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PVTx Measurements for Water + Toluene Mixtures in the Near-Critical and Supercritical Regions

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The *PVTx* relationships of dilute $(1 - x)$ water + x toluene mixtures were measured in the near-critical and supercritical regions, with a constant-volume piezometer immersed in a precision thermostat. The ITS-90 temperature was measured with a 10 Ω platinum resistance thermometer (PRT-10) with an uncertainty of 10 mK. Pressure was measured by means of a dead-weight gauge with an uncertainty of 1.5−2.0 kPa. Uncertainties of the density measurements are estimated to be 0.05−0.15%, depending on the experimental pressure and temperature. The uncertainty in composition measurement is 0.001 mole fraction. Measurements were made on near-critical and supercritical isotherms between 623 and 673 K at pressures from 11 to 46 MPa and densities between 54 and 579 $kg\cdot m^{-3}$ for three composition mole fractions of toluene (0.0008, 0.0022, and 0.0085). The measured *PVTx* data for $(1 - x)$ water + x toluene mixtures were compared with values calculated from a recently developed crossover equation of state and published measurements. The *PVTx* measurements were used to derive values of the Krichevskii parameter, excess volumes, and apparent molar volumes. The method of isochoric break points was used to extract the phase transition temperatures and pressures for each measured isochore. The critical anomalies of the supercritical $(1 - x)$ water + x toluene mixtures and the behavior of the Krichevskii function near the solvent's (water) critical point are discussed.

Introduction

Supercritical water (SCW; i.e., water at temperatures and pressures above its critical point, $T_C = 647.096$ K; $P_C = 22.064$ MPa) has continued to be a subject of intense scientific interest. This is due to its crucial role in a variety of natural processes and promising technological applications, including SCW oxidation destruction of hazardous waste such as toxic waste, chemical weapons, and nuclear processing waste. The advantages of SCW oxidation arise primarily from the unusual properties exhibited by water under supercritical conditions. The ionic product of SCW is many orders of magnitude smaller than that of ordinary liquid, and the dielectric constant drops to values (~2 at 25 MPa and 723 K) typical of organic solvents. Earlier work[1−4] has shown that organics are highly miscible with water above the critical temperature of pure water. Between 533 and 573 K benzene solubility[4] increases from a few percent to complete miscibility. An obstacle to the development of industrial-scale SCW technologies is the lack of reliable thermodynamic data of supercritical aqueous systems.

At this time, only limited experimental data for $(1 - x)$ water + x toluene mixtures in the near-critical and supercritical regions are available. Degrange[5] reported *PVTx* properties and enthalpies for dilute mixtures of $(1 - x)$ water + x toluene in a temperature range from room temperature to 685 K and at pressures between 10 and 33 MPa for compositions between 0.0012 and 0.0366 mol fraction of toluene. Degrange[5] measured differences between the density of toluene and water using a vibrating U-tube densimeter. The results were represented by a correlation of the form $\Delta\rho = (\rho_{sol} - \rho_w) = Am + Bm^2 + Cm^3$ (where m is concentration in $mol\cdot kg^{-1}$) for fixed temperatures and pressures. Uncertainty in temperature measurement was better than ±0.05 K. However, due to a small gradient between the vibrating tube and the resistance thermometer, the uncertainty in temperature measurements at high temperatures (600 K) is ±0.2 K. The pressure in the system was measured with an uncertainty of 0.3 MPa. The reproducibility of density measurements is ~0.05 $kg\cdot m^{-3}$ at temperatures below 450 K and ~0.14 $kg\cdot m^{-3}$ above 550 K.

In previous work,[6] we reported *PVTx* measurements near the water critical point for one dilute $(1 - x)$ water + x toluene mixture ($x = 0.0278$ toluene) in a temperature range from 623 to 673 K and at pressures up to 39 MPa. We also reported a crossover model for $(1 - x)$ water + x toluene mixtures near the solvent's (water) critical point based on our measured *PVTx* data and the data reported by Degrange.[5] We expect the present *PVTx* measurements to be useful to improve and recalculate the parameters of the crossover model.

Phase equilibrium for this system has been reported previously. Chandler et al.[7] measured three-phase vapor−liquid−liquid (VLL) equilibria in $(1 - x)$ water + x toluene mixtures at temperatures from 473 to 548 K and at pressures up to 17.2 MPa. Anderson and Prausnitz[3] reported mutual solubilities and vapor pressure for binary aqueous systems containing toluene in the temperature

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range from 373 to 473 K and at pressures up to 2.4 MPa. The results of Anderson and Prausnitz[3] at 473 K were shown to be in good agreement with the measurements of Chandler et al.[7] Roof[2] reported pressure and temperature of the three-phase (VLL) critical point from visual observations for binary systems of water and toluene. Roof[2] made measurements in both rising- and falling-temperature runs. The differences between those runs were observed to be about 1 K and 0.014 MPa. The different fillings of the capillary gave values of temperature agreeing within 1 K and of pressure within 0.015−0.2 MPa. The three-phase endpoint reported by Roof[2] is 558.2 K and 10.1 MPa. Connolly[1] reported solubility for (1 − *x*) water + *x* toluene mixtures up to their critical solution temperatures and at pressures from 10 to 80 MPa. Sharp maxima were observed in the solubility isotherms (solubility versus pressure curve) near the critical solution temperatures at pressures of ~30 MPa. The total uncertainty in the temperature measurements was ±0.02 K. The pressure was controlled to 0.05 MPa and was measured with an uncertainty of ~±0.2 MPa. The reported critical solution temperature was either the minimum temperature for mixing of two liquids (water and toluene) in all proportions or the maximum temperature of the binary system for two liquid phases in equilibrium. The uncertainty in the critical solution temperature was ~±2 K, and that of the corresponding pressure is ~±0.1 MPa. The measured values of *PTx* on the phase equilibrium curve were compared with data reported by Roof.[2] The agreement was good at a temperature of 553.2 K, whereas at 573.2 K the data revealed slight deviations. Chen and Wagner[8] measured the mutual solubility and three-phase vapor pressure for (1 − *x*) water + *x* toluene mixtures in a temperature range from 303 to 373 K and at pressures up to 0.35 MPa. Alwani[9] and Alwani and Schneider[10] measured the phase equilibria LL and LV for binary aqueous solutions of toluene over a temperature range from 533 to 639 K and up to a maximum pressure of 200 MPa. From these measurements, a part of the P_C-T_C critical locus has been deduced. Haruki et al.[11,12] reported phase equilibria for (1 − *x*) water + *x* toluene binary mixtures at temperatures between 553 and 573 K. Haruki et al.[11,12] used a modified Soave−Redlich−Kwong (MSRK) equation of state with an exponent-type mixing rule for the energy parameter and a conventional mixing rule for the size parameter to correlate the phase equilibria for four binary mixtures of (1 − *x*) water + *x* toluene. Optimal values of interaction parameters for (1 − *x*) water + *x* toluene at two temperatures were determined by Haruki et al.[11,12] by using measured VLE and LLE data.

