High-Pressure Vapor-Liquid Equilibria in the Propane-1-Propanol System

Andre L. Mühlbauer and J. David Raal
Dept. of Chemical Engineering, University of Natal, Durban 4001, South Africa

High-pressure isothermal vapor liquid equilibrium data were measured for the propane-1-propanol system at 81.6, 105.2, and 120.1°C in a static equilibrium cell with liquid-phase sampling by a piston-driven sampling rod and homogenizing the sample with a static jet mixer. The vapor phase was sampled by releasing it into an evacuated manifold, and the gas chromatograph was calibrated with a new variable volumetric device. Satisfactory modeling was achieved with the combined method (Wichterle, 1978b) using the UNIQUAC equation with equations of state: the group contribution EOS (Skjold-Jorgenson, 1986), Peng-Robinson EOS (Peng Robinson, 1976) or the two-parameter Virial EOS. Differences between the measured and calculated vapor-phase mole fractions, however, were significant for the lower pressure regions of the 81.6 and 120.1°C isotherms.

UNIQUAC parameters a_{ij}, hitherto unavailable, with fairly strong temperature dependence in the 81.6 to 120.1°C range are proposed for the system. The covariance matrix indicated a significant correlation among the parameters. The classical mixing rule interaction parameters, δ_{ij}, required for the original Peng-Robinson EOS in the combined method were obtained using the direct method (Wichterle, 1978a) and were temperature-independent for the isotherms for which the propane was supercritical. The possibility of propane/1-propanol immiscibility was theoretically examined according to the criteria of Baker et al. (1982). The plots of Gibbs energy of mixing vs. phase mole fractions did not indicate liquid-phase splitting, but the inferences are EOS-dependent and must await visual confirmation. Our earlier vapor-phase thermodynamic consistency test (1991a) indicated the data for all three data sets not to be inconsistent.

Introduction

Recently, the separation of alcohols from mixtures by liquid-liquid or gas-liquid extraction has received much attention in the hope of finding an alternative to the energy-intensive distillation process. In the rapidly developing technology of supercritical extraction, considerable interest has been shown in high-pressure vapor-liquid equilibria for systems with carbon dioxide (Takishima et al., 1986), light hydrocarbons [methane, ethane (McHugh et al., 1983)], and propane and other solvents [1,1 Difluoroethane (Nakayama et al., 1987)].

Propane has been measured with the alcohols methanol (Galivel-Solastiouk et al., 1986) and ethanol (Gomez Nieto and Thodos, 1978).

A review of *Chemical Abstracts* and the *Data Bibliography* (Wichterle et al., 1973) revealed one reference for the propane/1-propanol system (Nagahama et al., 1971). The data were measured at low pressures (1 to 8 bar) and low temperatures (19.85°C). The *IUPAC Solubility Data Series* (Kertes and Hayduk, 1986) and *Dechema Chemistry Data Series* (Knapp et al., 1982), as well as a search of recent literature, revealed no reference for the high-temperature–high-pressure propane/1-propanol binary. Suzuki et al. (1990) reviewed measured binaries of importance to the syngas industry. The authors made no mention of high-pressure–high-temperature data for the propane/1-propanol binary.

Correspondence concerning this article should be addressed to J. D. Raal.

Present address of A. L. Mühlbauer: Shell & BP Petroleum Refineries (Pty) Ltd., P.O. Box 3179, Durban 4000, South Africa.

The accurate measurement of high-pressure vapor liquid equilibrium data is a very demanding task. Some of the problems encountered in static, circulation or flow-through methods include:

- Attaining true equilibrium which can be adversely affected even by the smallest temperature or pressure gradients
- Sampling from a high-pressure region without disturbing the equilibrium
- Proper homogenization of the sample where relative volatilities of the components may differ greatly, and conveyance of the samples without change in composition to a gas chromatograph
- Attaining leak-free seals in moving parts in high-pressure-high-temperature work due to the attrition or deformation of the sealing materials.

Thermodynamic interpretation and modeling of high-pressure equilibrium data is a much more difficult proposition than for the low-pressure case. Modeling either by direct methods (which involve the use of equations of state to describe both the liquid and vapor phase) or by the combined method (which involves the description of the liquid-phase nonideality via an activity coefficient) presents many problems not encountered in low-pressure analysis. These include finding an appropriate model for the Gibbs free energy, iterative methods for estimating the vapor-phase fugacity coefficients which are composition-dependent, evaluation of liquid molar volumes as a function of pressure and temperature and the problem of defining appropriate reference states for the fugacity when one component is noncondensable. In selecting an equation of state to model either the vapor phase (combined method) or both phases (direct method), difficulties arise in choosing appropriate mixing rules for the mixture for equations other than the virial equation of state. Such mixing rules are empirical and tend to become system-specific.

Relatively few researchers attempt thermodynamic consistency testing of high-pressure VLE data, probably because the procedures are complex and tedious and involve estimates of several quantities such as liquid- and vapor-phase fugacities and liquid molar volumes, all of which may be subject to greater or lesser error.

Experimental Equipment

Static experimental equipment

The experimental equipment was the result of much experimentation and has been described in detail (Mühlbauer and Raal, 1991; Mühlbauer, 1991).

Measurements were made in a 350 cm^3 static equilibrium cell capable of operating at up to 200 bar and 180°C. The equilibrium cell was mounted in an air bath with internal copper cladding to provide an isothermal environment, Figure 1. Considerable precautions were taken in the design of the bath to remove vertical temperature gradients induced by conduction and heater element radiation.

The sampling procedures were designed to cause minimal disturbance to the equilibrium condition. The vapor phase was sampled by releasing it into a 0.9 cm^3 evacuated manifold. A liquid-phase sample was obtained via a piston-driven sampling rod which removed an 8.8 mm^3 sample and released it into a previously evacuated jet mixer.

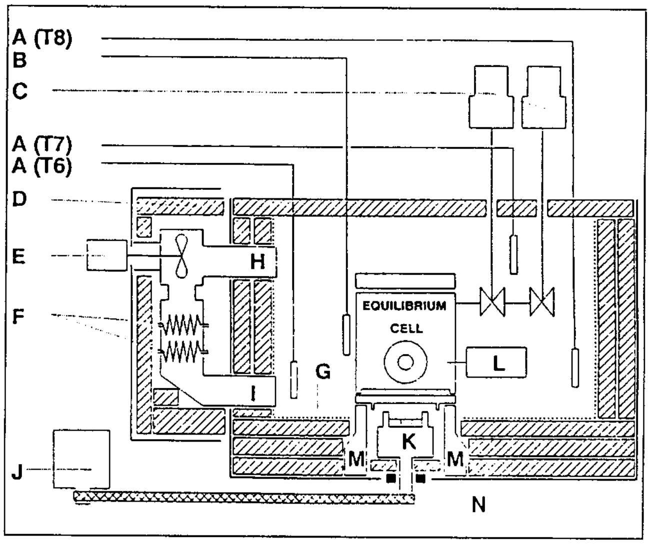

Figure 1. Equilibrium cell and air bath arrangement.

