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Density Measurements of Binary Supercritical Fluid Ethane/Cosolvent Mixtures

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Densities of binary supercritical mixtures of ethane with cosolvents, ethanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol, have been measured by a constant volume apparatus. Measurements were made in the range 0.7 to 2.0 mol % cosolvent and at pressures from 49.8 to 105.7 bar at 308.2 K. Despite the low cosolvent composition, all mixture densities deviate significantly from the density of pure ethane in the highly compressible region. Mixture densities calculated by the PR-EOS give only a qualitative representation of the experimental data.

Introduction

Supercritical fluid (SCF) solvents can be tailored for a specific process by the addition of small amounts of polar or protic cosolvents (Knutson et al., 1995; Eckert and Knutson, 1993; Gurdial et al., 1993) and thus can lead to increased loading of solute in the fluid phase. The contributing factors to solubility enhancement can be understood better when the solute solubility data are plotted against the mixture density, such that the solubility enhancement due to increases in density can be removed, and any solute/cosolvent interaction can be distinguished (Foster et al., 1993). In addition, accurate mixture density data are also important for modeling of SCF systems, as conventional equation of state treatments can provide only a qualitative description of the phase behavior of SCF mixtures. In this study, experimental densities of binary supercritical fluid ethane ($T_c = 305.3$ K, $P_c = 48.7$ bar) + cosolvent systems were measured. Three highly protic cosolvents were selected: ethanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol.

Experimental Section

The sources and purities of the compounds used in this study are listed in Table 1. All reagents were used as received. A schematic diagram of the apparatus used is depicted in Figure 1. The density measurements were performed in a constant volume apparatus which incorporated a high-pressure sight gauge (Jerguson, Model 11-T-32), a K-type thermocouple (calibrated to within ±0.1 K), and a pressure transducer (Druck, Model PDCR 911) with 0.25% full scale accuracy. The internal volume of the apparatus was calibrated against pure N_2, and pure CO_2, using a wet test meter (Alexander Wright, Model Midget) with a reported accuracy of 0.25% full scale. The estimated internal volume of the apparatus is 57.7 ± 0.3 mL.

The apparatus was submerged in a constant temperature water bath controlled to ±0.1 K using a PID controller (Bayley, Model 123). A known mass of cosolvent was first injected into the sight gauge using a 5 mL gastight syringe; then ethane was slowly pumped into the system to the desired operating pressure using a high-pressure syringe pump (ISCO 260D). The mixture was agitated with a magnetic stirrer for 1 h to ensure thorough mixing, and the agitation was maintained throughout the entire experiment. After the system has reached equilibrium, a small volume (0.5 L to 1.5 L at standard temperature and pressure) of the mixture was released from the system through a metering valve and measured by a wet test meter. This procedure was repeated every 10 min provided the mixture was homogeneous, as determined by visual observations of the mixture through the sight gauge.

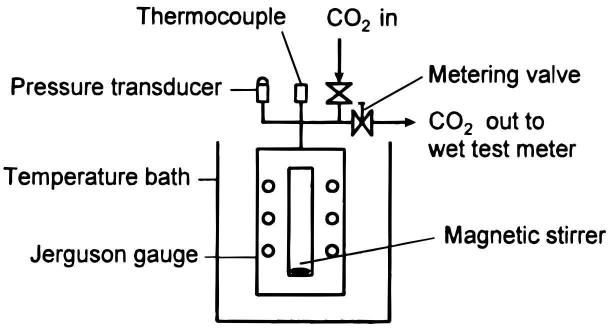

Figure 1. Schematic diagram of the experimental setup.