The phase behavior of a (1 − *x*) water + *x* toluene system is classified as type III. Figure 1 shows a *P*−*T* phase diagram for the (1 − *x*) water + *x* toluene mixture. Figure 1 includes all of the available experimental data on the three-phase (LLV) curve, the L−G critical curves, UCEP coordinates, vapor pressure curves for pure components, and phase equilibria (*P*−*T*) curves for some selected compositions reported by Alwani[9] and Connolly.[1]

Majer et al.[13] reported the partial molar volumes at infinite dilution for (1 − *x*) water + *x* toluene mixtures at temperatures up to 623 K and at pressures to 30 MPa. These authors tested the following three types of correlations: the model of Helgesen−Kirkhan−Flowers using dielectric properties of water; semiempirical equations using the compressibility of water; and equations based on fluctuation solution theory. The partial molar volumes at infinite dilution (1 − *x*) water + *x* toluene were obtained by extrapolation of the apparent molar volumes correlated as a function of concentration. The uncertainty of derived values of partial molar volumes was 3−6 cm^3·mol^{-1} at temperature >573 K.

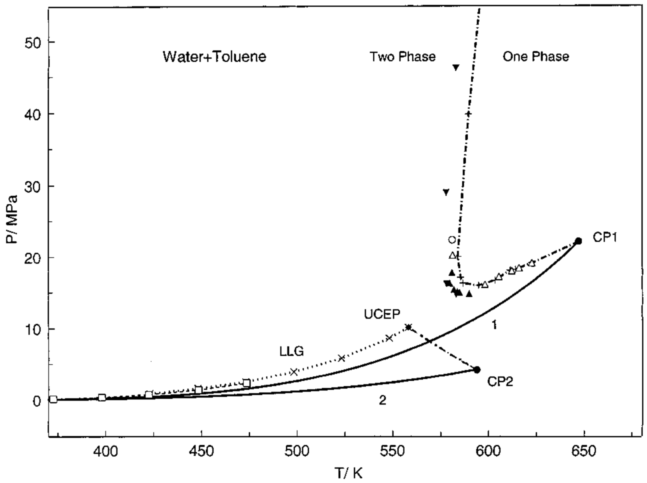

Figure 1. Pressure−temperature (*P*−*T*) phase diagram for (1 − *x*)water + *x* toluene mixture: CP1, critical point of pure water; CP2, critical point of pure toluene; 1, vapor pressure curve of pure water (IAPWS-95[18]); 2, vapor pressure curve of pure toluene (Lemmon and Jacobsen[21]); ○, LG critical point (Connolly[1]); ×, LLG (Chandler et al.[7]); · − ·, LG critical curve (Alwani[9]); □, LLG (Anderson and Prausnitz[3]); ▼, *x* = 18 wt % toluene (Connolly[1]); +, LG critical points (Alwani and Schneider[10]); △, *x* = 30 wt % toluene (Alwani[9]); ▲, *x* = 50 wt % (Alwani[9]); ◆, LG critical points (Roof[2]).

Experimental Section

Apparatus and Procedures. The *PVTx* properties for (1 − *x*) water + *x* toluene mixtures were measured by using a constant-volume method with direct mass measurements of the sample. The apparatus details were described in our previous work.[14] The method of measurements, experimental procedures, and construction of the piezometer have been discussed in detail in previous publications.[15−17] The apparatus for *PVTx* measurements consisted chiefly of an air thermostat, a piezometer, lines for filling and extracting samples, temperature control and temperature measuring devices, and pressure measuring instruments. The temperature inside the thermostat was maintained uniform within 5 mK with the aid of guard heaters located between the thermostat walls and a regulating heater, which was mounted inside the thermostat. The fluid temperature (ITS-90) was detected by a platinum resistance thermometer (PRT-10) with a precision of 10 mK. The pressure in the piezometer (±2 kPa precision) was transmitted to a liquid-octane system through a diaphragm-type null indicator, which was mounted on the end of the piezometer. The mixture in the piezometer was heated in the thermostat until its temperature reached the prescribed value and pressure reached a maximum value of ~50 MPa. After thermal equilibration, the *PVTx* measurements along an isotherm were made, starting from a maximum pressure of ~50 MPa. Measurements were continued by extracting a small amount of sample from the piezometer through a needle valve. The extracted samples were collected in a separate collector and weighed using a high-precision balance with an uncertainty of 0.05 mg. Thus, a number of data points were taken along each isotherm until the system pressure dropped to ~10 MPa. The density of a

Table 1. Experimental *PVTx* Data for $(1 - x)$ Water + x Toluene Mixtures

	P/MPa at T/K of									
ρ/kg·m^{-3}	623.15	628.15	633.15	638.15	643.15	647.10	648.15	653.15	663.15	673.15
					$x = 0.0085$					
555.32						30.25	30.85	33.97	39.74	46.04
482.37						24.31	24.75	26.98	31.55	36.28
372.03						22.57	22.85	24.36	27.46	30.72
290.44						22.37	22.64	23.83	26.21	28.77
186.49						21.60	21.76	22.56	24.15	25.75
104.36						17.92	17.97	18.42	19.30	20.17
54.790						11.38	11.45	11.83	12.58	13.32
					$x = 0.0022$					
578.85	18.04	21.01	24.08	27.51	31.47	35.15	36.33	42.01		
565.61	17.40	19.92	22.55	25.37	28.67	31.41	32.15	35.77		
515.12	16.84	18.47	20.12	22.00	24.10	25.75	26.25	28.84		
438.16	16.79	17.89	19.07	20.30	21.71	22.79	23.18	25.20		
278.13	16.54	17.66	18.79	19.97	21.16	22.10	22.41	23.65		
161.19	16.39	17.45	18.50	19.46	20.37	20.95	21.17	21.95		
65.710	12.71	12.95	13.16	13.40	13.67	13.83	13.99	14.33		
					$x = 0.0008$					
546.35						28.25	28.98	32.10	37.17	43.33
498.42						24.67	25.11	27.58	32.00	37.21
422.84						22.48	22.83	24.66	28.40	32.33
192.54						21.52	21.75	22.85	24.65	26.32
135.71						20.04	20.25	20.87	21.92	22.98
108.31						18.35	18.40	18.97	19.88	20.74
66.480						14.08	14.20	14.57	14.97	15.67

sample at a given temperature T and pressure P is determined from the simple relationship

$$\rho_i = M_i/V_{TP}, \quad M_i = m_{\text{tot}} - m_{\text{coll}}, \quad m_{\text{tot}} = m_1 + m_2 + m_3 + \dots m_N, \tag{1}$$

