Volumetric Properties of Near-Critical and Supercritical Water + Pentane Mixtures: Molar, Excess, Partial, and Apparent Volumes

Ilmutdin M. Abdulagatov,*,† A. R. Bazaev, E. A. Bazaev, M. B. Saidakhmedova, and A. E. Ramazanova

Institute for Geothermal Problems of the Dagestan Scientific Center of the Russian Academy of Sciences, 367030 Makhachkala, Kalinina 39 A, Dagestan, Russia

We present new *PVTx* measurements for water (A) + pentane (B) mixtures at the critical temperature of water (T_C = 647.05 K) in the pressure range 4 MPa to 41 MPa at x_b = 0, 0.028, 0.042, 0.061, 0.088, 0.184, 0.391, 0.694, and 1.0. The measurements were performed with a constant-volume piezometer. The sample was confined to a 36.8 cm³ cylindrical cell of a corrosion-resistant steel alloy, provided with a steel ball for stirring. The cell was separated from the rest of the fill and pressure measurement system by a diaphragm-type null indicator. The temperature was measured by a 10 Ω platinum resistance thermometer. The uncertainty in the temperature measurement is less than ±5 mK. Pressure was measured by means of a dead-weight gauge with a precision of ±2 kPa. The composition was determined with an uncertainty of ±0.002 in mole fraction. The volume of the cell was corrected for temperature expansion and elastic deformation by means of the known expansion coefficients of the cell. Taking into account the errors of temperature, pressure, and concentration measurements, the total experimental uncertainty of density, $\delta\rho$, was estimated to be less than ±0.5%. From the *PVTx* results, the excess, partial, and apparent molar volumes were determined. Analysis of the results for dilute water + pentane mixtures showed that partial molar volume of pentane (solute) and excess molar volume of the mixture near the critical point of pure water (solvent) exhibit the behavior predicted by theory. A nonclassical (scaled) asymptotic relation has been used for the analysis of the partial and molar volumes behavior along the critical isotherm–isobar.

1. Introduction

This work is part of an experimental program to determine the thermodynamic properties of water + hydrocarbon mixtures at near-critical and supercritical conditions. In this paper, we present new measurements of the homogeneous *PVTx* surface for pure water, pentane, and their mixtures near the critical point of pure water.

Water, the most important solvent in nature, has surprising properties as a reaction medium in its supercritical state. Near-critical and supercritical fluids, as well as near-critical and supercritical water in particular, are widely used as a solvent or reaction medium for a number of technological applications (Kiran and Levelt Sengers, 1993; Kiran and Brennecke, 1993; Bright and McNally, 1992; Johnston and Penninger, 1989; Abdulagatov et al., 1994a). Near-critical and supercritical water is used for destruction of hazardous wastes and has been explored as a solvent medium to carry out chemical reactions or biological degradations without char formation (Model et al., 1982; Staszak et al., 1982; Tester et al., 1991). Water + hydrocarbon mixtures are important in a wide range of industrial processes, including coal gasification, oil recovery, steam distillation, steam reforming, and combustion.

Binary aqueous fluid mixtures with hydrocarbons are interesting combinations of polar and nonpolar molecules. The near-critical local environment (microstructure) around an infinitely dilute solute can be dramatically different from the bulk average. The aim of this work was to use

PVTx measurements of dilute water + pentane mixtures near the critical point of pure water to study the anomalous critical behavior of the partial molar volume of pentane in the critical point of pure water (solvent).

Very little has been published concerning the *PVTx* properties of water + hydrocarbon mixtures at supercritical conditions owing to the experimental difficulties in their measurement. In previous papers (Abdulagatov et al., 1993a,b, 1994, 1995, 1996), we reported *PVTx* data of five water + hydrocarbon binary mixtures (water + methane, + hexane, + heptane, + octane, + benzene) at supercritical conditions. The new *PVTx* data for water + pentane systems in the immediate vicinity of the solvent's critical point provide additional information on the effects of temperature, pressure, and composition on the *PVT* relation in such systems, which could lead to improved understanding of the process near the solvent's critical point. However, the *PVTx* data for the system water + pentane at near-critical and supercritical conditions are scarce. A number of phase-equilibrium (PTx) studies have been made on water + alkane mixtures (Alwani and Schneider, 1967; Rebert and Hayworth, 1967; de Loos et al., 1982; de Loos and Dorp, 1983; Brunner, 1990; Connoly, 1966; Brollos et al., 1970; Yiling et al., 1991). Most of the measurements were performed at temperatures up to the critical point of pure water.