A = bath profiles
B = Eurotherm 818 controller Pt 100
C = vapor sampling valves
D = fiberglass insulation
E = Siflo fan
F = heaters
G = copper lining
H = air inlet
I = air outlet
J = variable speed motor
K = magnetic stirrer
L = jet mixer.

Homogeneity of the vapor and particularly of the liquid samples, an especially acute problem due to the volatility difference between the components, was ensured by the use of jet mixers (Figure 2). The liquid sample flashed into the initially evacuated jet mixer through the nozzle at high velocity to produce a swirling recirculating flow until the pressure became uniform. Further mixing was subsequently produced by flushing helium carrier gas through a passage in the cell wall into the mixer at a controlled pressure. The mixer was heated electrically to ±60° above the equilibrium temperature. The interior volume was dictated by the liquid sample size. A sensitive flush-mounted pressure transducer provided useful indications of the operation of the device. The compactness of the design and the absence of moving parts are distinct advantages for high-temperature work, and the device is recommended for other workers in the field.

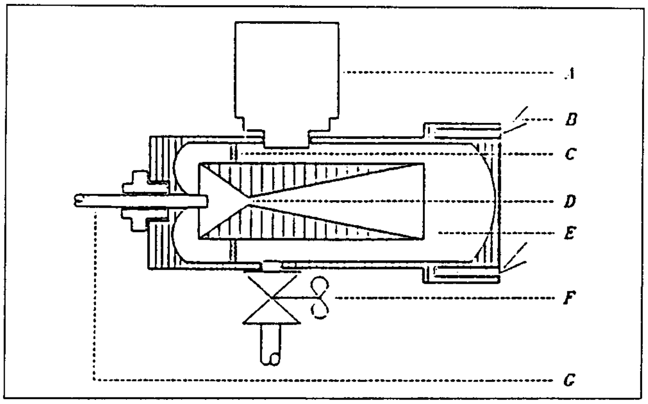

Figure 2. Jet mixer for vapor homogenization.

A = Sensotec pressure transducer
B = heating elements
C = nozzle support
D = nozzle orifice
E = mixing chamber
F = outlet valve
G = inlet from equilibrium cell

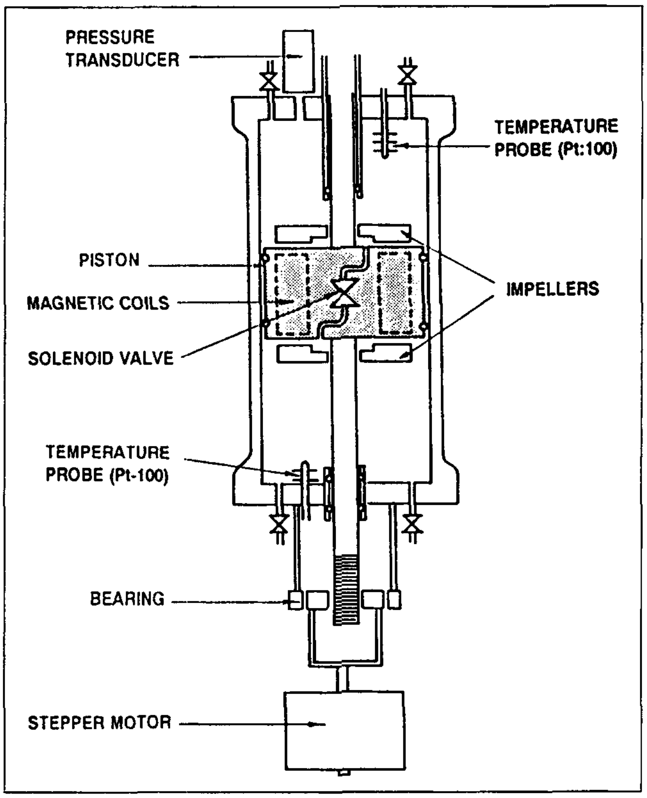

Figure 3. Gas chromatograph calibration device.

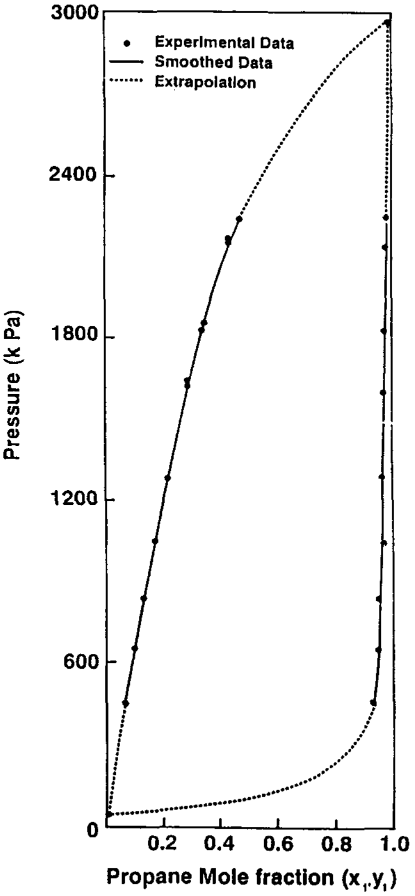

Figure 4. Phase equilibrium data at 81.6°C.

Auxiliary Equipment

Gas compression device

Since propane is subcritical at room temperature, the quantity of gas that can be added to the equilibrium cell is limited. A rough estimate of the amount could be obtained from the ideal gas law using the vapor pressure of propane at room temperature. Since the vapor pressure of propane at room temperature is 8 bar, the final pressure in the equilibrium cell, which may be achieved by simple heating as in the case of a supercritical gas such as carbon dioxide, is limited.

A procedure was therefore required to pressurize the propane/nonvolatile binary in the equilibrium cell. A simple device was designed (Mühlbauer, 1991) to heat and compress propane, supplied from a gas cylinder, to pressures above its bottle pressure. The heated and compressed propane was then forced into the equilibrium cell, thereby pressurizing the cell contents.

Gas chromatograph detector calibration device

Accurate GC (gas chromatograph) detector calibration is essential for accurate data. Calibration of the detectors for small quantities of propane in 1-propanol was possible by a unique gas detector calibration device, which was described in detail elsewhere (Raal, 1992). In essence, it incorporates variable-volume magnetically-stirred gas mixing chambers of patented design (Figure 3). These permit reproducible volume increments as small as 0.01% or less. Mixing is done at atmospheric pressure, and small corrections for nonideal gas behavior of the pure component is readily handled using the virial equation of state. Small quantities of propane were accurately diluted in a large quantity of nitrogen as diluent and analyzed. This is not the preferred operating procedure for the device, since peak areas still depended on the reproducibility of the amount injected, but the method gave satisfactory accuracy. (A further development of the detector calibration device incorporates a microliquid-droplet dispenser discharging onto an appropriate evaporating surface—this will permit more accurate calibration of liquid gas mixtures.)