where V_{TP} is the temperature- and pressure-dependent volume of the piezometer, M_i is the mass of the mixture in the piezometer, m_{coll} is the mass of sample extracted from the piezometer and stored in the collector during the runs, m_{tot} is the total mass or initial mass of the sample in the piezometer, and N is the number of extractions. After the last extraction, the total mass, m_{tot}, of the mixture in the piezometer was calculated. The mass of toluene, m_{tol}, was determined from the difference between the total mass, m_{tot}, of the mixture extracted from the piezometer during the run and the known initial mass m_{w} of pure water in the piezometer, $m_{\text{tol}} = m_{\text{tot}} - m_{\text{w}}$. The toluene composition of the mixture was calculated from $w = 1 - m_{\text{w}}/m_{\text{tot}}$. The uncertainty of the mass m of the sample can be estimated from those of m_{tot} and m_{coll} to be 0.01%. The experimental uncertainty in the composition is estimated to be <0.001 mole fraction. The volume of the piezometer was previously calibrated from the known density of a standard fluid (pure water) with well-known PVT values (IAPWS-95 formulation[18,19]) at a temperature of $T_0 = 673.15$ K and a pressure of $P_0 = 40.32$ MPa. The volume at these conditions was $V_{P_0T_0} = (32.68 \pm 0.01)$ cm^3. Variations of the volume with temperature T and pressure P were calculated with the equation

$$V_{TP} = V_{T_0P_0}[1 + 3\alpha(T - T_0) + \beta(P - P_0)] \tag{2}$$

where $\alpha = 1.3 \times 10^{-5}$ K^{-1} is the thermal expansion coefficient of alloy (EI-437BU-VD), which is virtually temperature-independent in a broad temperature range from 500 to 700 K, and $\beta = 4.12 \times 10^{-5}$ MPa^{-1} is the pressure expansion coefficient of the piezometer. The maximum uncertainty in volume of the piezometer δV_{TP} at a given temperature T and pressure P is related to the measured uncertainties of $V_{T_0P_0}$, α, and β, which were $\delta V_{T_0P_0} = 0.03\%$, $\delta\alpha = 0.0012\%$, and $\delta\beta = 0.0005\%$, respectively. In the worst case the value of δV_{TP} is ~0.032%. The total experimental uncertainty in density was estimated to range from 0.05 to 0.15%, depending on the temperature T and pressure P.

A high-purity (HPLC grade, 99.8 mol %) toluene sample was used in this study. The water was twice distilled and degassed and had an electric conductivity of $\sim 10^{-4}\ \Omega^{1-}\cdot\text{m}^{-1}$.

Results and Discussion

***PVTx* Measurements.** Measurements of the $PVTx$ relationship of the $(1 - x)$ water + x toluene mixtures were performed along five to eight near-critical and supercritical isotherms between 623 and 673 K for each mole fraction (0.0008, 0.0022, and 0.0085) of toluene. The density ranged from 54 to 579 kg·m^{-3}, and the pressure ranged from 11 to 46 MPa. The experimental temperatures, densities, pressures, and compositions for near-critical and supercritical mixtures are presented in Table 1. Measured results for selected near-critical and supercritical isotherms are also shown in Figures 2−4. Figure 2 shows the dependence of density on pressure along near-critical and supercritical isotherms for various compositions together with values calculated from the crossover equation of state by Kiselev et al.,[6] known as CREOS. As one can see from Figure 2, the agreement between the present experimental data and values calculated from CREOS[6] is good in the density range from 95 to 500 kg·m^{-3}. At densities >500 kg·m^{-3} the calculated values of pressure are systematically higher than measured values, but this density range is outside the range of validity of CREOS.[6] Figure 3 shows projections at constant composition (isopleths) in the $Z-P$ planes, where $Z = PV_{\text{m}}/RT$ is the compressibility factor at the critical temperature (647.10 K) of pure water. Figure 3 also contains the results for pure water calculated from the CREOS model by Kiselev and Friend.[20] To check the reproducibility, the measurements at three selected isotherms (623.15, 647.1, and 673.15 K) were repeated. The differences between these measurements are within the experimental uncertainties (0.14, 0.33, and 0.12% in density). Figure 4 demonstrates the temperature dependence of pressure of the mixtures along various isochores and