Experimental Section

The experimental apparatus was designed for measuring the *PVTx* data of supercritical fluids and fluid mixtures at high temperatures and high pressures. The constant-

† Present address: Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, Colorado 80303. E-mail: ilmutdin@boulder.nist.gov or kvadro@sinol.ru.
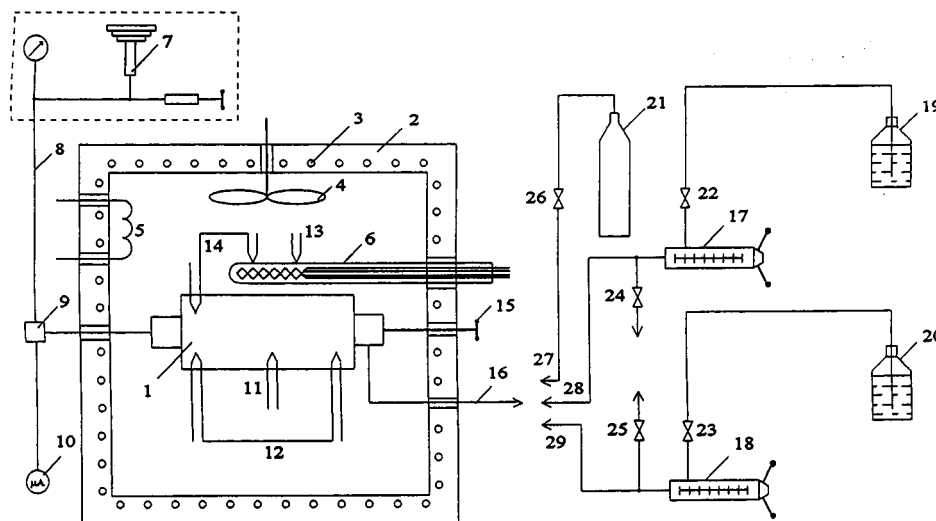
Figure 1. Schematic diagram of the experimental apparatus for the *PVTx* measurements of the supercritical mixtures: (1) air thermostat, (2), (20) electrical heaters, (3) regulating heater, (4) platinum resistance thermometer, (5) piezometer, (6) dead-weight gauge, (7), (8) samples, (9), (10) hand-operated screw press, (11) Ar cylinder, (12), (13), (16) capillary tube, (14), (15), (17)−(19) valves, (21)−(24) thermocouples, (25) stirrer, (26) adapter, (27) microammeter.

volume piezometer has been used in the past several years to measure the *PVTx* proreties of pure hydrocarbons (methane, hexane, heptane, octane, benzene) and their aqueous mixtures in the near-critical and supercritical conditions, and it was described in detail by Abdulagatov et al., 1993a,b, 1994b, 1995, 1996). The apparatus used in the present measurements of water + pentane mixtures near the critical point of pure water is schematically shown in Figure 1.

The main part of the apparatus consisted of an air thermostat, a piezometer, lines for filling and extracting samples, temperature-control and temperature-measuring devices, and pressure-measuring instruments. The air thermostat has double walls, and it has an inside volume of 65 dm³. Guard heaters have been located between the walls of the thermostat for setting the desired temperature inside the thermostat. The regulating heater was mounted inside the thermostat to avoid thermal losses. The thermostat temperature is controlled automatically to within ±10 mK. The automated temperature controller has been described in detail in previous paper by Bazaev (1993). The temperature is measured by a 10 Ω platinum resistance thermometer. The thermometer used in the present study has been calibrated within an accuracy of ±1 mK at the VNIIFTRI (Moscow), against ITS-90. The uncertainty in the temperature measurement when local temperature gradients and temperature stability are taken into account is less than ±5 mK. To minimize temperature gradients in the air thermostat, two electrically driven high-speed fans were provided.

The piezometer is located horizontally in the center of the air thermostat. The cylindrical piezometer was made from a heat- and corrosion-resistant high-strength alloy (EI-437B4) and contains a volume of about 36.8 cm³. On one of the ends of the piezometer, a diaphragm-type null indicator is mounted and, on the other end, a high-pressure valve. The diaphragm (40 mm in diameter and 0.08 mm thick) was made from type 321 stainless steel. The diaphragm-type null indicator is connected with a dead-weight pressure gauge MP-600 by a stainless steel tube filled with liquid octane. The dead-weight pressure gauge MP-600 has an effective piston area of 0.05 cm². The sample was isolated from the pressure-transmitting liquid octane system by a stainless steel diaphragm in the null

indicator. The pressure measurements have an uncertainty of ±2 kPa.

All parts of the experimental apparatus in contact with the fluid and fluid mixture were carefully cleaned initially with acetone. The piezometer was evacuated with the aid of a vacuum pump.

The water in the piezometer was heated until its temperature reached the desired value and the pressure reached about 50 MPa. When pressure and temperature equilibrium was reached the *PVT* measurements along the prescribed isotherm were made for pure water. To reach equilibrium fast, the electric heater was switched on and the sample was stirred with a steel ball bearing, which was rotated rapidly in the sample by a mechanical rotation of the piezometer. Measurements were continued by extracting a prescribed amount of water from the piezometer through valve. The extracted water was collected in a vessel cooled with liquid nitrogen. The mass of the extracted water was measured with a precision chemical balance with an uncertainty of ±0.5 mg. From the mass of the collector before and after extraction, the mass of the extracted water has been determined. The density of the sample water at a given temperature and pressure is determined from the simple relation

$$\rho = m/V_{TP}, \quad m = m_1 + m_2 + m_3 + \ldots \quad (1)$$

where m_i is the mass of water at each extraction from the piezometer during the run, m is the total mass of the water in the piezometer, and V_{TP} is the temperature- and pressure-dependent volume of the piezometer.

