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High-Pressure Vapor–Liquid Equilibria of the Binary Mixtures Nitrogen + *n*-Butane and Argon + *n*-Butane

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High-pressure vapor–liquid equilibrium composition and density data of the binary systems nitrogen + *n*-butane (at 339.4 and 380.2 K) and argon + *n*-butane (at 340.0 and 380.1 K) are reported. The data sets were fit with the Peng–Robinson equation of state using both generalized and fluid-specific temperature-dependent parameters. The binary interaction parameters so obtained are reported.

Introduction

This study continues our research on the vapor–liquid equilibrium of mixtures of molecules asymmetric in size and critical properties (*1*, *2*). The data obtained in this study, in addition to being of direct interest, are of use for testing and improving equations of state and their mixing rules, especially for the simultaneous prediction of the equilibrium compositions, densities, and other thermodynamic properties of mixtures.

Experiment

A dynamic high-pressure vapor–liquid equilibrium apparatus (maximum pressure 5000 psi and maximum temperature 300 °F), which allows the simultaneous measurement of the compositions and densities of the coexisting phases, was used to obtain the data reported below. Shibata et al. (*1*) give a detailed description of the apparatus and its operation.

Grade 5 nitrogen, argon with a purity of 99.998%, and instrument grade *n*-butane, supplied by Matheson were used for the measurements. As described earlier (*1*), temperatures are measured with an error of less than 0.05 K and pressures with an error of 0.1 psi in the range below 800 psi and 2 psi above 800 psi. The error in the measurement of the phase compositions with a calibrated gas chromatograph is smaller than 0.005 mole fraction. Densities were measured with calibrated Mettler/Paar vibrating tube densimeters with an error of less than 0.0001 g/cm^3.

Table I. Experimental Data for the Nitrogen + *n*-Butane System at 339.4 K

T, K	P, bar	x_N	y_N	ρ_L, g/cm^3	ρ_V, g/cm^3
339.37	12.41	0.023	0.342	0.5242	0.0263
339.18	18.82	0.024	0.524	0.5230	0.0333
339.26	26.17	0.038	0.632	0.5226	0.0413
339.43	34.35	0.051	0.700	0.5212	0.0514
339.36	41.66	0.068	0.738	0.5203	0.0596
339.41	56.16	0.092	0.781	0.5190	0.0766
339.41	68.26	0.117	0.800	0.5175	0.0916
399.33	89.18	0.165	0.822	0.5144	0.1196
339.39	103.42	0.180	0.826	0.5120	0.1356
339.57	120.52	0.211	0.824	0.5095	0.1578
339.35	135.96	0.249	0.824	0.5042	0.1788
339.37	152.17	0.282	0.815	0.4869	0.2001
339.50	168.85	0.315	0.801	0.4810	0.2249
339.48	182.64	0.352	0.792	0.4746	0.2479
339.37	193.88	0.381	0.778	0.4685	0.2649
339.35	199.95	0.400	0.761	0.4640	0.2770
339.35	206.29	0.424	0.751	0.4563	0.2888
339.15	215.18	0.459	0.726	0.4467	0.3098
339.35	221.05	0.505	0.688	0.4201	0.3360

Table II. Experimental Data for the Nitrogen + *n*-Butane System at 380.2 K

T, K	P, bar	x_N	y_N	ρ_L, g/cm^3	ρ_V, g/cm^3
380.15	17.58	0.000	0.000	0.4518	0.0483
380.02	24.27	0.020	0.190	0.4501	0.0566
380.20	31.92	0.037	0.319	0.4478	0.0649
380.26	39.44	0.051	0.400	0.4458	0.0748
380.07	51.64	0.077	0.483	0.4409	0.0904
380.09	65.50	0.109	0.540	0.4348	0.1105
380.21	82.74	0.153	0.573	0.4254	0.1349
380.20	103.42	0.211	0.586	0.4097	0.1700
380.20	124.04	0.287	0.563	0.3833	0.2153
380.30	130.66	0.317	0.544	0.3634	0.2369
380.25	134.45	0.349	0.514	0.3489	0.2560
380.35	135.76	0.373	0.500	0.3370	0.2707