Measuring devices

The equilibrium cell temperature was measured with a platinum resistance thermometer, calibrated against a Hewlett Packard 2801A Quartz thermometer. The temperature was within 0.25 K. The pressure was measured with either a 0-500 psi (0-3.4 MPa) or 0-5,000 psi (0-34.5 MPa) Heisse Bourdon pressure gauge factory calibrated to 0.1% of full scale. Sample analysis was by gas chromatography using a Varian 3000 Chromatograph employing both thermal and flame ionization detectors in series. Results from the two detectors were in close agreement. A 2.5-m-long, 3.175-O-D stainless-steel column, packed with 50 to 80 mesh Poropak Q, was used as the separating column. The conversion of peak area to moles resulted in an uncertainty in the calibrated mole fraction of ±2.5%.

Results

Chemicals

Certified instrument-grade propane, with a minimum stated purity of 99.5%, was supplied from Air Products (USA). 1-

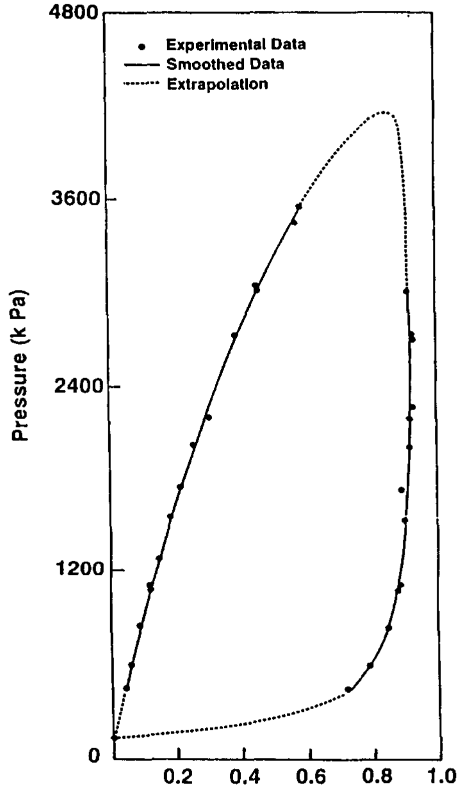

Figure 5. Phase equilibrium data at 101.1°C.

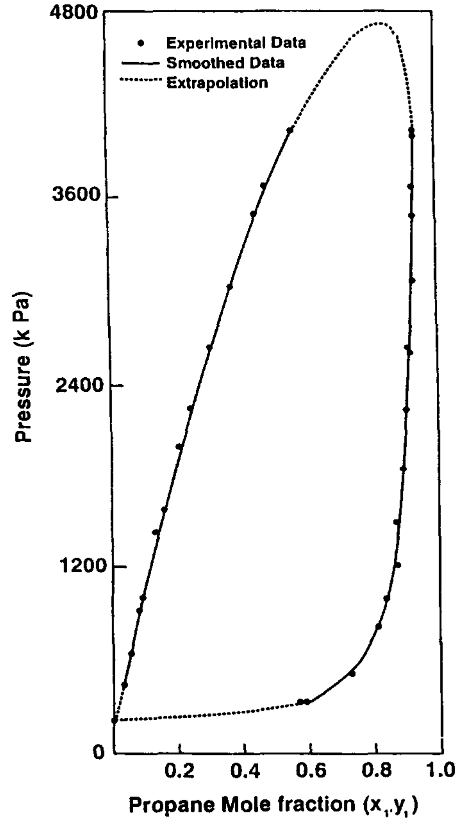

Figure 6. Phase equilibrium data at 120.1°C.

Table 1. Isothermal Phase Equilibrium Data for the Propane/1-Propanol System: Results for the 81.6°C Isotherm

Pres. bar (*a*)	Temp. °C	Propane Mole Fraction
	Liquid Phase (*x*)	
22.39	81.64	0.4709
22.39	81.64	0.4765
21.70	81.64	0.4346
21.70	81.64	0.4336
21.49	81.60	0.4353
18.53	81.58	0.3468
18.25	81.57	0.3378
16.18	81.64	0.2883
16.11	81.71	0.2876
12.80	81.62	0.2198
10.53	81.65	0.1690
8.18	81.67	0.1258
6.53	81.67	0.0973
4.53	81.60	0.0646
	Vapor Phase (*y*)	
22.39	81.71	0.9819
22.39	81.50	0.9843
21.35	81.66	0.9796
21.35	81.63	0.9760
18.11	81.56	0.9752
18.11	81.73	0.9719
15.97	81.66	0.9714
15.97	81.68	0.9687
12.80	81.65	0.9665
10.39	81.54	0.9665
8.18	81.63	0.9530
6.46	81.62	0.9472
6.46	81.64	0.9404
4.53	81.61	0.9264

Propanol, glass-distilled and filtered through 0.5-μ filters of HPLC grade, with minimum purity of 99.9%, was supplied from Aldrich. The main impurity was water with 0.3%.

Refractive index measured with a high-precision refractometer was 1.38449 for 1-propanol (at 19.9°C) compared to the literature value of 1.3850 (20°C) (Weast et al., 1984). Gas chromatograph analyses for the 1-propanol showed no trace of impurities. The purity of the propane supplied by Air Products was determined by gas chromatography analysis to be 99.48% compared with the stated purity of 99.5%. The main impurities were ethane with 0.01%, isobutane with 0.35%, and *n*-butane with 0.3%.

Experimental phase equilibrium results

The experimental phase equilibrium measurements for the propane/1-propanol system at temperatures of 81.62, 105.22 and 120.05°C are shown in Figures 4 to 6 and Tables 1 to 3. Vapor and liquid mole fractions are given separately. When total system pressure was affected by vapor or liquid sampling, the system was reequilibrated before further sampling and the data are thus not given in pairs at exactly the same pressure.

Cell temperature and pressure changes

The temperature varied approximately 0.2, 0.8 and 0.4 K over the entire run for the three isotherms at 81.62, 105.22 and 120.05°C, respectively. The liquid-phase mole fractions, measured at the same pressure, were reproducible to within

Table 2. Isothermal Phase Equilibrium Data for the Propane/1-Propanol System: Results for the 105°C Isotherm

Pres. bar (*a*)	Temp. °C	Propane Mole Fraction
	Liquid Phase (*x*)	
35.49	105.53	0.5886
35.49	105.53	0.5864
34.45	105.22	0.5758
34.45	105.22	0.5746
30.32	105.02	0.4588
30.14	105.23	0.4584
27.21	105.31	0.3874
23.08	105.24	0.3071
20.25	105.18	0.2552
17.49	105.19	0.2139
15.56	105.14	0.1877
12.80	105.33	0.1484
11.05	105.19	0.1220
10.80	105.24	0.1219
8.46	105.28	0.0887
6.11	105.40	0.0610
5.00	105.40	0.0601
	Vapor Phase (*y*)	
29.97	105.25	0.9161
27.21	105.22	0.9296
27.14	105.23	0.9294
23.08	105.16	0.9230
32.08	105.38	0.9204
23.08	105.24	0.9159
20.18	105.36	0.9067
17.49	105.25	0.8935
15.49	105.19	0.9014
11.15	105.26	0.8864
11.15	105.18	0.8871
10.80	105.16	0.8779
8.46	105.16	0.8513
8.46	105.12	0.8489
6.05	105.16	0.7924
4.58	105.15	0.7209