Since the inner volume V_{TP} of the piezometer is subjected to the effects of both temperature and pressure, it is essential to make appropriate corrections for these influences. The inner volume of this piezometer was calculated taking into consideration the corrections of the elastic deformation and thermal expansion. The volume of the piezometer was previously calibrated from the known density of standard fluid (pure water) with a well-known *PVT* (Haar et al., 1984) at temperature $T_0 = 673$ K and at pressure $P_0 = 13.4$ MPa. The volume at these conditions was $V_{P_0T_0} = 36.80 \pm 0.002$ cm³. The volume of piezometer at given T and P was calculated from the equation

$$V_{TP} = V_{P_0 T_0}[1 + 3\alpha(T - T_0) + \beta(P - P_0)] \qquad (2)$$

where $\alpha = 1.4 \times 10^{-5}$ K^{-1} is the thermal expansion coefficient of alloy (EI-437B4) which is virtually temperature-independent in a broad temperature range from 500 K to 700 K, and $\beta = 3.06 \times 10^{-11}$ Pa^{-1} is the pressure expansion coefficient of the piezometer. The values of thermal expansion coefficient α and pressure expansion coefficient β for this cell were determined in this work experimentally.

Next, the mass of a mixture in the piezometer at given T and P was determined in a similar way. The mass, m_w, of the pure water at a given temperature and pressure was obtained by $m_w = V_{TP} \cdot \rho_w$, where ρ_w is the pure water density, which was determined previously. Then, the fill line of the piezometer was connected with line of the gas injector and the second component (pentane) was injected into the piezometer until the desired pressure was reached. The mass of pentane was determined from the difference in mass of the extracted mixture and the known initial mass m_w of pure water in the piezometer. The density of the sample mixture for given composition at a given temperature and pressure was determined using eq 1.

Taking into account the errors of temperature, pressure, and concentration measurements, the total experimental uncertainty of density, $\overline{\delta\rho}$, could be calculated as follows

$$\overline{\delta\rho} = \delta\rho + \frac{100}{\rho}\left[\left(\frac{\partial\rho}{\partial P}\right)_{T,x}\Delta P + \left(\frac{\partial\rho}{\partial T}\right)_{P,x}\Delta T + \left(\frac{\partial\rho}{\partial x}\right)_{P,T}\Delta x\right] \quad (3)$$

where $\delta\rho = 100|\Delta\rho/\rho| = 0.024\%$, $\Delta P = \pm 0.002$ MPa, $\Delta T = \pm 1$ mK, and $\Delta x = \pm 0.002$ mole fraction are our estimates based on experiments. Values for the partial derivatives $(\partial\rho/\partial P)_{T,x}$, $(\partial\rho/\partial T)_{P,x}$, and $(\partial\rho/\partial x)_{P,T}$ have been calculated using correlating equations for various experimental paths (isotherm−isopleth, isobar−isopleth, and isotherm−isobar). In the present study, the total uncertainty of density was estimated to be less than $\pm 0.5\%$.

The operational range of the instrument covers the temperature range from 295 K to 700 K and pressure up to 100 MPa.

The water was triply distilled and degassed and had an electric conductivity of about 10^{-4} Ω^{-1} m^{-1}. Pentane was 99.2 mol percent pure.

3. Results

The *PVTx* experimental values for water + pentane mixtures and their pure components are given in Table 1. The measurements cover the pressure range from 4 MPa to 41 MPa. About six to nine *PVT* measurements were made at mole fraction of pentane: 0.0, 0.0283, 0.0420, 0.0608, 0.0880, 0.1840, 0.3907, 0.6938, 1.0.

The measurements of pure components (water and pentane) were carried out in order to confirm the reliability of the present apparatus. The *PVT* data are well-known for these fluids. To check the apparatus, density measurements on the pure components have been carried out also on the isotherm 647.05 K. The test measurements for pentane are in excellent agreement, namely, clearly within $\pm 0.4\%$, with the densities measured by Grigor'ev et al., 1986).

Test measurements on pure water and pure pentane have confirmed the estimated total uncertainty in density of less than $\pm 0.5\%$.

4. Discussion

From the experimental mixture molar volume values and the corresponding values for the pure components, the