Table 1. Reagents and Purities

reagent	source	% purity
ethane	Matheson	99.0
ethanol	Quantum Chemical	99.9
2,2,2-trifluoroethanol	Aldrich	99.5
1,1,1,3,3,3-hexafluoro-2-propanol	Aldrich	99.8

The system temperature, pressure, and amount of gas released were recorded at each stage. Mixture density and composition were obtained by measuring the total amount of gas released from the system and the total amount of cosolvent injected originally into the system. From a total mass balance, the mole fraction of cosolvent present was calculated. All experimental data were obtained in the one-phase region; therefore, the mole fraction of cosolvent present was constant during slow depressurization throughout this region. The amount of cosolvent released during each step was then proportional to the amount of gas released at the same time. From this, a mass balance calculation performed at each stage of gas release allowed the total mass, hence, the mixture density, to be obtained.

The visible system described above has the advantage of continuously monitoring the phase behavior of the mixture, such that the reliability of the experimental data will not be affected in the event of phase separation.

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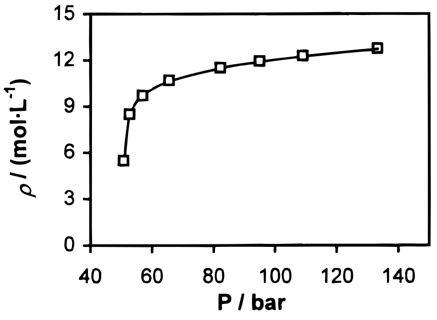

Figure 2. Density of pure ethane at 308.2 K: (□) experimental; (—) literature data.

Results and Discussion

The density of pure ethane was measured to verify the reliability of the experimental procedure used in this study. A comparison of the measured ethane densities, at various pressures, and the literature values (Younglove and Ely, 1987) is given in Figure 2; all the measured data are in good agreement with the literature values, less than ±0.5% deviation for $P > 55$ bar and ±3.3% for $P < 55$ bar, the literature data have uncertainties of ±0.2% away from the critical region and ±5% in the critical region. This set of data has been duplicated and shown to be reproducible. The deviation between the measured and literature data for pure ethane density provides a good estimate of the uncertainty associated with the experimental procedure.

Mixture densities are compared with pure ethane densities in Table 2. At low cosolvent concentrations, mixture densities are close to the pure solvent densities in the higher pressure region but deviate significantly in the highly compressible region. Hence, the usual assumption that the density of supercritical solvent + cosolvent mixtures may be approximated by that of the pure solvent may result in serious error, even at very low cosolvent concentration.

Mixture densities were correlated by the Peng–Robinson equation of state (PR-EOS) (Peng and Robinson, 1976), using van der Waals mixing rules with one adjustable parameter, as shown

$$P = \frac{RT}{v - b_{\mathrm{m}}} - \frac{a_{\mathrm{m}}}{v^2 + 2b_{\mathrm{m}}v - b_{\mathrm{m}}^2}$$

$$a_{\mathrm{m}} = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2}(1 - k_{ij}) \tag{1}$$

$$b_{\mathrm{m}} = \sum_i y_i b_i$$

where P is the pressure, R is the gas constant, T is the temperature, v is the molar volume, a_{m} and b_{m} are mixture constants for the Peng–Robinson EOS, y is the mole fraction, and k_{ij} is the binary interaction parameter.

Optimization was carried out by minimizing the average absolute relative deviation (AARD) between the experimental and correlated density (ρ^{exp}, ρ^{corr}) values defined in eq 2. An example of the experimental and correlated data

$$\mathrm{AARD} = \frac{1}{N}\sum \left|\frac{(\rho^{\mathrm{corr}} - \rho^{\mathrm{exp}})}{\rho^{\mathrm{exp}}}\right| \tag{2}$$

is illustrated in Figure 3. As shown in the figure, PR-EOS is incapable of correlating the density data quantitatively, in particular, in the highly compressible region. The highly nonideal nature of this region and the asymmetry of solute and cosolvent molecules cannot be adequately described by the use of conventional mixing rules. This further illustrates the importance of experimental density measurements for supercritical solvent + cosolvent systems.

