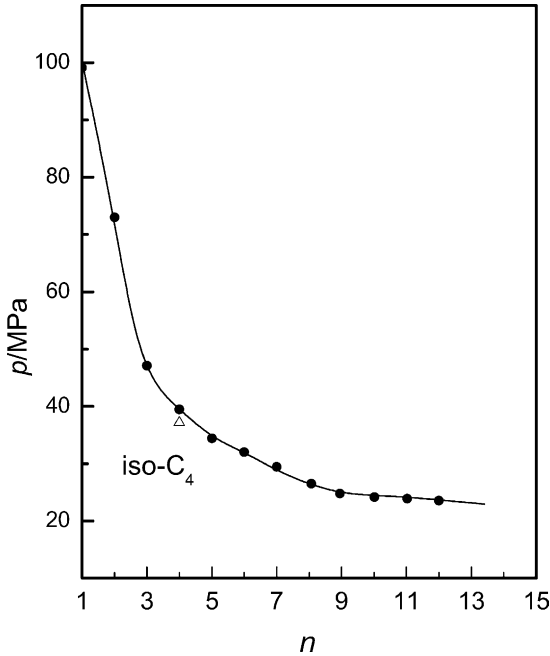| System	$T_{c\ min}$ (K)	p_c (MPa)	x_c
$CH_4 + H_2O$	626	99.0	0.75
$C_2H_6 + H_2O$	623	73.0	0.78
$C_3H_8 + H_2O$	622	47.1	0.88
$C_4H_{10} + H_2O$	624	39.5	0.89
iso-$C_4H_{10} + H_2O$	623	37.5	0.86
$C_5H_{12} + H_2O$	624	34.4	–
$C_6H_{14} + H_2O$	625	32.0	0.90
$C_7H_{16} + H_2O$	626	29.4	–
$C_8H_{18} + H_2O$	630[a]	26.5[a]	–
$C_9H_{20} + H_2O$	632[a]	24.8[a]	–
$C_{10}H_{22} + H_2O$	634[a]	24.1[a]	–
$C_{11}H_{24} + H_2O$	635[a]	23.9[a]	–
$C_{12}H_{26} + H_2O$	638[a]	23.5[a]	–

[a] Estimated values.

Fig. 6. (Gas + gas) equilibria for water + n-alkane: pressure at the temperature minimum of the critical curve as a function of the number n of C-atoms in the n-alkane (($\triangle$) iso-butane).

3.2. Excess molar volume and Gibbs energy for water + n-butane system

From the mixture density values determined at certain temperature, pressure and concentration, the deviations of the system from the ideal solution behavior were calculated. The excess molar volume, V^E, is defined as

$$V^E(T,\ p,\ x) = V_m(T,\ p,\ x) - \{x_1 V_{m,1}^*(T,\ p) + x_2 V_{m,2}^*(T,\ p)\} \tag{1}$$

where V_m is the experimentally determined molar volume of the mixture of concentration x at T and p, $V_{m,1}^*$ and $V_{m,2}^*$ are the molar volumes of the pure components at the same temperature and pressure.

Figs. 7 and 8 show results for V^E at 600 and 620 K for different pressures in dependence of the water fraction. It indicates that the V^E have different maximum values for different pressure at the same temperature. At 600 K and 40 MPa the V^E has a maximum of 34 cm^3/mol corresponding $x(H_2O) = 0.58$, but at 620 K and 40 MPa the V^E has a maximum of
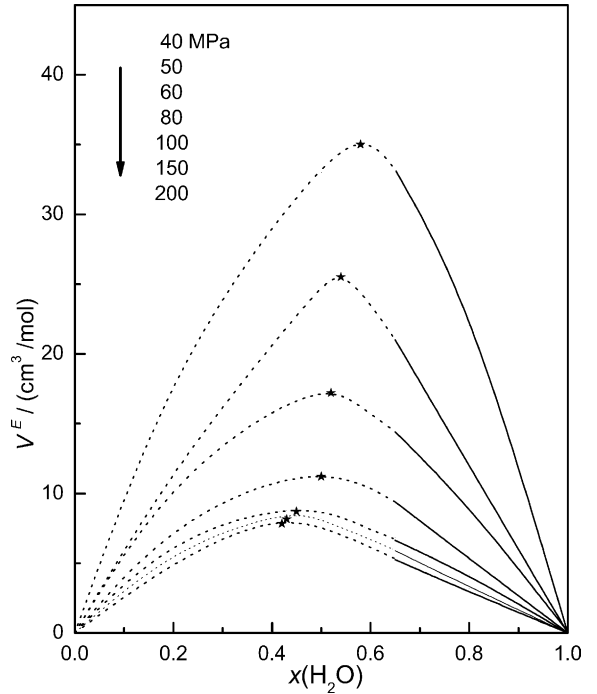

Fig. 7. Excess volume V^E of water + n-butane system in phase equilibrium boundary surface for 600 K. ($\star$) The broken line is basis on the previous work of Tian et al. [14].