Table 1. Experimental *PVTx* Properties of Water + Pentane

		$T = 647.05$ K		
P/MPa	ρ/kg·m^{-3}	V/cm^3·mol^{-1}	x/mole fraction of pentane	$Z = PV/RT$
5.434	20.000	900.800	0.0000	0.9099
9.824	40.000	450.400		0.8225
15.909	80.000	225.200		0.6660
20.312	140.000	128.686		0.4859
25.423	520.000	34.646		0.1637
36.830	600.000	30.027		0.2056
4.700	18.913	1033.427	0.0283	0.9028
10.386	46.702	418.510		0.8080
14.918	76.703	254.817		0.7066
18.690	114.492	170.713		0.5931
22.125	177.721	109.977		0.4523
24.815	298.104	65.565		0.3024
27.150	388.043	50.369		0.2542
30.170	447.267	43.700		0.2451
38.492	521.150	37.504		0.2683
4.635	18.981	1068.98	0.0420	0.9210
10.315	47.164	430.208		0.8249
14.849	76.959	263.652		0.7278
18.483	111.564	181.871		0.6249
21.799	163.015	124.470		0.5044
25.010	255.714	79.348		0.3689
26.997	326.130	62.215		0.3122
30.895	410.575	49.419		0.2838
38.984	492.579	41.192		0.2985
4.690	20.098	1060.283	0.0608	0.9243
10.374	49.925	426.835		0.8231
14.831	80.395	265.059		0.7308
18.528	114.748	185.708		0.6396
21.408	153.138	139.153		0.5538
23.815	200.234	106.423		0.4711
27.220	289.964	73.490		0.3719
30.459	360.844	59.055		0.3344
39.612	462.950	46.030		0.3389
4.625	21.090	1080.096	0.0880	0.9285
10.390	52.136	436.916		0.8438
14.872	83.283	273.515		0.7562
18.673	118.711	191.889		0.6661
21.875	159.317	142.980		0.5814
25.1606	215.845	105.535		0.4936
30.031	312.588	72.873		0.4068
39.993	428.538	53.156		0.3952
4.617	25.3732	1102.657	0.1840	0.9464
10.481	63.967	437.380		0.8522
14.766	98.031	285.400		0.7834
18.756	134.406	208.160		0.7257
21.969	169.948	164.626		0.6723
25.022	208.032	134.489		0.6255
30.856	281.772	99.293		0.5695
40.877	376.166	74.377		0.5652
4.344	36.514	1072.627	0.3907	0.8662
9.810	86.558	452.480		0.8251
16.262	147.040	266.362		0.8052
22.328	211.244	185.405		0.7695
29.827	283.359	138.219		0.7664
40.382	356.589	109.834		0.8245
4.629	50.494	1100.553	0.6938	0.9469
9.446	109.912	505.596		0.8878
14.904	180.423	308.004		0.8533
22.444	264.057	210.450		0.8780
29.943	323.204	171.938		0.9570
37.891	367.126	151.367		1.0662
3.560	54.306	1328.512	1.0000	0.8792
7.445	127.477	565.954		0.7832
9.975	178.234	404.783		0.7506
14.967	260.380	277.080		0.7709
22.189	332.957	216.683		0.8937
30.062	380.411	189.653		1.0598
41.130	423.239	170.462		1.3033

departure of the water + pentane mixtures from ideal solution behavior has been calculated. The excess (V_m^E) and apparent ($^\phi V_m$) molar volumes are defined as

Table 2. Excess and Apparent Molar Volumes for Aqueous Solutions of Pentane

				$T = 647.05$ K			
				x/mole fraction of pentane			
P/MPa	0.028	0.042	0.061	0.088	0.184	0.391	0.694
				$V_{\rm m}^{E}$/cm$^3\cdot$mol^{-1}			
5.0	−21.339	2.315	−1.814	10.589	38.463	−28.760	86.885
7.5	−3.150	10.192	10.599	24.120	32.878	−0.394	69.326
10.0	−0.364	8.482	8.505	21.216	29.344	17.792	59.737
12.5	1.316	9.800	9.320	19.093	26.017	26.771	47.079
15.0	3.233	10.093	10.130	19.033	26.090	31.291	37.899
17.5	4.567	10.780	12.877	19.961	29.511	33.387	32.459
20.0	8.042	14.556	19.601	26.056	37.045	38.144	31.587
22.05	50.752	57.828	64.311	70.696	78.017	69.133	45.576
22.5	58.123	65.630	72.686	79.177	86.170	75.263	48.387
25.0	23.762	37.281	47.271	57.093	68.316	62.703	41.203
27.5	11.399	19.522	28.539	38.528	53.090	51.966	35.030
30.0	7.468	12.658	18.735	27.058	41.859	43.796	30.200
32.5	5.687	9.405	14.181	20.942	34.108	37.727	26.543
35.0	4.590	7.495	11.292	16.775	28.472	32.893	23.642
37.5	3.896	6.135	9.149	13.570	23.925	28.847	21.373
				$^{\phi}V_{\rm m}$/cm$^3\cdot$mol^{-1}			
5.0	140.642	951.099	866.182	1016.327	1104.984	822.382	1021.222
7.5	450.254	804.319	735.936	835.853	740.391	560.736	661.668
10.0	391.146	605.889	543.798	645.123	563.462	449.556	490.120
12.5	369.617	556.299	476.221	540.019	464.409	391.562	390.902
15.0	391.074	516.877	443.135	492.942	418.412	356.736	331.277
17.5	410.432	505.354	460.413	475.621	409.132	334.229	295.564
20.0	513.954	575.753	551.450	525.410	430.599	326.933	274.836
22.05	2013.808	1593.694	1274.289	1020.723	641.244	394.267	283.019
22.5	2272.465	1777.145	1409.704	1114.870	683.306	407.716	284.833
25.0	1045.822	1092.037	981.627	853.529	575.921	365.195	264.103
27.5	600.028	661.178	665.578	634.371	485.013	329.539	247.028
30.0	454.145	491.066	497.711	497.293	417.253	301.894	233.333
32.5	385.536	408.061	417.279	422.209	369.552	280.777	222.477
35.0	341.893	357.818	365.006	370.052	334.129	263.608	213.498
37.5	313.224	321.326	325.678	329.518	305.308	249.139	206.116
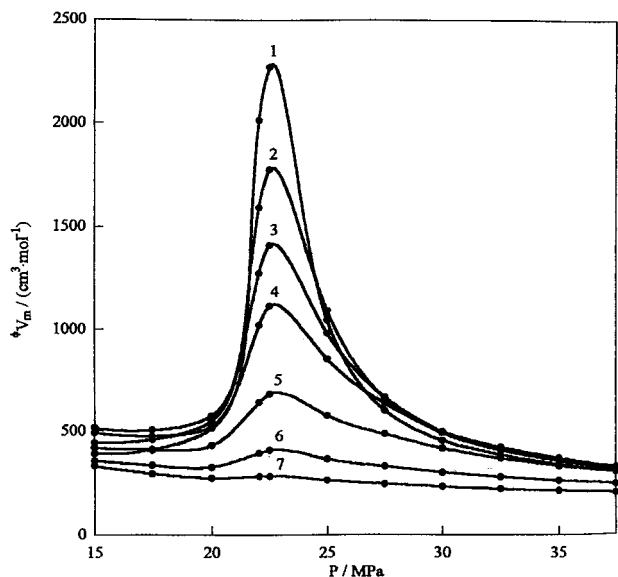
Figure 2. Apparent molar volumes $^{\phi}V_{\rm m}$ of pentane as a function of pressure *P* at critical isotherm 647.05 K for various compositions. 1, *x* = 0.028; 2, *x* = 0.042; 3, *x* = 0.061; 4, *x* = 0.088; 5, *x* = 0.184; 6, *x* = 0.391; 7, *x* = 0.694 molar fraction.