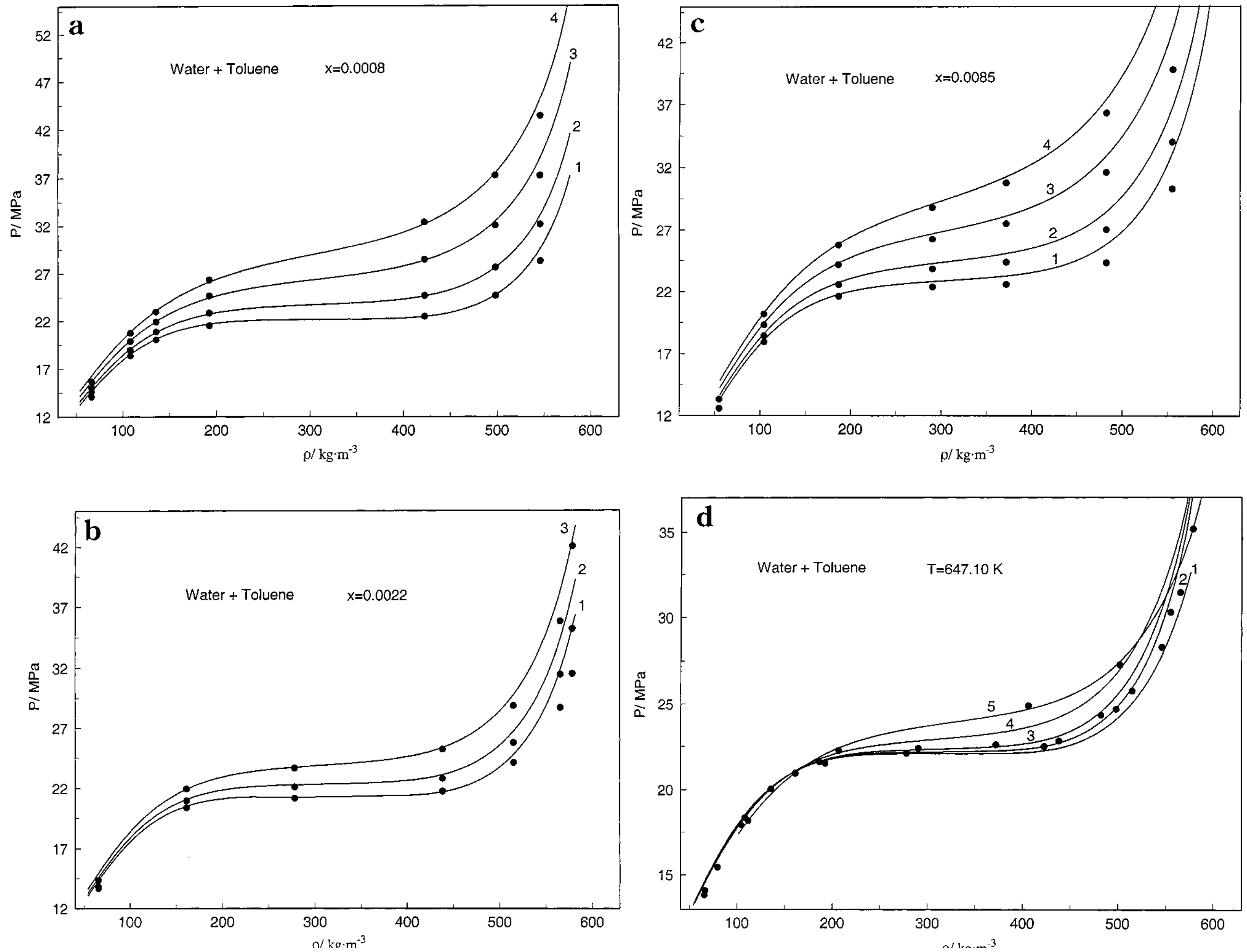

Figure 2. Pressure P of $(1 - x)$water + x toluene mixture as a function of density ρ along near-critical and supercritical isotherms for various compositions together with values calculated from the crossover model (Kiselev et al.[6]): (a) 1, 647.10 K; 2, 653.15 K; 3, 663.15 K; 4, 673.15 K; (b) 1, 643.15 K; 2, 647.10 K; 3, 653.15 K; (c) 1, 647.10 K; 2, 653.15 K; 3, 663.15 K; 4, 673.15 K; (d) 1, $x = 0$ (pure water); 2, $x = 0.0008$; 3, $x = 0.0022$; 4, $x = 0.0085$; 5, $x = 0.0287$; ●, this work; —, CREOS (Kiselev et al.[6]).

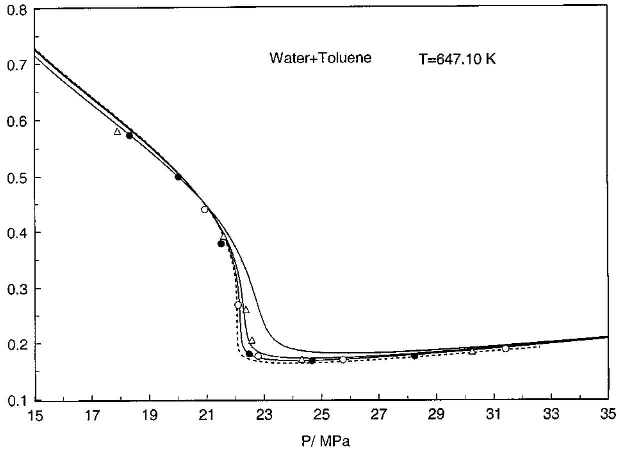

Figure 3. Compressibility factor $Z = PV/RT$ of $(1 - x)$water + x toluene mixture as a function of pressure P along the critical isotherm for various compositions together with values of Z for pure water from CREOS (Kiselev and Friend[20]): △, $x = 0.0085$; ○, $x = 0.0022$; ●, $x = 0.0008$; —, CREOS (Kiselev et al.[6]); – – –, Kiselev and Friend.[20]

compositions. For each of these measured isochores, a break point (liquid−vapor phase transition points) was observed. The values of temperature T_S, pressure P_S, and density ρ_S at the break points for two composition (0.0022 and 0.0287) mole fractions are given in Table 2 and shown in Figure 4. A comparison of the experimental isothermal and isobaric data for $(1 - x)$ water + x toluene mixtures measured in the present work with values reported by Degrange[5] are plotted in Figure 5. The agreement of density between the present and Degrange[5] measurements is good (<0.35%).

To check and confirm the accuracy of the method, *PVT* measurements were made on the pure components (water and toluene) along the near-critical and supercritical isotherms. The measured values of density and pressure along selected isotherms for pure water and pure toluene are shown in Figures 6 and 7 together with values calculated from the equations of state (IAPWS-95 formulation[18] for water and Lemmon and Jacobsen[21] EOS for toluene) and previously reported high-accuracy experimental *PVT* data for pure water[22−25] and pure toluene.[26−29] For this work, deviation statistics for the measured densities are as follows: (for water) AAD = 0.44%, bias = 0.16%, SD = 0.46%, SE = 0.12%, and maximum deviation = 0.7%; (for toluene) AAD = 0.65%, bias = 0.64%, SD = 0.59%, SE = 0.06%, and maximum deviation = 2.18%. One can see from Figures 6 and 7 that the present data show good agreement with published data.

Molar Volumes. Figure 8 shows the experimental values of molar volumes V_m of $(1 - x)$ water + x toluene mixtures as a function of composition at the critical tem-

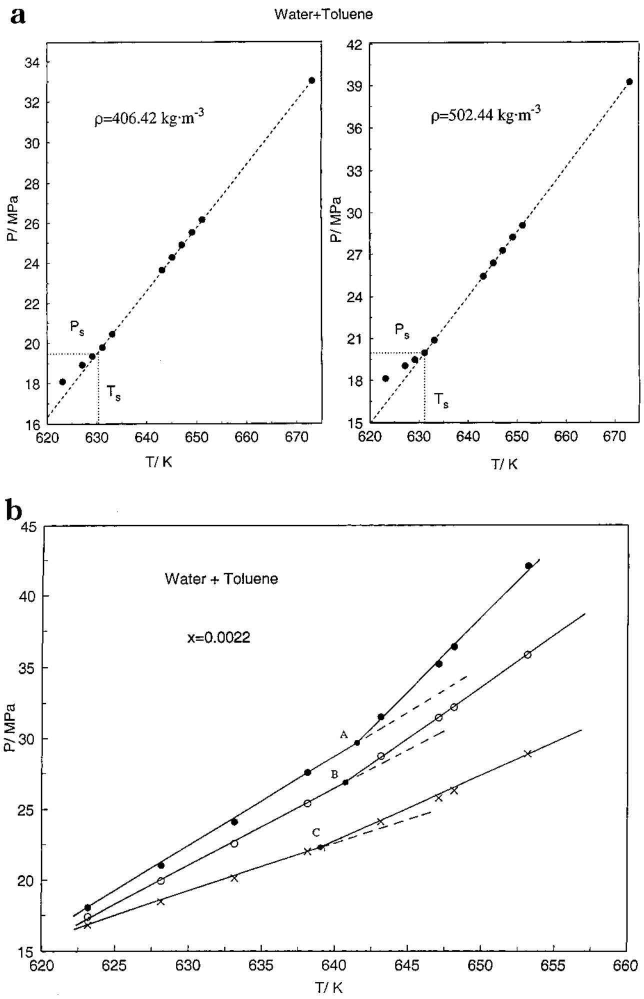

Figure 4. Break points of the pressure−temperature ($P-T$) experimental isochores for $(1-x)$water + x toluene mixtures for various compositions: (a) $x = 0.0287$, $\rho_S = 406.42$ kg·m^{-3}, $T_S = 630.35$ K, $P_S = 19.48$ MPa; $x = 0.0287$, $\rho_S = 502.44$ kg·m^{-3}, $T_S = 631.15$ K, $P_S = 19.97$ MPa); (b) ○, 578.85 kg·m^{-3}; ●, 565.61 kg·m^{-3}; ×, 515.12 kg·m^{-3}; A ($T_S = 641.33$ K, $P_S = 28.85$ MPa); B ($T_S = 639.00$ K, $P_S = 25.67$ MPa); C ($T_S = 638.17$ K, $P_S = 21.83$ MPa).