Results and Discussion

Tables I and II give the unsmoothed data for the equilibrium compositions and densities for the nitrogen + *n*-butane system at 339.4 and 380.0 K, respectively; these same data are plotted in Figures 1 and 2. The data for the argon + *n*-butane system at the same temperatures are shown in Tables III and IV and in Figures 3 and 4. The data were fit with the Peng–Robinson equation of state (PR-EOS) (*3*) with both generalized parameters and the fluid-specific temperature-dependent parameters of Xu and Sandler (*4*). The PR-EOS can be written as

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \qquad (1)$$

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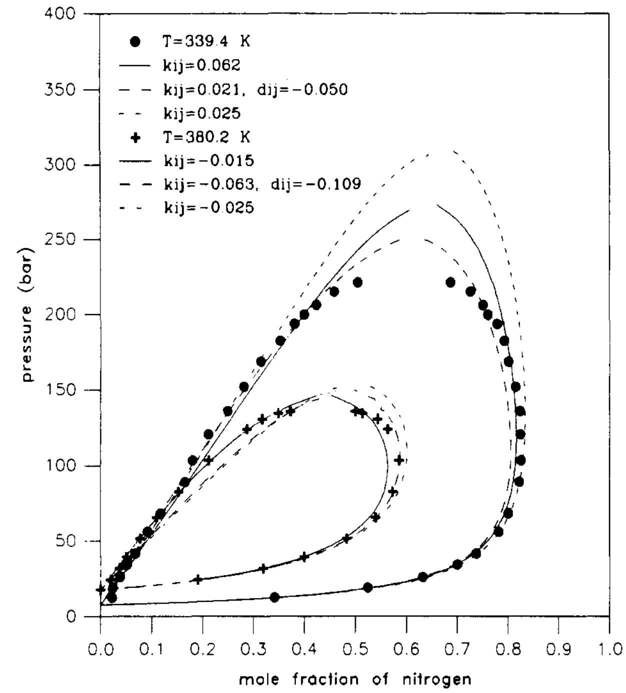

Figure 1. P-x-y data for nitrogen + n-butane at T = 339.4 and 380.2 K. The data have been fit with the PR-EOS. The line --- results from the use of the generalized equation of state parameters, while the lines — and -- result from the use of the fluid-specific parameters with one and two binary parameters, respectively.

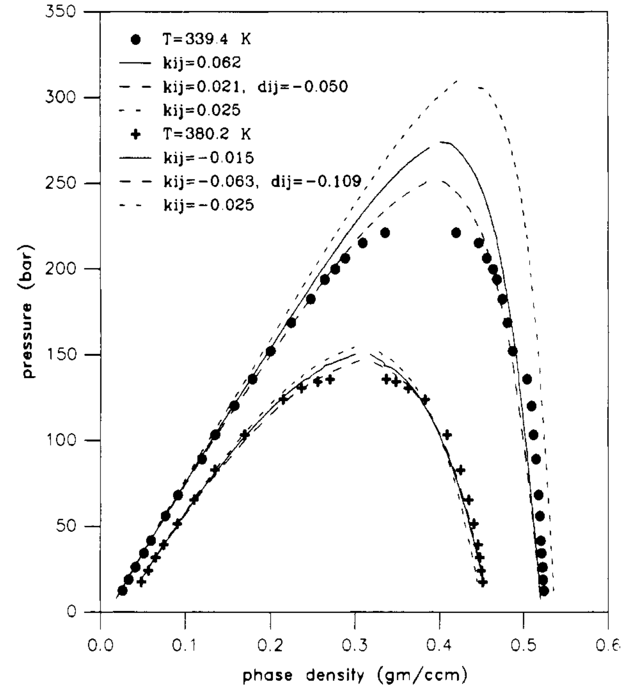

Figure 2. Pressure–density data for nitrogen + n-butane at T = 339.4 and 380.2 K. The lines result from the PR-EOS with binary parameters fit to the composition data. Line legend as in Figure 1.