$$V_{\rm m}^{E}(P, T, x) = V_{\rm m}(P, T, x) - xV_{\rm m}(P, T, 1) - (1 - x)V_{\rm m}(P, T, 0) \quad (4)$$

$$x^{\phi}V_{\rm m}(P, T, x) = V_{\rm m}(P, T, x) - V_{\rm m}^{w}(P, T)(1 - x) \quad (5)$$

where $V_{\rm m}(P, T, x)$ is the experimentally determined molar volume of the mixture of concentration *x* at temperature *T* and pressure *P*, $V_{\rm m}(P, T, 1)$, and $V_{\rm m}(P, T, 0)$ are the volumes of the pure components at the same *P* and *T*, and $V_{\rm m}^{w}(P, T)$ is the molar volume of water.

Table 2 shows the results for $V_{\rm m}^{E}$ at the temperature 647.05 K for various pressures in dependence on the pentane mole fraction. Figure 2 and Table 2 shows the apparent molar volumes $^{\phi}V_{\rm m}$ as a function of pressure. As one can see from Figure 2 near the critical point of pure water (at pressures about 22 MPa), the pressure dependence increase rapidly and the $^{\phi}V_{\rm m}$ go through a maximum that changes with pressure like the compressibility of pure water K_T.

The partial molar volumes $\bar{V}_i$, $i = 1, 2$, are obtained from the slope of the tangent $(\partial V_{\rm m}/\partial x)_{PT}$ as follows

$$\bar{V}_1 = V_{\rm m} - x\left(\frac{\partial V_{\rm m}}{\partial x}\right)_{P,T}, \quad \bar{V}_2 = V_{\rm m} + (1 - x)\left(\frac{\partial V_{\rm m}}{\partial x}\right)_{P,T} \quad (6)$$

The anomalies in the partial molar volume of the solute near the solvent's critical point can be explained in terms of critical point phenomena (Chang et al., 1984; Chang and Levelt Sengers, 1986; Levelt Sengers, 1991a,b; Harvey and Levelt Sengers, 1991). In the limit $T \to T_C$ and $P \to P_C$, the tangent $(\partial V_{\rm m}/\partial x)_{PT}$ approaches the vertical and therefore $\bar{V}_2^{\infty} \to +\infty$. The asymptotic behavior of the molar volume $V_{\rm m}$ in the limit $x \to 0$ along critical isotherm–isobars near the pure solvent's critical point can be expressed by the asymptotic relation

$$V_{\rm m} = V_0 x^{\epsilon} \quad (7)$$

where V_0 is the asymptotic critical amplitude and $\epsilon = 1 - \gamma/\beta\delta \approx 0.21$ is the universal critical exponent ($\gamma = 1.24$,
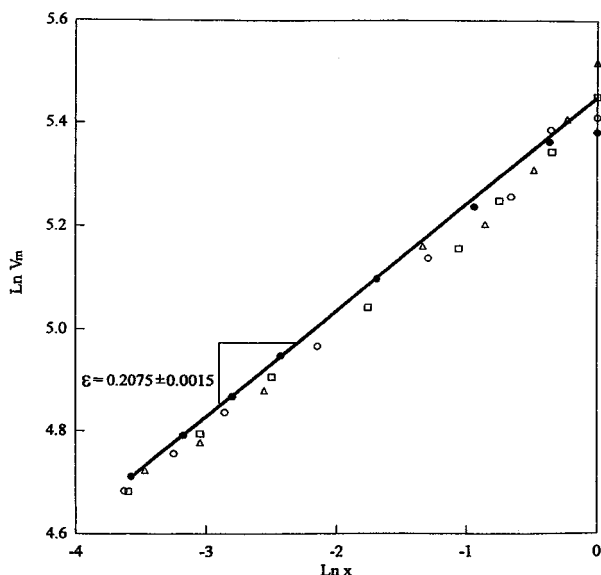
Figure 3. Molar volumes ln V_m against concentrations ln x for water + alkane mixtures at critical isotherm−isobar (T_C = 647.05 K and P_C = 22.05 MPa) for various near-critical pressures: (●) water + pentane (this work); (□) water + heptane; (△) water + octane; (○) water + hexane (Abdulagatov et al., 1996).