Table 2. Pressures (P_S), Temperatures (T_S), and Densities (ρ_S) on the Liquid−Gas Two-Phase Boundary from Measured *PVTx* Data for $(1-x)$ Water + x Toluene Mixtures

x	T_S/K	P_S/MPa	ρ_S/kg·m^{-3}
0.0022	638.17	21.83	515.12
0.0022	639.00	25.67	565.61
0.0022	641.33	28.85	578.85
0.0287	630.35	19.48	406.42
0.0287	631.15	19.97	502.44

perature and critical pressure of pure water. As this figure shows, the tangent of the V_m-x curve becomes very steep as $x \rightarrow 0$, and thus values of the derivative $(\partial V_m/\partial x)^{\infty}_{PT}$ dominate the calculation of partial molar volume $\bar{V}_2^{\infty}$. Because the partial molar volume $\bar{V}_2^{\infty}$ of solute (toluene) is obtained from the tangent $(\partial V_m/\partial x)^{\infty}_{PT}$ (refs 30−35), the partial molar volume of an infinitely dilute $(1-x)$ water + x toluene mixture near the critical point of pure water tends to plus infinity ($\bar{V}_2^{\infty} \rightarrow +\infty$). For other relatively nonvolatile solutes, the partial molar volume has been observed to tend to minus infinity ($\bar{V}_2^{\infty} \rightarrow -\infty$).[36] The mechanism that induces these infinite values has been explained in previous work.[30−35,37,38] Some physical models have been proposed to describe the behavior.[37,38] This

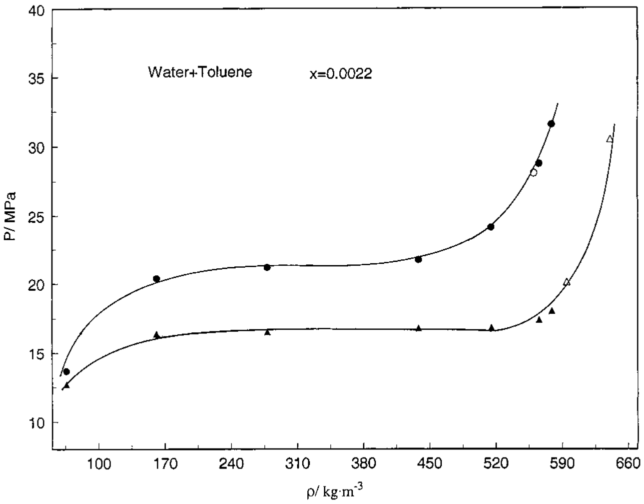

Figure 5. Comparison of measured values of *PVTx* for $(1-x)$ water + x toluene mixtures with the data reported by Degrange[5] along the two near-critical isotherms: ●, 643.15 K (this work); ▲, 623.15 K (this work); ○, 643.15 K (Degrange[5]); △, (Degrange[5]). The solid curves are guides for the eye.

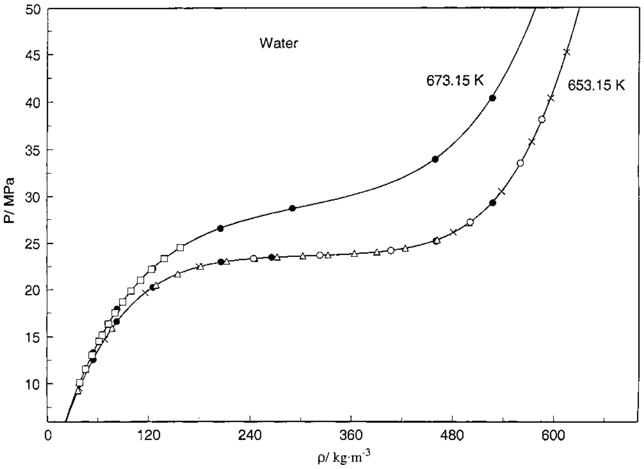

Figure 6. Comparison of measured *PVT* data for pure water with values calculated from IAPWS-95 formulation:[18] ○, Hanafusa et al.;[22] △, Rivkin and Troyanovskaya;[25] ●, this work; ×, Alexandrov et al.;[23] □, Kell et al.;[24] —, IAPWS-95 formulation.[18]

anomaly is a result of the divergence of the isothermal compressibility K_T of the solvent and is common to all dilute near-critical mixtures.[30−35] From the expansion of the Helmholtz free energy,[32,35,37,39] $A(V,T,x)$, around the solvent's critical point, we can also calculate values of the derivative $(\partial V_m/\partial x)^{\infty}_{PT} = -A_{VX}/A_{VV}$, where A_{VV}^{-1} at $x \rightarrow 0$ is K_T of the pure solvent (water), which diverges strongly at its own critical point. Therefore, $(\partial V_m/\partial x)^{\infty}_{PT}$ becomes proportional to A_{VV}^{-1} or K_T and $(\partial V_m/\partial x)^{\infty}_{PT}$, and $\bar{V}_2^{\infty}$ diverge strongly at the solvent's critical point. According to the classical model, both $(\partial V_m/\partial x)^{\infty}_{PT}$ and $\bar{V}_2^{\infty}$ diverge as $x^{-2/3}$ (refs 30−35, 37, and 38). However, real fluids behave nonclassically. Therefore, the asymptotic behavior of the mixture molar volume V_m at T_C and P_C in the limit $x \rightarrow 0$ can be expressed by the simple power law

$$V_m(P_C,T_C,x) = V_0 x^{-\epsilon} \qquad (3)$$

where $\epsilon = 1 - \gamma/\beta\delta$, γ, β, amd δ are the universal critical exponents (refs 40−42). For the classical case $\gamma = 1$, $\beta = 0.5$, $\delta = 3$, and $\epsilon = 0.3333$, and for the nonclassical case $\gamma = 1.24$, $\beta = 0.325$, $\delta = 4.83$, and $\epsilon = 0.21$. Figure 9

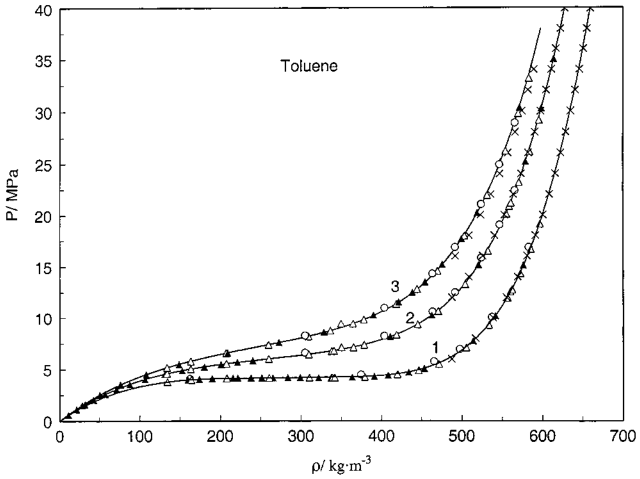

Figure 7. Comparison of measured *PVT* data for pure toluene with values calculated from the Lemmon and Jacobsen[21] EOS: ○, this work; ▲, Akhundov and Abdullaev;[27] △, Straty et al.;[26] ●, Mamedov et al.;[51] ×, Mamedov and Akhundov;[52] —, Lemmon and Jacobsen[21] EOS.