Table 2. Densities of Binary Supercritical Ethane + Cosolvent Mixtures at 308.2 K

Ethane (A) + 1,1,1,3,3,3-Hexafluoro-2-propanol (B)

$x_B = 0.0068$				$x_B = 0.0136$			
P/bar	ρ_{mixture}/ (mol/L)	ρ_{pure}^{a}/ (mol/L)	% dev^{b}	P/bar	ρ_{mixture}/ (mol/L)	ρ_{pure}^{a}/ (mol/L)	% dev^{b}
102.3	11.97	12.08	−0.9	103.3	12.04	12.10	−0.5
84.6	11.49	11.55	−0.5	87.7	11.64	11.66	−0.2
76.8	11.20	11.24	−0.4	76.4	11.25	11.23	0.18
69.5	10.86	10.88	−0.2	68.0	10.86	10.78	0.7
62.5	10.41	10.37	0.4	61.7	10.47	10.29	1.8
57.1	9.87	9.72	1.5	56.4	9.99	9.61	4.0
53.7	9.28	8.87	4.6	54.7	9.76	9.22	5.9
52.0	8.76	7.60	15.3	52.2	9.28	7.88	17.8
51.3	8.31	6.29	32.1	51.1	8.89	5.78	53.8
50.7	7.62	5.31	43.5				
50.5	7.09	5.09	39.3				

Ethane (A) + 2,2,2-Trifluoroethanol (B)

$x_B = 0.0098$				$x_B = 0.0198$			
P/bar	ρ_{mixture}/ (mol/L)	ρ_{pure}^{a}/ (mol/L)	% dev^{b}	P/bar	ρ_{mixture}/ (mol/L)	ρ_{pure}^{a}/ (mol/L)	% dev^{b}
103.2	12.07	12.10	−0.2	102.6	11.97	12.09	−1.0
84.2	11.55	11.54	0.1	84.6	11.50	11.55	−0.4
76.9	11.27	11.25	0.2	76.9	11.23	11.24	−0.1
69.9	10.95	10.90	0.5	69.9	10.94	10.90	0.4
63.3	10.55	10.44	1.1	62.9	10.54	10.40	1.3
57.5	10.00	9.79	2.1	57.0	10.04	9.71	3.4
54.1	9.47	9.03	4.9	53.8	9.59	8.90	7.8
52.5	9.03	8.17	10.5	51.9	9.22	7.38	24.9
51.4	8.48	6.43	32.0	50.7	8.67	5.23	65.8
50.7	7.51	5.23	43.6	49.8	8.11	4.59	76.7
50.4	6.70	4.97	34.8				

Ethane (A) + Ethanol (B)

$x_B = 0.0168$			
P/bar	ρ_{mixture}/ (mol/L)	ρ_{pure}^{a}/ (mol/L)	% dev^{b}
105.7	12.27	12.16	0.9
84.2	11.72	11.54	1.6
76.5	11.45	11.23	2.0
69.8	11.17	10.89	2.6
62.7	10.78	10.38	3.9
56.3	10.26	9.57	7.2
53.4	9.91	8.81	12.5
51.9	9.60	7.38	30.1
50.6	9.18	5.16	77.9
49.7	8.72	4.51	93.3

[a] Younglove and Ely, 1987. [b] % dev = $(\rho_{\mathrm{mixture}} - \rho_{\mathrm{pure}}) \times 100/\rho_{\mathrm{pure}}$.

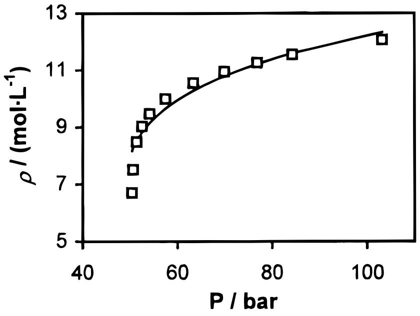

Figure 3. Experimental and correlated mixture densities of binary ethane (A) + 2,2,2-trifluoroethanol (B), $x_B = 0.0098$: (□) experimental; (—) PR-EOS.

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