Table 3. Critical Exponents and Amplitudes for Four Water + Alkane Mixtures

| | | ϵ | | |
system	$V_0/$ (cm³·mol⁻¹)	experimental	scaling theory	classical theory
water + pentane	232.7116	0.2075 ± 0.0015		
water + heptane	224.3932	0.2058 ± 0.0011		
water + hexane	225.1350	0.2045 ± 0.0017	0.21	0.33
water + octane	225.4729	0.2076 ± 0.0013		
water + benzene	180.0798	0.1933 ± 0.0018		

β = 0.325, δ = 4.83). In the classical case (mean field theory), ϵ = 1 − $2/3$ ≈ 0.3333. The asymptotic scaling relation (eq 7) was fitted to our experimental (V_m, x, P_C, T_C) data by the weighted linear least-squares procedure at $x \to 0$ (dilute mixtures). The molar volumes V_m of water + pentane dilute mixtures as a function of ln x along the critical isotherm−isobar together with our earlier results for water + alkane mixtures are presented in Figure 3. From our experimental results we have deduced values for exponent ϵ and amplitude V_0. The results given in Table 3 are in good agreement with the values predicted by scaling theory.

Thus, the measurements of the molar volumes $V_m(P_C, T_C, x)$ at the critical isotherm−isobar (T_C = 674.05 K and P_C = 22.05 MPa) in the wide concentration ranges (from 0 to 1) have been correlated as a function of the concentration x by scaling equation

$$V_m(x) = V_0 e^{-x} \sum_{i=1}^{N} \frac{x^{i-\gamma/\beta\delta}}{(i-\gamma/\beta\delta)} + (1-x) V_{mc}(P_c, T_c) + x V_{12} \quad (8)$$

where N = 3, $V_{mc}(P_c, T_c)$ = 59.223 cm³·mol⁻¹ is the critical volume of pure water, V_0 and V_{12} are nonuniversal adjustable parameters. From our experimental $PVTx$ data, we have deduced values for V_0 and V_{12} at the critical isotherm−isobar. Our results are V_0 = 26.5097 cm³·mol⁻¹ and V_{12} = 193.643 cm³·mol⁻¹. From eq 8 for derivative $(\partial V_m/\partial x)_{PT}$ we obtain
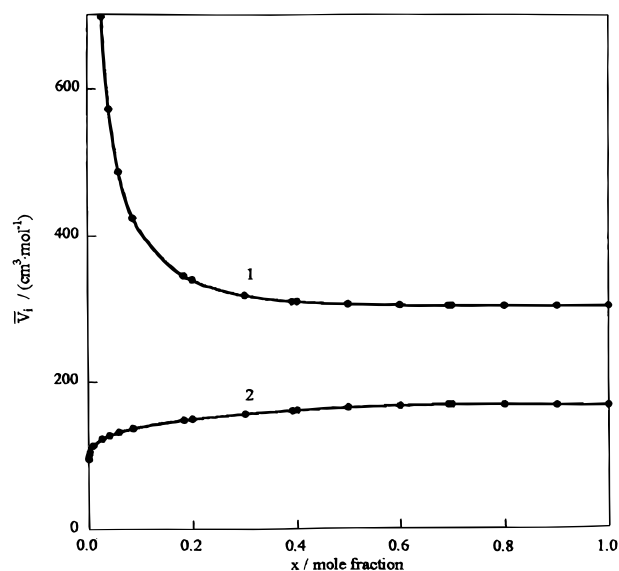

Figure 4. Partial critical isothermal−isobaric molar volumes $\bar{V}_1$ (curve 2) and $\bar{V}_2$ (curve 1) as a function of composition for water + pentane mixture.
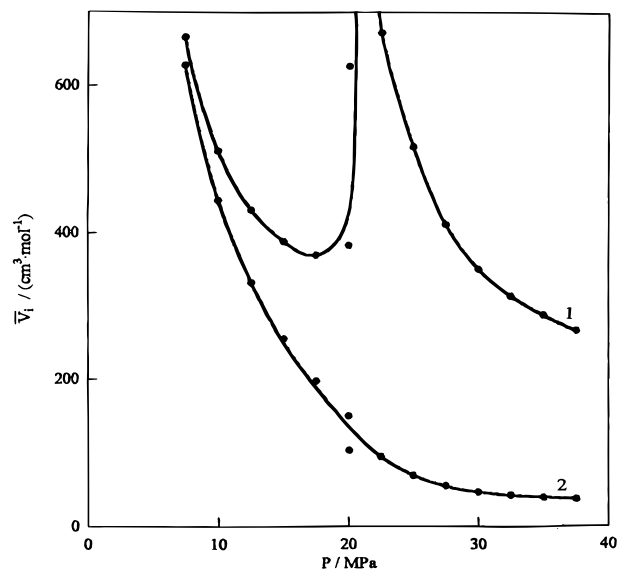

Figure 5. Partial molar volumes $\bar{V}_1$ (curve 2) and $\bar{V}_2$ (curve 1) at critical isotherm−isobar as a function of pressure for water + pentane mixture.