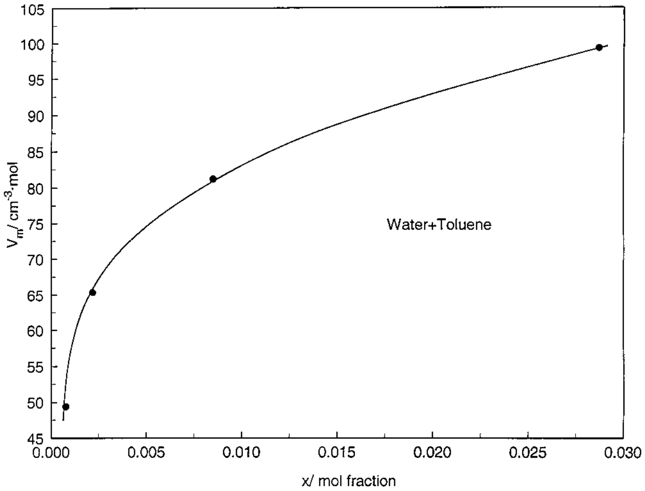

Figure 8. Molar volumes V_m of $(1 - x)$ water + x toluene mixtures as a function of composition x along the critical isotherm–isobar ($T_C = 647.1$ K; $P_C = 22.1$ MPa). The solid curves are guides for the eye.

shows $\ln(V_m)$ as a function of $\ln(x)$ for $(1 - x)$ water + x toluene mixtures at T_C and P_C of the pure solvent (water). These data were fitted with the simple expression $\ln(V_m) = \ln(V_0) + \epsilon \ln(x)$. The fitting parameters are $\ln(V_0) = (5.403 \pm 0.03)$ and $\epsilon = (0.207 \pm 0.005)$, which is very close to the nonclassical value of critical exponent $\epsilon = 0.21$. Therefore, the present *PVTx* measurements for dilute $(1 - x)$ water + x toluene mixtures at the critical temperature and critical pressure of the pure solvent (water) are consistent with the nonclassical behavior of the singularity of partial molar volume $\bar{V}_2^\infty$ predicted by theory. At the solvent's critical temperature and critical pressure, from the expansion of the Helmholtz free energy[32,35,37,39] $A(V,T,x)$ around the solvent's critical point, we can calculate the values of derivative $(\partial V_m/\partial x)^\infty_{PT}$ with the equation[37]

$$\left(\frac{\partial V_m}{\partial x}\right)^{\infty}_{PT} = \frac{1}{3}\left(-\frac{6A^C_{VX}}{A^C_{4V}}\right)^{1/3} x^{-2/3} \tag{4}$$

where $A^C_{VX} = -(\partial P/\partial x)^C_{TV}$. Therefore, the sign of the derivative $(\partial V_m/\partial x)^\infty_{PT}$ and partial molar volume $\bar{V}_2^\infty$ is determined

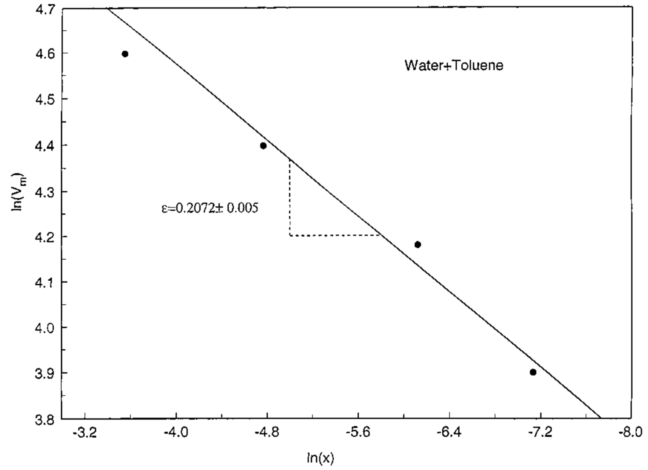

Figure 9. Molar volumes $\ln(V_m)$ of $(1 - x)$ water + x toluene mixtures against composition $\ln(x)$ along the critical isotherm–isobar ($T_C = 647.1$ K; $P_C = 22.1$ MPa).

by the sign of $A^C_{VX} = -(\partial P/\partial x)^C_{TV}$, which is the Krichevskii parameter. Adding a solute will most likely raise the pressure, $(\partial P/\partial x)^C_{TV} > 0$, and will cause the partial molar volume $\bar{V}_2^\infty$ to approach $+\infty$. For $(1 - x)$ water + x toluene mixtures, a positive divergence of the derivative $(\partial V_m/\partial x)^\infty_{PT}$ was observed. Therefore, the Krichevskii parameter for this system is positive, $(\partial P/\partial x)^C_{TV} > 0$. Values of partial molar volume $\bar{V}_2^\infty$ can be calculated from values of the derivatives $(\partial P/\partial x)^\infty_{TV}$ using the relationship[31]

$$\bar{V}_2^\infty = V_{H_2O}\left[1 + K_{TH_2O}\left(\frac{\partial P}{\partial x}\right)^{\infty}_{TV}\right] \tag{5}$$

where K_{TH_2O} is the isothermal compressibility of pure water and V_{H_2O} is the molar volume of pure water.

Krichevskii Parameter. The thermodynamic behavior of infinitely dilute mixtures near the solvent's critical point is fully characterized by values of the Krichevskii parameter, $(\partial P/\partial x)^\infty_{T_C V_C}$, and near-critical properties of the pure solvent.[31] The thermodynamic behavior of a near-critical dilute solution is very important to understand the molecular interactions and the microscopic structure of the solution. In the limit of infinite dilution, many partial molar properties of the solute ($\bar{V}_2^\infty$, $\bar{H}_2^\infty$, and $\bar{C}^\infty_{P2}$) diverge strongly at the solvent's critical point.[43] Levelt Sengers[44] proposed a description of the thermodynamic behavior of dilute near-critical solutions based on $(\partial P/\partial x)^\infty_{TV}$. Japas et al.[45] denoted $(\partial P/\partial x)^\infty_{TV}$ as the Krichevskii function. The value of $(\partial P/\partial x)^\infty_{TV}$ at the critical point is, by definition, the Krichevskii parameter.[46] This parameter is very important to describe the thermodynamic behavior of a dilute solution near the solvent's critical point. For example, the Krichevskii function is related to direct correlation functions[47] and accounts for effects of intermolecular interactions between solvent and solute molecules, which determine the properties of their solution. Figure 10 shows the pressure of the $(1 - x)$ water + x toluene mixtures as a function of concentration along the various near-critical densities at the solvent's (water) critical temperature. The slope $(\partial P/\partial x)^\infty_{T_{CV}}$ of the isothermal–isochoric lines (Krichevskii function) changes with solution density. At low (vapor) densities, the slope is negative, whereas at high (liquid) densities the slope is positive. At near-critical densities, the slope of a $P-x$ curve is small. The slope of a $P-x$ curve for dilute $(1 - x)$ water + x toluene mixtures ($x \to 0$) at the