Table 3. Isothermal Phase Equilibrium Data for the Propane/1-Propanol System: Results for the ±120°C Isotherm

Pres. bar (*a*)	Temp. °C	Propane Mole Fraction
	Liquid Phase (*x*)	
40.45	120.27	0.5613
40.31	120.22	0.5652
40.31	120.41	0.5627
36.73	120.01	0.4782
34.97	120.03	0.4448
31.21	120.36	0.3689
31.21	120.32	0.3674
26.52	120.02	0.2999
22.46	119.33	0.2424
22.46	120.22	0.2402
19.97	120.04	0.2045
15.84	120.04	0.1585
13.29	120.00	0.1288
10.05	119.92	0.0904
9.22	119.94	0.0787
6.39	119.98	0.0493
6.39	120.17	0.0485
4.53	120.14	0.0297
	Vapor Phase (*y*)	
40.31	119.28	0.9355
40.11	120.21	0.9327
36.73	119.94	0.9273
34.80	120.25	0.9304
30.66	119.96	0.9199
30.66	120.21	0.9350
26.52	119.94	0.9100
26.18	119.96	0.9149
22.32	120.22	0.9036
22.32	120.03	0.8969
19.63	120.31	0.8900
16.11	119.98	0.8681
13.22	119.99	0.8701
10.05	120.17	0.8356
9.22	119.94	0.8144
6.32	120.17	0.7364
6.32	120.04	0.7122
4.53	119.86	0.5890
4.46	120.15	0.5762

1% of each other. The vapor pressures were reproduced to within 2.5%. During the sampling process, the internal cell temperature changes did not exceed 0.2 K.

Theoretical Analysis

Three computer programs were written: fitting program, correlation program, and consistency test program.

Fitting program

The fitting program was based on the combined method as suggested by Prausnitz et al. (1980). This program was used to fit VLE data at a given temperature to a liquid-phase model for activity coefficients. In the original Prausnitz program, the two-parameter virial equation of state was selected for the description of the vapor phase. The Prausnitz program was expanded in this project to accept the Peng Robinson and Group Contribution equations of state. This program yielded values of the UNIQUAC binary interaction constants a_{ij}, Eq. 1, for each temperature:

$$a_{ij}=\frac{\Delta U_{ij}}{R}\quad (R=83.147) \tag{1}$$

The most important feature of the Prausnitz et al. (1980) program is the attempt to properly account for all measurement errors. This is in contrast to other parameter estimation methods which give only estimates for the parameters and no measure of their uncertainty. The regression procedure was based on a general application of the maximum likelihood principle, as described by Anderson et al. (1978).

The Prausnitz et al. (1980) program uses the combined method:

$$x_i\gamma_i f_i^{OL}=y_i\phi_i^v P \tag{2}$$

to seek the parameters that minimize the objective function (S):

$$S=\sum_{j=1}^{m}\left|\frac{(P_i^c-P_i^e)^2}{\sigma_P^2}+\frac{(T_i^c-T_i^e)^2}{\sigma_T^2}+\frac{(x_i^c-x_i^e)^2}{\sigma_x^2}+\frac{(y_i^c-y_i^e)^2}{\sigma_y^2}\right|$$

where m is the number of data points, σ the estimated variance of the particular measurement, and superscripts c and e denote the calculated and experimental values, respectively.

The chosen parameter variance and covariance matrices, which give an indication of the uncertainties of the parameters, were obtained as a last step in the iterative calculation of the parameters. The percentage confidence ellipses (regions within which the parameters can be expected to lie at the confidence level associated with the ellipse) were then calculated from the eigenvalues and eigenvectors of the variance and covariance matrix.

In addition to the variance-covariance matrix, the maximum likelihood method also generates the calculated "true" values with respect to the model chosen of each measured variable in the course of the parameter estimation. The difference between these "true" values and experimentally measured values will be referred to as residuals. Examination of the residuals, when plotted against another system variable such as liquid mole fraction, may provide useful information on excessive experimental error, systematic error, "bad" data points or lack of model fit.

Correlation program

The correlation program permitted prediction of total pressures and vapor-phase compositions for given experimental temperatures and liquid-phase compositions by the combined method, which is essentially a bubble point computation. This constituted a test of the accuracy of the UNIQUAC parameters obtained from the fitting program.

Consistency test program

The consistency test program allowed for thermodynamic consistency testing of the data according to the vapor-phase (Mühlbauer and Raal, 1991) consistency test.

Liquid-phase fugacity

For the two highest isotherms (105.2°C and 120.1°C), propane was mildly supercritical. Even at the highest temperature, since $T/T_c = 1.06$, which is much below the upper limit of 1.8 recommended by Prausnitz et al. (1980), propane was considered a condensable gas: the symmetric convection for normalizing the activity coefficients was used for both components. Pressure-independent liquid-phase activity coefficients as defined by Prausnitz et al. (1980) were used in all calculations.

$$\gamma_i^{(pr)} = \gamma_i^{(p)} \exp \int_{p}^{p^r} \frac{\bar{V}_i^L}{RT} dp \tag{3}$$

In order that $\gamma_i^{(pr)} \to 1$ as $x_i \to 1$ for the condensable component, the standard state fugacity f_i^{OL} must be that of pure liquid i at the solution temperature and reference pressure $p^r \cdot f_i^{OL}$ is then given by:

$$f_i^{OL} = p_i^{\text{sat}} \phi_i^{\text{sat}} \exp \int_{p_i^{\text{sat}}}^{p^r} \frac{V_i^L}{RT} dp \tag{4}$$

Standard state fugacities consistent with Eq. 4 were computed as functions of temperature using a polynomial expression with constants evaluated by Prausnitz et al. (1980) for the pure components.

As in previous studies on another system (Mühlbauer and Raal, 1991), the reference pressure p^r is set equal to zero for both components. Since information for evaluating partial molar volumes is seldom available, it is assumed that $\bar{V}_i^L = V_i^L$.

Vapor-phase fugacity

The vapor-phase fugacity coefficient can be calculated using the integrated form of the exact thermodynamic relationship:

$$\ln \phi_i^v = \left(\frac{1}{RT}\right) \int_{V^v}^{\infty} \left[\left(\frac{\partial P}{\partial n_i}\right)_{(T,V,n_{j\neq i})} - \frac{RT}{V^v} \right] dV - \ln \left[\frac{PV^v}{n_T RT} \right] \tag{5}$$

together with any equation of state judged suitable for the system and conditions. In this study, it was decided to use the two-parameter truncated virial EOS, Peng and Robinson EOS in its original form (1976) and the group contribution EOS (Skjold-Jorgenson, 1986) for the propane/1-propanol system.