$$\left(\frac{\partial V_m}{\partial x}\right)_{PT} = -V_0 e^{-x} \sum_{i=1}^{N} \frac{x^{i-\gamma/\beta\delta}}{(i-\gamma/\beta\delta)} + V_0 e^{-x} \sum_{i=1}^{N} x^{i-\gamma/\beta\delta} - V_{mc} + V_{12} \quad (9)$$

which, with eq 6, yields the partial molar volumes $\bar{V}_1$ and $\bar{V}_2$. On the critical isotherm−isobar in the limit $x \to 0$, $(\partial V_m/\partial x)_{PT}$ diverges as $x^{-\gamma/\beta\delta}$. Consequently, $\bar{V}_2$ behaves as $x^{-\gamma/\beta\delta}$, which in good agreement with the nonclassical limiting behavior (Chang et al., 1984; Chang and Levelt Sengers, 1986; Levelt Sengers, 1991a,b; Harvey and Levelt Sengers, 1991).

In Figure 4 and Table 4, the partial molar volume for pentane $\bar{V}_2$ and water $\bar{V}_1$, derived from (eqs 6 and 9) using our experimental molar volumes, is shown as a function of concentration at the critical isotherm−isobar. The pressure dependences of the $\bar{V}_i$ (i = 1, 2) near the critical point of water are given in Figure 5.

The low densities and low pressures experimental values of $PVTx$ has been used for determining second and third

Table 4. Partial Molar Volumes of Water and Pentane Derived from *PVTx* Measurements

x/mole fraction	*P*/MPa						
	20.0	22.05	25.0	27.5	30.0	32.5	35.0
	$\overline{V}_1$/cm³·mol⁻¹						
0.0005	141.358	76.033	49.503	42.256	38.310	35.987	34.338
0.001	142.303	79.201	51.770	43.681	39.301	36.749	34.948
0.002	143.397	82.869	54.396	45.331	40.449	37.631	35.654
0.003	144.116	85.279	56.121	46.415	41.203	38.210	36.118
0.010	146.660	93.808	62.226	50.251	43.872	40.262	37.761
0.028	149.473	103.237	68.976	54.492	46.822	42.529	39.577
0.042	150.741	107.489	72.020	56.404	48.153	43.552	40.396
0.061	152.040	111.845	75.137	58.363	49.516	44.600	41.235
0.088	153.459	116.601	78.542	60.502	51.004	45.743	42.151
0.184	156.690	127.433	86.295	65.374	54.393	48.349	44.237
0.200	157.084	128.752	87.240	65.968	54.806	48.666	44.491
0.300	159.038	135.305	91.930	68.915	56.856	50.242	45.753
0.391	160.273	139.443	94.893	70.776	58.151	51.237	46.550
0.400	160.377	139.793	95.143	70.933	58.261	51.321	46.618
0.500	161.292	142.859	97.338	72.312	59.220	52.059	47.208
0.600	161.881	144.834	98.752	73.201	59.838	52.534	47.589
0.694	162.194	145.885	99.504	73.673	60.167	52.786	47.791
0.700	162.208	145.930	99.536	73.694	60.181	52.797	47.800
0.800	162.317	146.298	99.800	73.859	60.296	52.886	47.871
0.900	162.245	146.057	99.627	73.750	60.220	52.828	47.824
1.000	162.020	145.303	99.087	73.411	59.984	52.646	47.679

x/mole fraction	*P*/MPa						
	20.0	22.05	25.0	27.5	30.0	32.5	35.0
	$\overline{V}_2$/cm³·mol⁻¹						
0.0005	3456.601	10928.26	7891.661	5045.528	3574.755	2792.176	2272.201
0.001	2105.590	6399.138	4649.623	3008.478	2157.575	1702.903	1399.887
0.002	1324.067	3779.170	2774.195	1830.102	1337.775	1072.789	895.278
0.003	1030.184	2793.960	2068.961	1386.987	1029.499	835.842	705.525
0.010	552.198	1191.561	921.931	666.280	528.101	450.458	396.902
0.028	383.549	626.184	517.222	411.992	351.192	314.482	288.009
0.042	347.876	506.596	431.618	358.205	313.773	285.721	264.976
0.061	323.404	424.555	372.892	321.306	288.102	265.990	249.175
0.088	305.380	364.132	329.640	294.129	269.195	251.458	237.538
0.184	282.893	288.747	275.677	260.223	245.607	233.327	223.019
0.200	281.234	283.186	271.697	257.722	243.867	231.990	221.947
0.300	275.158	262.816	257.115	248.560	237.493	227.090	218.024
0.391	272.771	254.812	251.386	244.961	234.989	225.166	216.483
0.400	272.611	254.277	251.003	244.720	234.821	225.037	216.380
0.500	271.469	250.451	248.264	242.999	233.624	224.117	215.643
0.600	270.976	248.798	247.081	242.256	233.107	223.719	215.324
0.694	270.801	248.208	246.659	241.990	232.922	223.577	215.211
0.700	270.795	248.189	246.645	241.982	232.916	223.573	215.207
0.800	270.755	248.055	246.549	241.922	232.874	223.540	215.181
0.900	270.766	248.092	246.575	241.938	232.886	223.549	215.188
1.000	270.777	248.128	246.601	241.954	232.897	223.558	215.195

virial coefficients for water + pentane mixtures and their pure components. The truncated virial equation of state