40 cm^3/mol corresponding $x(H_2O) = 0.69$.

$$V^E(p \to 0,\ T,\ x)$$
$$= 2x_1 x_2 B^E(T)$$
$$= x_1 x_2 \{2B_{12}(T) - [B_{11}(T) + B_{22}(T)]\} \tag{2}$$

where B_{11} and B_{22} are the second virial coefficients of the pure components, while B_{12} is the second virial coefficient of the mixture:

$$B_{12} = \frac{RT_c}{p_{c,12}}(B^0 + \omega_{12} B') \tag{3}$$

where B^0 and B' are the same functions of $T_{c,12}$, as given by Prausnitz [20],

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \tag{4}$$

$$T_{c,12} = (T_{c,1} T_{c,2})^{1/2}(1 - k_{12}) \tag{5}$$

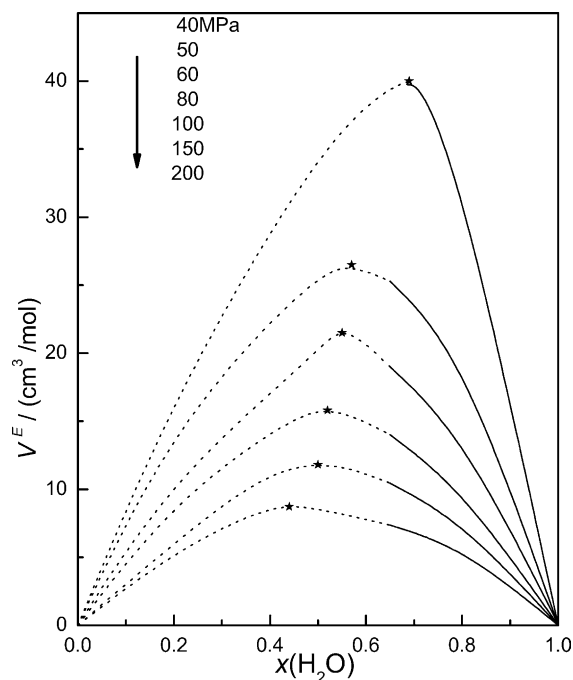$$p_{c,12} = \frac{Z_{c,12} RT_{c,12}}{V_{c,12}} \tag{6}$$

Fig. 8. Excess volume V^E of water + n-butane system in phase equilibrium boundary surface for 620 K. (★) The broken line is basis on the previous work of Tian et al. [14].

$$Z_{c,12} = 0.291 - 0.08 \left(\frac{\omega_1 + \omega_2}{2} \right) \qquad (7)$$

$$V_{c,12} = \left(\frac{V_{c,1}^{1/3} + V_{c,2}^{1/3}}{2} \right)^3 \qquad (8)$$

The ω_1 and ω_2 are acentric factors of the pure components. The k_{12} is the characteristic constant for unlike pairs, which is determined by the data of cross virial and density of liquid solutions. The value of k_{12} used in this work was equal to 0.42. B_{11}, B_{22}, $V_{m,1}^*$ and $V_{m,2}^*$ were calculated on the basis of existing data [21] and the proposed procedures [22]. The result are $B_{11} = 10.4$ cm^3/mol for 600 K, $B_{12} = 10.2$ cm^3/mol for 620 K.

As can be observed from Figs. 7 and 8, the value of V^E remained positive throughout the entire region investigated. From the values of $V^E = f(p)$ (at constant T) the excess Gibbs energy G^E can be determined by

$$G^E(T, P, x) = \int_0^p V^E (T, p', x) \, dp' \qquad (10)$$

Table 5
Values of constants C, D and the values of G^E corresponding the maxima of V^E at 600 and 620 K for different pressures

T (K)	P (MPa)	C (kJ/mol)	D (kJ/mol)	V_{max}^E [a] (cm^3/mol)	G^E (kJ/mol)
600	40	5.46	3.09	34 (0.58)	1.45
	100	7.49	2.83	11.2 (0.50)	1.89
	150	8.34	2.77	8.4 (0.45)	2.11
	200	10.17	2.19	8.0 (0.42)	2.54
620	40	6.96	3.71	40.0 (0.69)	1.79
	80	8.64	3.63	15.8 (0.52)	2.17
	100	9.88	3.24	11.8 (0.50)	2.38
	200	11.04	2.51	8.7 (0.44)	2.57

[a] The values in the parenthesis are the corresponding fraction of water.

Table 5 given the values of constants C, D and the values of G^E corresponding the maxima of V^E at 600 and 620 K for different pressures. Similar behavior was found for the water + *iso*-butane system.

Acknowledgements

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