The virial EOS is attractive as it is soundly-based theoretically, and the mixture second virial coefficient B_{mix} is related to the pure component and cross second virial coeffficients by an exact expression.

The correlating ability of the virial EOS is limited to low to moderate pressures, for example, $P < 20$ bar. System-specific interaction parameters, which would not be available for an unmeasured system, are not required. As in the Prausnitz et al. (1980) program, the B_{ij}'s were evaluated as functions of temperature from the Hayden and O'Connel (1975) corresponding states correlation.

The Peng and Robinson EOS (and its several modifications) has been widely used for phase equilibrium correlations. An important drawback in using this EOS for the vapor-phase description is the necessity for interaction parameters in the attraction and covolume parameters:

$$a = \sum \sum_j y_i y_j (1 - \delta_{ij}) a_i^{0.5} a_j^{0.5} \tag{6}$$

$$b = \sum_j y_i b_i \tag{7}$$

Binary interaction parameters δ_{ij} for the "classical mixing rule," Eq. 6, were not available for the temperature range of interest. The δ_{ij}'s for the propane/1-propanol system were generated from experimental VLE data in a manner similar to that used by Mohammed and Holder (1987) and by Ng and Robinson (1978).

The Group Contribution EOS is attractive in that it does away with the need for binary interaction parameters and can describe polar substances. For high pressures, this EOS is considered superior to the two-parameter virial EOS.

For the group contribution EOS the propane/1-propanol components had to be dissected into their appropriate groups. The groups chosen to represent the above two molecules are listed in Table 4.

UNIQUAC parameters obtained from the fitting program

Using the virial, Peng-Robinson and group contribution EOS, the UNIQUAC interaction parameters obtained from

Table 4. Pure Group Parameters for Group Contribution EOS for Propane and *n*-Propanol*

Component	Group	Designated Component**	v_j^i
Propane	C_3H_8	34	1
1-Propanol	CH_3	1	1
	CH_2	2	1
	CH_2OH	20	1

* From Skjold-Jorgensen (1988).
** Component reference number.

the fitting program on the experimental data sets in Tables 1 to 3 are shown in Figures 7 and 8 and Table 5.

Analysis of the covariance matrix for the various data sets permitted the plotting of the 90% and 95% confidence regions as described by Beck and Arnold (1977). They were elongated shapes indicating that the two parameters were highly correlated. The correlation matrices with diagonal values in the region of 0.9 also indicated a high degree of parameter correlation.

All parameters for this binary are strongly temperature-dependent, as was the case with the carbon dioxide/toluene system (Mühlbauer and Raal, 1991). The UNIQUAC parameters were found to be vapor-phase-description-dependent. Interestingly enough for the propane/1-propanol binary the parameters follow the same trend, Figures 7 and 8, for two of the EOS (virial and GC). The virial- and GC-derived parameters also lie within overlapping confidence regions. The exceptions are a_{12} and a_{21} derived with the Peng Robinson EOS.

A high degree of correlation implies that many sets of parameters can represent the data equally well. Realistic data reduction can therefore determine only the parameters within a region. The "nonuniqueness" of parameters is not confined to the combined method. Fink and Hershey (1990) obtained P-R EOS parameters for the carbon dioxide/toluene binary from various literature sources using the direct method. They reported the interaction parameter values to be data-origin-dependent. *P*, *T*, *x* and *y* residuals (not shown) were obtained for the three EOS. The *P*, *T* and *x* residuals appeared to be randomly distributed and had zero means. The *y* residuals for this binary, in contrast to the carbon dioxide/toluene binary for example, were all positive and decreased with increasing pressure.

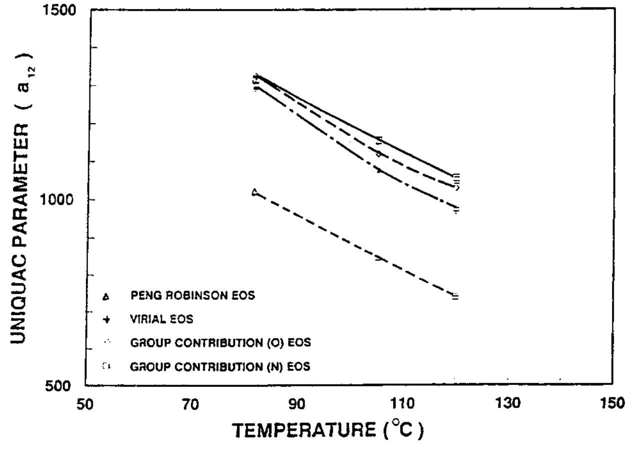

Figure 7. UNIQUAC parameter a_{12} as a function of temperature.

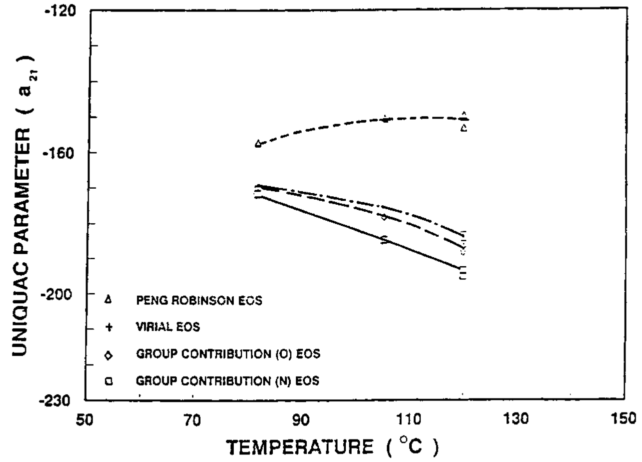

Figure 8. UNIQUAC parameter a_{21} as a function of temperature.

Pressure and vapor-phase composition prediction

The predicted vapor-phase compositions and total pressures generated from the correlating program are shown in Figures 9 to 11. A plot of the *K* values for the group contribution EOS and UNIQUAC correlation is given in Figure 12. Surprisingly, significant differences between the measured and calculated vapor-phase mole fractions are observed for the lower pressure regions for the 81°C and 120°C isotherms. This would suggest that the measured pressure was either too low if the composition was measured correctly or the measured vapor mole fraction too high if the pressure was measured correctly or a combination of both. The maximum differences certainly are larger than can be accounted for by uncertainties in the experimental measurements. The reason for the observed discrepancy is not clear, but may be due to one of the following possibilities:

Table 5. Propane and 1-Propanol System: UNIQUAC Parameters as a Function of Temperature

Temp. °C	Regression Type	Equation of State Virial	 GC*	 PR**
		UNIQUAC Parameter a_{12} (K)		
81.62	PTXY	1,371	1,325	1,021
81.62	PTX	1,313	1,322	1,020
105.11	PTXY	1,153	1,118	846
105.11	PTX	1,155	1,119	847
120.05	PTXY	1,055	1,028	747
120.05	PTX	1,049	1,022	739
		UNIQUAC Parameter a_{21} (K)		
81.62	PTXY	−171.8	−170.0	−157.2
81.62	PTX	−171.5	−169.6	−156.9
105.11	PTXY	−184.7	−178.2	−150.3
105.11	PTX	−184.9	−178.4	−150.6
120.05	PTXY	−195.1	−188.4	−153.1
120.05	PTX	−193.5	−186.8	−149.5

* Group contribution EOS.
** Peng and Robinson EOS.