$$\frac{Z-1}{\rho_\mathrm{m}} = B_\mathrm{m}(T, x) + C_\mathrm{m}(T, x)\rho_\mathrm{m} \qquad (10)$$

where $Z = PV_\mathrm{m}/RT$ is the compressibility factor, was fitted to these experimental $[(Z-1)/\rho_\mathrm{m}]_\mathrm{exptl}$ data for each isopleth for constant temperature $T = 647.05$ K. The values of virial coefficients B_m and C_m found from the analyses of the $(Z-1)/\rho_\mathrm{m}$ data for each mixture concentrations are given in Table 5. From the values of the second B_m and third C_m virial coefficients of the mixtures and the known composition of the mixture x, the one interaction second virial coefficient B_{12} and two interaction third virial coefficients C_{112} and C_{221} were obtained from the equations

$$B_\mathrm{m} = x^2 B_{11} + 2x(1-x)B_{12} + (1-x)B_{22} \qquad (11)$$

$$C_\mathrm{m} = x^3 C_{111} + 3x^2(1-x)C_{112} + 3x(1-x)^2 C_{122} + (1-x)^3 C_{222} \qquad (12)$$

Table 5. Second B_m and Third C_m Virial Coefficients of Water + Pentane Mixtures and Their Pure Components at Temperature $T = 647.05$ K for Various Compositions

x/mole fraction	B_m/(cm³·mol⁻¹)	C_m/(cm⁶·mol⁻²)
0.000	−84.4984	2269.478
0.028	−84.3146	2444.030
0.042	−80.9817	2400.784
0.061	−81.8879	2765.142
0.088	−72.8351	1789.969
0.184	−71.4995	2909.051
0.391	−75.1568	6059.477
0.694	−92.1707	14535.56
1.000	−185.997	34839.91

where B_{11}, B_{22}, C_{111}, C_{222} are the second and third virial coefficients of the pure components. The results for interaction second and third virial coefficients values are

B_{12}/(cm³·mol⁻¹)	C_{112}/(cm⁶·mol⁻²)	C_{122}/(cm⁶·mol⁻²)
−16.8596	5616.6804	3171.5148

Figure 6 shows the temperature dependence of pure and interaction second virial coefficients for water + pentane
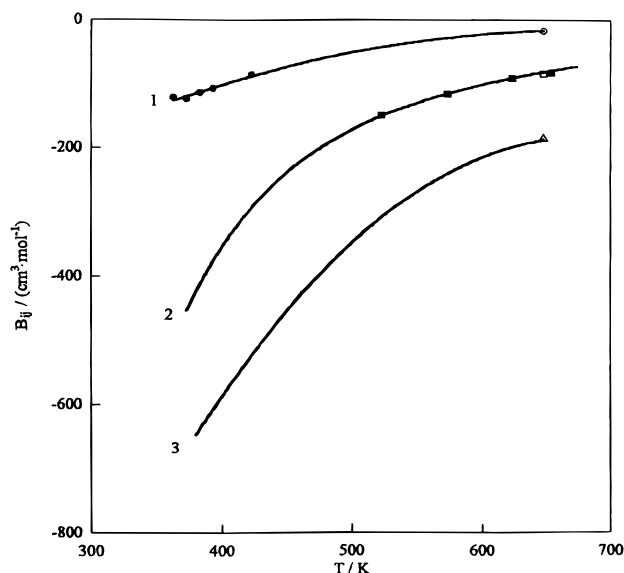
Figure 6. Second virial coefficients of the pure water and pentane together with cross-term second virial coefficients as a function of temperature derived from the *PVTx* data: 1, Cross-term second virial coefficients (○, this work from *PVTx* measurements; ●, Wormald and Lancaster, (1988) from excess enthalpies measurements); 2, recommended values of second virial coefficients for pure water (Eubank et al., 1988); ■, our earlier experimental result (Abdulagatov et al., 1996); □, this work); 3, recommended values of second virial coefficients for pure pentane (Dymond and Smith, 1980); △, this work.

mixtures together with earlier literature results. As can see from Figure 6, B_{12} values obtained from this work by volumetric (*PVTx*) measurements are in good agreement with B_{12} derived from calorimetric (excess enthalpies) measurements.

5. Conclusion

The *PVTx* properties in the near-critical range for the binary mixtures of water and pentane have been measured using the cylindrical constant-volume piezometer immersed in an air thermostat. The measurements cover the pressure range from 4 MPa to 41 MPa and at the temperature $T = 647.05$ K. From six to nine *PVT* properties have been obtained at each of the compositions 0.0 (pure water), 0.028, 0.042, 0.061, 0.088, 0.184, 0.391, 0.694, and 1.0 (pure pentane) of mole fraction of pentane. The accuracy of the present results was estimated as molar density, ±0.5%; pressure, ±0.15%; temperature, ±10 mK; concentration, ±0.002 mole fraction. Using our experimental results, the excess, partial, and apparent molar volumes were determined. The anomalous critical behavior of the partial molar volume of pentane near the critical point of pure water (solvent) was found.

By using experimental *PVTx* data, the values of second $B_m(T, x)$ and third $C_m(T, x)$ pure and mixtures virial coefficients at the temperature $T_C = 647.05$ K for seven compositions has been determined.

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