where P is the pressure, T is the temperature, R is the gas constant, v is the molar volume, and a and b are the temperature-dependent parameters. The van der Waals one-fluid mixing rules

$$a = \sum\sum x_i x_j a_{ij} \qquad (2)$$

$$b = \sum\sum x_i x_j b_{ij} \qquad (3)$$

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}) \qquad (4)$$

$$b_{ij} = \tfrac{1}{2}(b_i + b_j)(1 - d_{ij}) \qquad (5)$$

Table III. Experimental Data for the Argon + n-Butane System at 340.0 K

T, K	P, bar	x_A	y_A	ρ_L, g/cm^3	ρ_V, g/cm^3
339.90	7.45	0.000	0.000	0.5221	0.0175
340.00	13.93	0.021	0.402	0.5238	0.0291
340.10	24.13	0.046	0.612	0.5256	0.0434
340.05	34.47	0.076	0.703	0.5274	0.0623
340.10	48.26	0.109	0.763	0.5295	0.0833
340.10	68.95	0.163	0.794	0.5318	0.1185
340.11	82.74	0.203	0.808	0.5344	0.1430
340.10	96.53	0.238	0.813	0.5350	0.1689
339.98	110.32	0.275	0.816	0.5353	0.1944
339.95	124.04	0.314	0.813	0.5353	0.2213
340.00	137.96	0.356	0.807	0.5344	0.2508
339.99	151.55	0.401	0.795	0.5297	0.2831
339.67	165.34	0.443	0.778	0.5227	0.3160
340.10	178.71	0.507	0.744	0.5099	0.3614
340.15	184.85	0.550	0.713	0.4746	0.3924

Table IV. Experimental Data for the Argon + n-Butane System at 380.1 K

T, K	P, bar	x_A	y_A	ρ_L, g/cm^3	ρ_V, g/cm^3
379.98	17.51	0.000	0.000	0.4518	0.0467
380.20	24.34	0.026	0.196	0.4514	0.0594
380.15	34.96	0.060	0.370	0.4509	0.0763
379.98	48.26	0.093	0.477	0.4494	0.0997
380.06	62.26	0.132	0.543	0.4456	0.1237
380.19	75.84	0.173	0.579	0.4421	0.1502
380.22	89.63	0.220	0.593	0.4358	0.1794
380.09	103.42	0.271	0.588	0.4278	0.2140
380.25	112.87	0.311	0.572	0.4132	0.2420
380.15	122.86	0.378	0.539	0.3821	0.2842

Table V. Binary Interaction Parameters for the PR-EOS for the Nitrogen + n-Butane System

	genlzd param	fluid-specific param		
	1 param	1 param	2 param	
T, K	k_{ij}	k_{ij}	k_{ij}	d_{ij}
339.4	0.025	0.062	0.021	−0.050
380.2	−0.025	−0.015	−0.063	−0.109

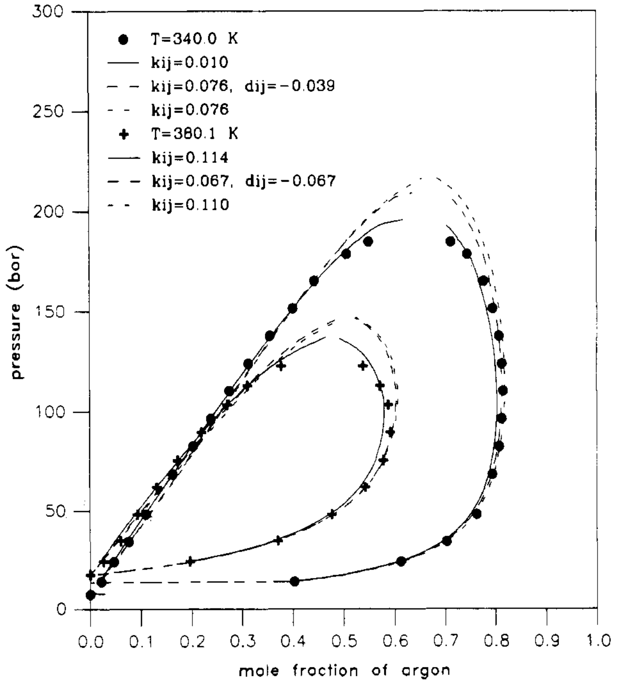

Figure 3. P-x-y data for argon + n-butane at T = 340.0 and 380.1 K. Line legend as in Figure 1.