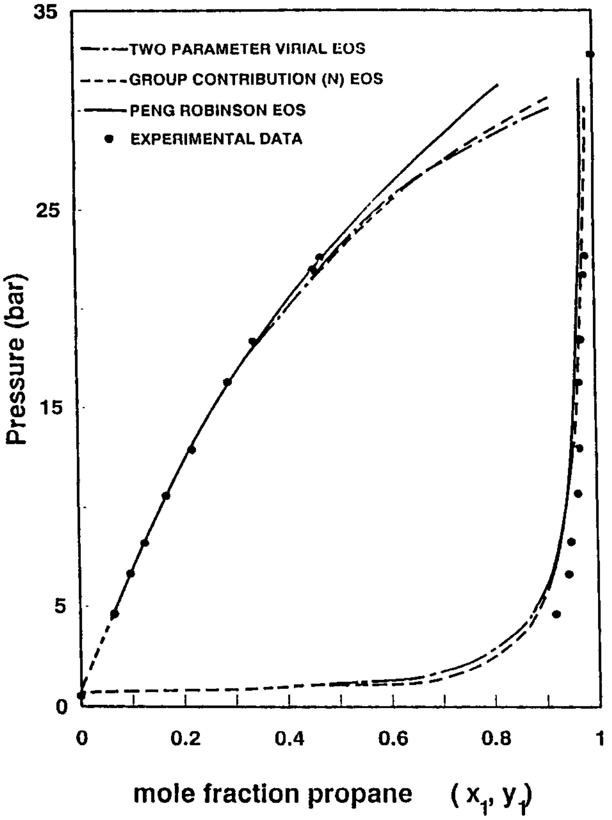

Figure 9. Comparison between predicted and experimental VLE at 81.6°C.

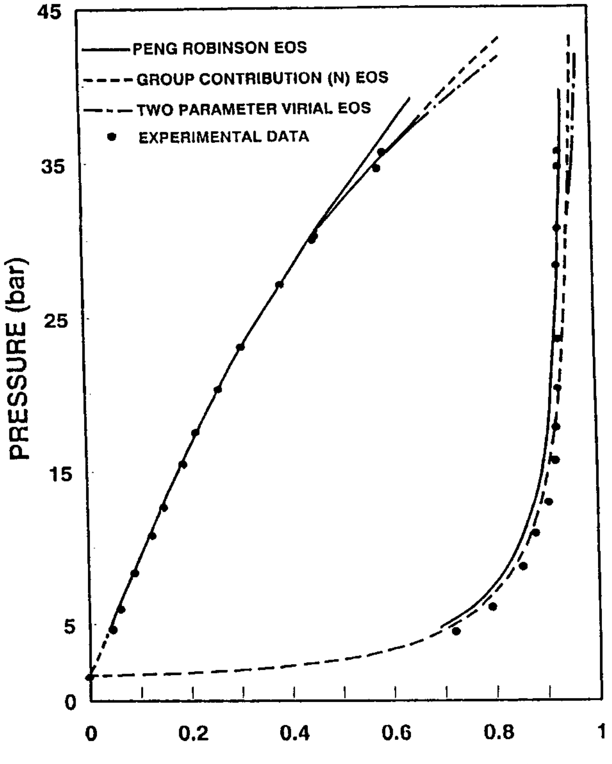

Figure 10. Comparison between predicted and experimental VLE at 105.1°C.

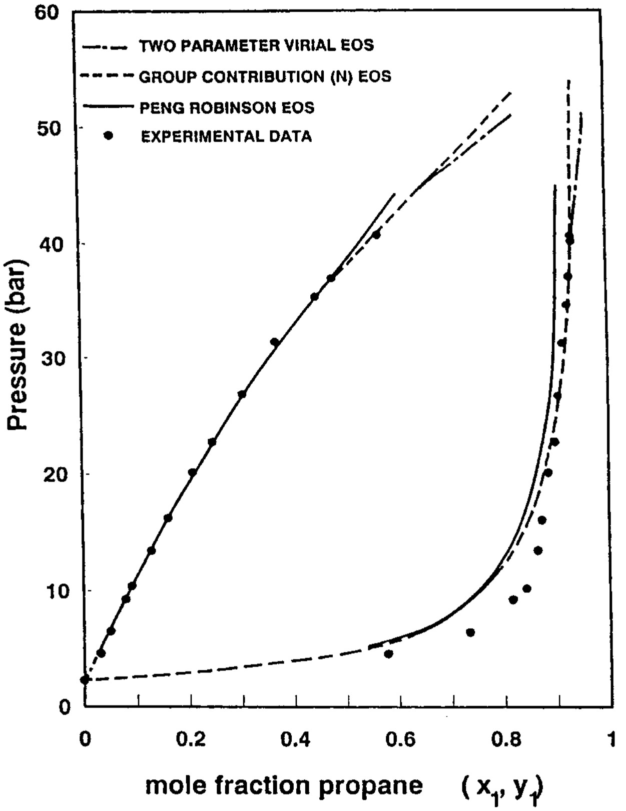

Figure 11. Comparison between predicted and experimental VLE at 120.1°C.

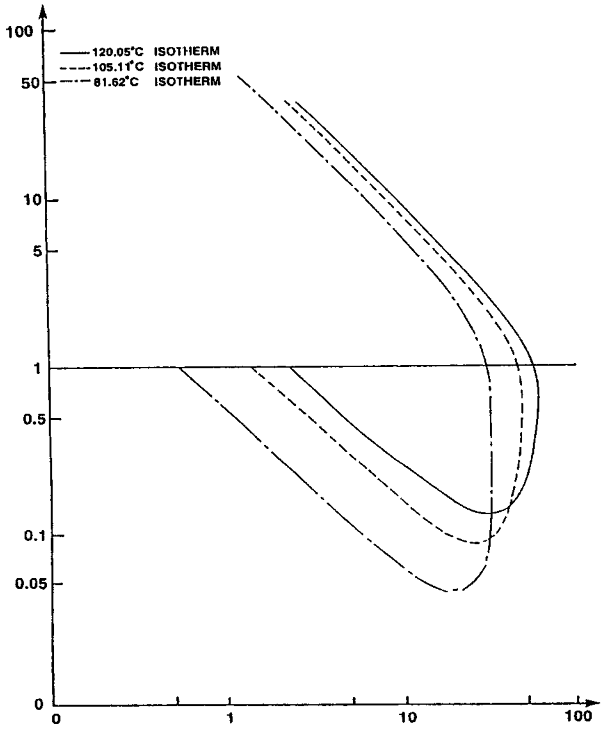

Figure 12. Equilibrium *K* values vs. pressure using the group contribution EOS.