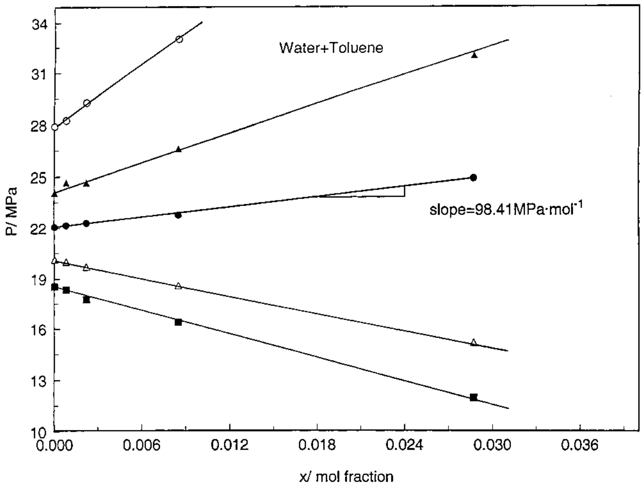

Figure 10. Pressure P of $(1 - x)$ water + x toluene mixtures as a function of composition x along the various near-critical densities at fixed critical isotherm of pure water ($T_C = 647.1$ K).

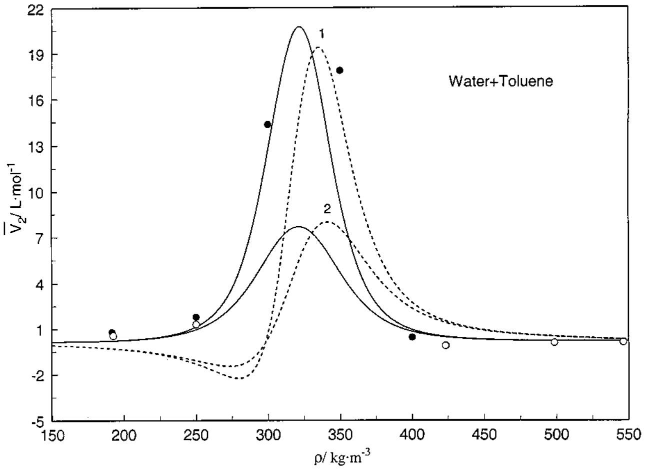

Figure 11. Comparison of the partial molar volume $\bar{V}_2^\infty$ calculated with the crossover model (solid line) and with the semiempirical equation by Majer et al.[13] (dashed line) and the values derived from the present experimental *PVTx* data along the near-critical isotherms: 1, 647.10 K; 2, 648.0 K.

critical temperature and critical density of pure water defines the value of the Krichevskii parameter $(\partial P/\partial x)^\infty_{T_CV_C}$. From this work, the experimental value of $(\partial P/\partial x)^\infty_{T_CV_C}$ is 98.4 MPa·mol^{-1}. This value agrees closely with a value of 105 ± 10 MPa·mol^{-1} estimated by Plyasunov and Shock,[48] whereas the values of the Krichevskii parameter calculated from the crossover equation of state (136.3 MPa·mol^{-1}; Kiselev et al.[6]) differ from the present results by 38 MPa·mol^{-1} (39%). Values of the Krichevskii parameter for $(1 - x)$ water + x toluene mixtures were estimated by Plyasunov and Shock[48] from the empirical relationship

$$\left(\frac{\partial P}{\partial x}\right)^\infty_{T_CV_C} = 88.7 + 4.11\Delta_h G^0$$

where $\Delta_h G°$ is the Gibbs energy of a solute at 298.15 K and 0.1 MPa and from the partial molar volume values $\bar{V}_2^\infty$ derived by Degrange[5] from *PVTx* measurements. The derived values are (105 ± 10) from the values of partial molar volumes and 107 from the Gibbs energy data. The value of this parameter was also estimated from the initial slopes of the critical lines for $(1 - x)$ water + x toluene mixtures and the values of the vapor pressure slope of pure water at its critical point. The initial slopes of the critical lines are related to the Krichevskii parameter as[31,46]

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{x}}\right)^{\mathrm{C}}_{\mathrm{V_CT_C}} = \left(\frac{\partial P_C}{\partial x}\right)^{\mathrm{C}}_{\mathrm{CRL}} - \left(\frac{\mathrm{d}P_S}{\mathrm{d}T}\right)^{\mathrm{C}}_{\mathrm{CXC}}\left(\frac{\partial T_C}{\partial x}\right)^{\mathrm{C}}_{\mathrm{CRL}} \tag{6}$$

or, equivalently

$$\left(\frac{\partial \mathrm{P}}{\partial x}\right)^{\mathrm{C}}_{\mathrm{V_CT_C}} = \left[\left(\frac{\mathrm{d}P_C}{\mathrm{d}T_C}\right)^{\mathrm{C}}_{\mathrm{CRL}} - \left(\frac{\mathrm{d}P_S}{\mathrm{d}T}\right)^{\mathrm{C}}_{\mathrm{CXC}}\right]\left(\frac{\mathrm{d}T_C}{\mathrm{d}x}\right)^{\mathrm{C}}_{\mathrm{CRL}} \tag{7}$$

where $(\partial P_C/\partial x)_{\mathrm{CRL}}$ and $(\partial T_C/\partial x)^{\mathrm{C}}_{\mathrm{CRL}}$ are the initial slopes of the critical lines (T_C-x and P_C-x). $(\mathrm{d}P_S/\mathrm{d}T)^{\mathrm{C}}_{\mathrm{CXC}} > 0$ is the slope of the solvent's vapor pressure curve evaluated at the critical point of the solvent (always positive). The near-critical behavior of mixtures depends on the signs and the magnitudes of the derivatives [initial slopes of the critical lines (T_C-x and P_C-x) and the vapor pressure curve (P_S-T_S) at the critical point] in these equations. The value of the Krichevskii parameter for the dilute $(1 - x)$ water + x toluene mixtures was estimated from eq 7 using critical lines (T_C-x and P_C-x) calculated from the crossover model and experimental T_C-P_C data reported by Alwani[9] and Alwani and Schneider[10] and a vapor pressure equation (P_S-T_S) by Levelt Sengers.[49] The results are $(\mathrm{d}P_S/\mathrm{d}T)^{\mathrm{C}}_{\mathrm{CXC}} = 0.2682$ MPa·K^{-1}, $(\partial P_C/\partial x)_{\mathrm{CRL}} = -91.0$ MPa·mol^{-1}, $(\partial T_C/\partial x)^{\mathrm{C}}_{\mathrm{CRL}} = -853.5$ K·mol^{-1}, and $(\mathrm{d}P_C/\mathrm{d}T_C)^{\mathrm{C}}_{\mathrm{CRL}} = 0.107$ MPa·K^{-1}, and the Krichevskii parameter is $(\partial P/\partial x)^\infty_{T_CV_C} = 137.7$ MPa·mol^{-1}. Therefore, there is good agreement between the values of the Krichevskii parameter calculated from eq 7 using the critical locus properties of the mixture and pure solvent's (water) vapor pressure properties at critical point and values calculated from the crossover model. On the basis of the high uncertainties associated with the estimates, we would recommend the experimental value of the Krichevskii parameter of 98.4 MPa·mol^{-1}.