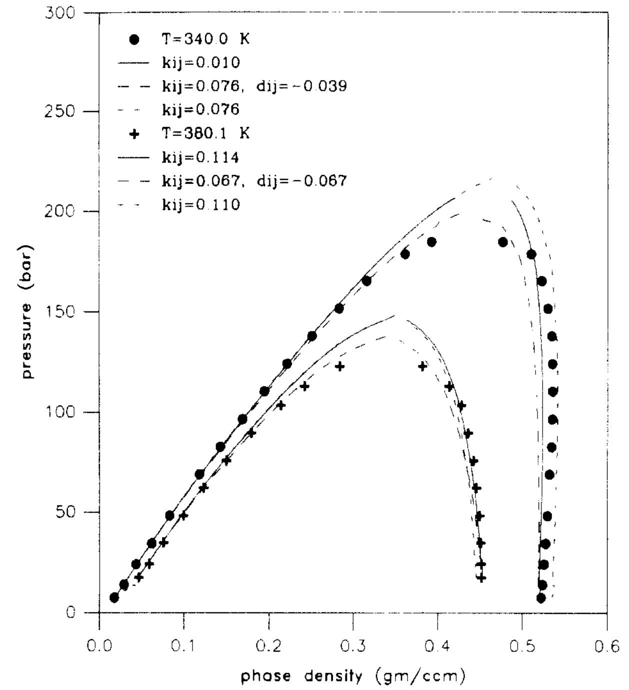

Figure 4. Pressure-density data for argon + *n*-butane at T = 340.0 and 380.1 K. The lines result from the PR-EOS with binary parameters fit to the composition data. Line legend as in Figure 1.

Table VI. Binary Interaction Parameters for the PR-EOS for the Argon + *n*-Butane System

	genlzd param	fluid-specific param		
	1 param	1 param	2 param	
T, K	k_{ij}	k_{ij}	k_{ij}	d_{ij}
340.0	0.076	0.010	0.076	-0.039
380.1	0.110	0.114	0.067	-0.067

were used to calculate the mixture parameters. The two adjustable binary interaction parameters, k_{ij} and d_{ij}, were obtained by fitting the data with the temperature and pressure as the independent variables and minimizing the errors in the vapor and liquid compositions simultaneously. The fitting procedure was done both for the case of $k_{ij} \neq 0$ and $d_{ij} = 0$, and for $k_{ij} \neq 0$ and $d_{ij} \neq 0$. Tables V and VI show the binary interaction parameters obtained in this way. It should be noted that the binary interaction parameters were fit just to the phase composition data, not to the phase densities.

Correlations for the systems we measured using the PR-EOS with generalized parameters (*3*) are not very good in the near-critical region and, in particular, results in an overprediction of the mixture critical pressure. Using the Xu-Sandler parameters (*4*) results in no significant difference in the average deviation between calculated and experimental compositions for both phases for each of the data points, but a mixture critical point that is in better agreement with experiment.

As suggested by Shibata and Sandler (*5*), using the Xu-Sandler parameters with two adjustable binary parameters gives a better correlation of the mixture behavior than when using just one parameter as seen in Figure 1, though the fits with one adjustable parameter give slightly better liquid volumes. This difference between the one- and two-parameter fits is evident for the system argon + *n*-butane in Figure 3. Figures 1 and 3 show the $P-x-y$ data for both systems compared with the best calculated results obtained by using the Xu-Sandler equation of state parameters with two binary interaction parameters, and Figures 2 and 4 show the density data for these same systems.

The fits of the nitrogen + *n*-butane data are similar to those of Shibata et al. (*1*) for this mixture at 310 and 410 K, respectively. Also, the overprediction of the mixture critical pressure for the argon + *n*-butane system increases with increasing temperatures. Though the critical temperature of argon is approximately 25 K higher than the critical temperature of nitrogen, the critical molar volume of argon is much smaller than that of nitrogen. Since the PR-EOS fit of the argon + *n*-butane data is not as good as that for the nitrogen + *n*-butane system, it appears that in this case the effect of the size difference dominates over that of the energy difference for these mixtures of relatively simple molecules.

Glossary

a, b	equation of state parameters
k_{ij}, d_{ij}	binary interaction parameters
P	pressure
R	gas constant
T	temperature
v	molar volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction
ρ	density

Registry No. Butane, 106-97-8; argon, 7440-37-1; nitrogen, 7727-37-9.

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Solubilities of α-Anhydrous Glucose in Ethanol/Water Mixtures

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Solubilities of α-anhydrous glucose in ethanol/water mixtures were determined at 35 °C. An isothermal method was used. The solubilities were modeled with a Redlich-Kister expansion.

Introduction

The solubility of D-glucose in solutions of ethanol and water has been studied and modeled in this work. Increased interest in biological molecules has revealed a need for thermodynamic properties of mixtures involving biological molecules. Despite the importance of sugars, relatively few thermodynamic data

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