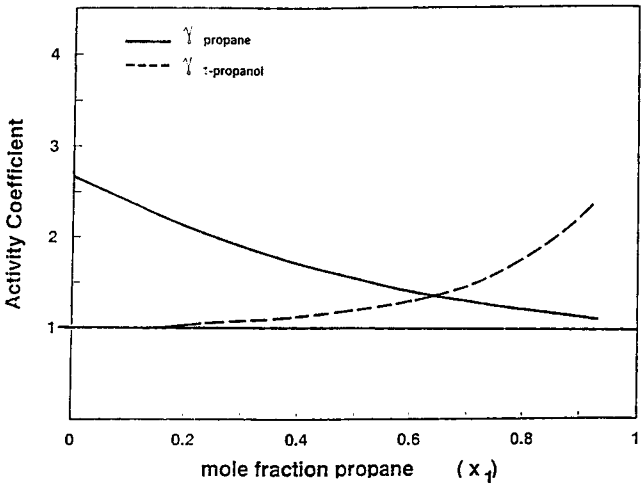

Figure 13a. Liquid-phase activity coefficients at 81.6°C.

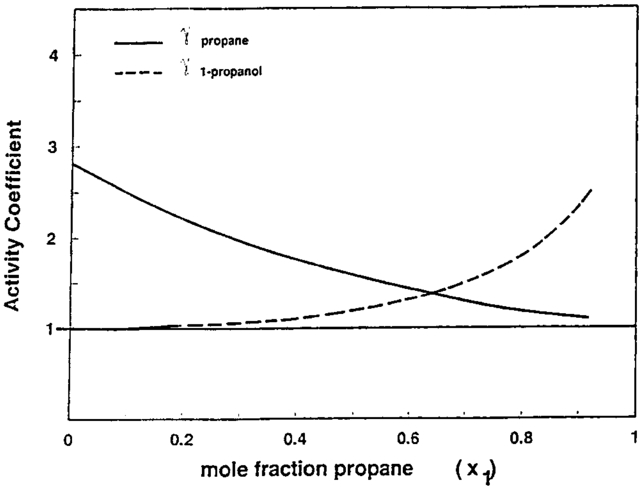

Figure 13b. Liquid-phase activity coefficients at 105.1°C.

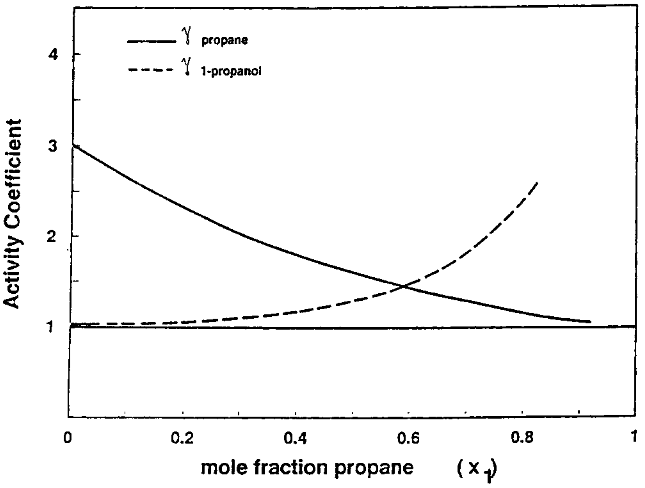

Figure 13c. Liquid-phase activity coefficients at 120.1°C.

- The liquid- and vapor-phase models chosen, that is, the UNIQUAC equation and the various EOS, were incapable of adequately describing the propane/1-propanol system. Since the predictions for all the different EOS's were similar this suggests that either the UNIQUAC equation or the various EOS's are not capable of describing the polar component, 1-propanol.
- The experimental data are incorrect. This is unlikely for experimental data, if measured carefully, are usually more reliable than theoretical predictions. This may be particularly true when EOS's are used for polar components such as 1-propanol. Also the same equipment and procedures previously produced very accurate data for other systems (for example, Mühlbauer and Raal, 1991).
- Another possible explanation is not related to the measurements or the theory but to the purity of the propane. As already explained, the highest purity propane available had minor contaminants of ethane and butane. The contaminants, effective diluents in the propane, may compete with 1-propanol at low pressures resulting in a lower 1-propanol presence in the vapor phase than those with pure propane. This explanation was deemed unlikely since it would not explain more satisfactory correlations for the 105°C data or the better fit at higher pressures. For the propane-water system (Mühlbauer and Raal, 1992), good agreement with literature values was obtained with a similar grade of propane.

The most likely explanation is therefore the inability of the UNIQUAC and/or the EOS to accurately describe the behavior of the polar/nonpolar binary mixture.

Activity coefficients

Liquid-phase activity coefficients are shown for three temperatures in Figures 13a, 13b, and 13c.

Additional numerical experiments

To resolve the discrepancy between measured and predicted $y_i(p)$ in the lower pressure range two further numerical experiments were performed. As an experiment, the data were fitted to the UNIQUAC equation by minimizing the objective function:

$$S=\sum_{i=1}^{m}\left|\frac{(P_i^c-P_i^e)^2}{\sigma_P^2}+\frac{(T_i^c-T_i^e)^2}{\sigma_T^2}+\frac{(x_i^c+x_i^e)^2}{\sigma_x^2}\right| \tag{8}$$

which is a regression of P-T-x data only.

The UNIQUAC parameters obtained, Table 5, differed only slightly from those obtained for the P-T-x-y data regression. The confidence regions were smaller, however, implying greater confidence in the calculated parameters. The residuals, however, still showed the same trends and were of similar magnitudes.

As a further experiment, experimental data were fitted using the NRTL equation for the liquid-phase parameters with the virial and group contribution EOS for the vapor phase. The third parameter in the NRTL equation, a, was set either to -1 or 0.3 according to the recommendations of Marina and Tassios (1973) and Behrens and Eckemann (1979) or allowed to vary freely. No satisfactory convergence was achieved in either case.

Liquid-liquid immiscibility

No convergence was achieved in the high-pressure regions when the correlation program was based on the UNIQUAC equation and the Peng-Robinson EOS. A very liberal pressure convergence criterion was adopted. The resulting pressure vs. propane mole fraction generated suggested the possible formation of a liquid-liquid equilibrium region much like the one shown in Vidal (1984) for the ethane/methane system. Swartzenruber et al. (1987) depicted unusual behavior near the critical point for the propane-methanol system and found systematic deviations in predicted vapor-phase compositions.

To test the possibility of liquid-liquid immiscibility, plots of the Gibbs energy of mixing vs. composition were constructed. The necessary and sufficient conditions for stability of phase equilibrium solutions have been developed by Baker et al. (1982). The plots based on the UNIQUAC equation and the virial and P-R EOS did not indicate liquid-phase splitting. The results, however, are equation-of-state-dependent and must await confirmation by visual observation, which was not possible in our equipment.