Partial Molar Volume. Figure 11 shows a comparison between values of partial molar volumes $\bar{V}_2^\infty$ derived from *PVTx* measurements and values calculated from a crossover model developed by Kiselev et al.[6] The calculations was carried using eq 5 and the semiempirical model using the compressibility of pure water[13]

$$\bar{V}_2^\infty = V_{\mathrm{H_2O}} + RTK_{T\mathrm{H_2O}}\rho_{\mathrm{H_2O}}[a_1 + a_2(\exp(v\rho_{\mathrm{H_2O}}) - 1)] \tag{8}$$

where $v = 5$ cm^3·g^{-1}, $\rho_{\mathrm{H_2O}}$ is the density of pure water, and a_1, a_2, and a_3 are the fitting parameters. The values of parameters a_i were determined using experimental partial molar volume values of toluene in an infinitely dilute $(1 - x)$ water + x toluene mixture.[41] Equation 8 is valid in the temperature range from 298 K to 623 K. We extrapolated this equation to high temperatures to compare with values calculated from the crossover model and with values derived from measured *PVTx* values. The results are shown in Figure 11. The partial molar volume values, calculated from eq 8, exhibit a maximum at a density of ~335 kg·m^{-3}, which is slightly higher than the critical density of pure water (322 kg·m^{-3}), as adopted by IAPWS.[50] The large differences near the critical point can be explained due to extrapolation properties of eq 8 or due to differences between the *PVT* relationship for pure water used by Majer et al.[13] and the IAPWS-95 formulation.[18] Far from the critical region (at densities <200 kg·m^{-3} and >400 kg·m^{-3}), the agreement between eqs 5 and 8 is satisfactory.

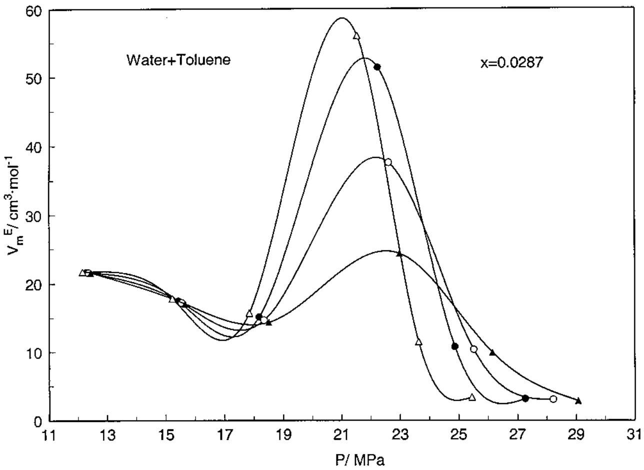

Figure 12. Excess molar volumes V^E_m of $(1 - x)$ water + x toluene mixture as a function of pressure P along near-critical and supercritical isotherms: ▲, 651.15 K; ○, 649.15 K; △, 643.15 K; ●, 647.10 K. The solid curves are guides for the eye.

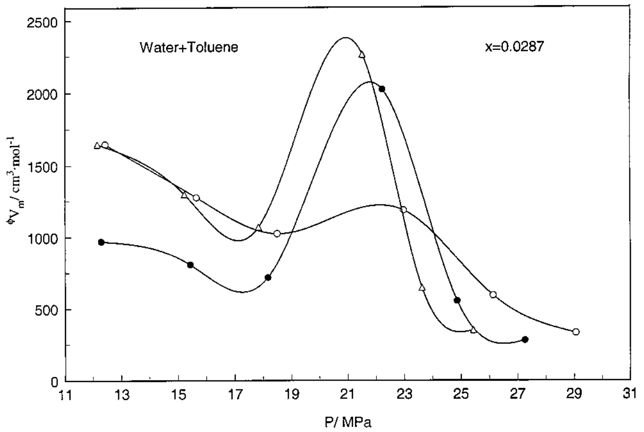

Figure 13. Apparent molar volumes $^{\Phi}V_m$ of $(1 - x)$ water + x toluene mixture as a function of pressure P along near-critical and supercritical isotherms: ○, 651.15 K; △, 643.15 K; ●, 647.10 K. The solid curves are guides for the eye.

From the experimental values of molar volumes $V_m(P,T,x)$ for $(1 - x)$ water + x toluene mixtures and the corresponding values for the pure components $V_m(P,T,0)$ (for pure-water) and $V_m(P,T,1)$ (for pure toluene), the values of excess $V^E_m(P,T,x)$ and apparent $^{\Phi}V_m(P,T,x)$ molar volumes are defined by[35]

$$V^E_m(P,T,x) = V_m(P,T,x) - x\, V_m(P,T,1) - (1 - x)V_m(P,T,0) \quad (9)$$

and

$$x^{\Phi}V_m(P,T,x) = V_m(P,T,x) - (1 - x)V_m(P,T,0) \quad (10)$$

In the limit of infinite of dilution, the apparent molar volume of the solute $^{\Phi}V_m(P,T,x)$ becomes equal to the partial molar volume $\bar{V}_2^{\infty}(\lim_{x\to 0}{}^{\Phi}V_m = \bar{V}_2^{\infty})$. Figures 12 and 13 show the results for $V^E_m(P,T,x)$ and $^{\Phi}V_m(P,T,x)$ at near-critical and supercritical isotherms. Near the critical pressure (~22.1 MPa) experimental values of $V^E_m(P,T,x)$ and $^{\Phi}V_m(P,T,x)$ for $(1 - x)$ water + x toluene mixtures show a large positive anomaly. This is universal behavior in any dilute near-critical mixture.

Conclusion

The *PVTx* properties for water + toluene were measured in a range of temperatures from 623 to 673 K and pressures from 11 to 46 MPa with an estimated uncertainty of 0.05−0.15% for three compositions (0.0008, 0.0022, and 0.0085 mole fractions) of toluene. The measured data show good agreement of densities (within ±0.35%) with other measurements (Degrange[5]) and with calculations with a crossover model (Kiselev et al.[6]). The accuracy of the method was confirmed by measurements of the *PVT* properties of pure water and pure toluene in the critical and supercritical regions. From measured values of *PVTx*, the values of the Krichevskii parameter and partial, excess, and apparent molar volumes were calculated. Large positive values of apparent molar volume of solute (toluene) in the vicinity of solvent's (water) critical point were observed. The partial molar volume of solute (toluene) in the solvent's (water) critical point have anomalous nonclassical behavior with nonclassical values of the critical exponent $\epsilon = (0.207 \pm 0.005)$. The experimental behavior of the Krichevskii function near the solvent's (water) critical point was discussed.

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