Peng-Robinson-interaction parameters

The experimental data obtained in this work made it possible to calculate the Peng-Robinson EOS binary interaction parameter for the propane/1-propanol system. The procedures, although complex, are well known (see, for example, Smith and Van Ness, 1987) and are based on the equality of fugacities in the liquid and vapor phases, $y_i\hat{\phi}_i^v = x_i\hat{\phi}_i^L$. The optimum interaction parameter δ_{ij} in Eq. 6 for evaluating parameter a_m in the P-R EOS was determined with a Simplex nonlinear least-squares regression program.

Due to the nature of the Simplex program, regression on only one dependent variable was possible. Since pressure is a crucial measurement in isothermal systems, it was chosen as the dependent variable. The vapor mole fraction was chosen for the convergence criterion. Therefore, the value of δ_{ij} obtained was the one that gave the minimum deviation between the experimental and predicted bubble point pressures in the direct method using the objective function:

$$S = \sum_{i=1}^{m} (P_i^{\text{calc}} - p_i^{\text{exp}})^2$$

The secant method was used to obtain the calculated pressure corresponding to the estimate of δ_{ij} in each successive regression iterational loop by solving for:

$$\sum (y_i - 1) \leq 0.0001$$

The Peng-Robinson interaction parameters obtained are listed in Table 6.

Thermodynamic consistency test

A consistency test based only on vapor-phase properties and compositions was derived by Mühlbauer and Raal (1991):

$$\int_{y_2=0}^{y_{2_c}} \ln(\hat{\phi}_2^v/\hat{\phi}_1^v)dy_2 + \int_{p_1^{\text{sat}}}^{p_c} \frac{V^v}{RT}dp = [\ln \hat{\phi}_1^v P + y_2 \ln \hat{\phi}_2^v/\phi_1^v]_{y_2=0}^{y_{2_c}} \quad (9)$$

Table 6. Peng and Robinson Interaction Parameter

Temp. (°C)	δ_{ij}
81.62	0.05870
105.11	0.06859
120.05	0.06831

This test requires neither liquid-phase volumetric data nor limiting values of the equilibrium constant ratio K_1/K_2. The results, Table 7, are appreciably model-dependent, but confirm that the data are not thermodynamically inconsistent. In particular, it may be noted that the indicated consistency for the data at 120°C is at least as good as for the data at 105.2°C.

Conclusion

Experimental studies

The static equilibrium equipment described was designed to measure vapor-liquid equilibrium data for temperatures and pressures of up to 200°C and 20 MPa, respectively. The results obtained for the very demanding carbon dioxide/toluene test system with the same equipment were in good agreement with published data. This gives a high degree of confidence in the new data for the propane/1-propanol system.

Isothermal bath conditions were achieved with a copper-clad air bath incorporating an external air circulation loop. The loop shielded the equilibrium cell from direct radiative interchange with the heaters. The individual samples were fully homogenized and showed no concentration profile over successive flushing to the gas chromatograph. The incorporation of two static jet mixers with no moving parts and relying only on carrier gas to homogenize the liquid sample is a particularly novel and successful feature.

Theoretical: fitting and correlation

In view of the tedious nature and expense of high-pressure vapor-liquid equilibrium data gathering, it is highly desirable to obtain the largest prediction capability from the minimum number of experiments. Modified *regression fitting* and *correlation* programs were developed based on those published by Prausnitz and coworkers for the combined method for low to moderate pressure analysis. These were implemented, with greater success for the carbon dioxide/toluene binary than for the propane/1-propanol binary. The noncondensable component in each case was treated as a condensable one whose properties could be found by extrapolation. Temperature-dependent values of the UNIQUAC interaction parameter a_{ij}, hitherto not available, are proposed for the propane/1-propanol system for temperatures in the 80°C to 120°C range.

For the propane/1-propanol binary use of the UNIQUAC, a_{ij} parameter values gave progressively less satisfactory modeling when combined with the group contribution, virial and Peng-Robinson equations of state in the fitting and correlation programs. The deviation between experimental and theoretically calculated values was most marked in the lower-pressure regions of the vapor-liquid coexistence curve. The thermodynamic consistency tests performed on the data showed marginally higher absolute inconsistencies than for the carbon dioxide/toluene binary (Mühlbauer and Raal, 1991), for example. This can most likely be ascribed to the inability of the

Table 7. Interval Comparison of Vapor-Phase Consistency Test Propane/1-Propanol System

Mole Fraction Propane y	Area 1	Area 2	LHS	RHS	% Diff.
Temperature: 81.62°C					
		Vapor-Phase Model: Two-Parameter Virial			
0.8200	0.0275	1.6649	1.6924	1.6727	1.17
0.9665	0.0333	2.9408	2.97413	2.8777	3.29
0.9831	0.0357	3.6925	3.7282	3.5239	5.63
		Vapor-Phase Model: Group Contribution			
0.8200	0.0117	1.6681	1.6798	1.6660	0.82
0.9665	0.0164	2.8877	2.9040	2.8740	1.03
0.9831	0.0192	3.5318	3.5511	3.5168	0.97
Temperature: 105.22°C					
		Vapor-Phase Model: Two-Parameter Virial			
0.4000	0.0225	0.6913	0.7138	0.6965	2.46
0.8489	0.0528	1.1812	1.8711	1.7952	4.13
0.8489	0.0597	2.5431	2.6028	2.4547	5.85
0.9300	0.0620	3.0849	3.1469	2.9011	8.12
		Vapor-Phase Model: Group Contribution			
0.4000	0.0199	0.6833	0.6953	0.6914	0.56
0.8489	0.0367	1.7647	1.8014	1.7852	0.90
0.8489	0.0459	2.4190	2.4649	2.4443	0.84
0.9300	0.4977	2.8523	2.9021	2.8797	0.77
Temperature: 120.05°C					
		Vapor-Phase Model: Two-Parameter Virial			
0.4000	0.0278	0.5120	0.5339	0.5208	3.60
0.8200	0.0575	1.4112	1.4688	1.3979	4.94
0.8999	0.0662	2.3020	2.3682	2.1997	7.37
0.9335	0.0732	2.8849	2.9581	2.663	10.37
		Vapor-Phase Model: Group Contribution			
0.4000	0.0136	0.5019	0.5155	0.5140	0.28
0.8200	0.0326	1.3650	1.3976	1.3857	0.85
0.8999	0.0408	2.1666	2.2074	2.1884	0.86
0.9335	0.0498	2.6149	2.6647	2.6439	0.78

equations of state to describe the polar 1-propanol component. Some of the many modifications of the P-R EOS (for example, Stryjek and Vera, 1986) may give improved predictions for the system studied, which may well require an EOS with two adjustable parameters.

Classical mixing rule interaction parameters (δ_{ij}) for the Peng-Robinson EOS were obtained for the propane/1-propanol system. The value of δ_{ij} obtained was the one that gave the minimum deviation between the measured and predicted bubble point pressures. The value of δ_{ij} obtained for the supercritical propane isotherms were temperature-independent.

Consistency Testing

The newly developed equal-area vapor-phase test showed the data sets not to be inconsistent. All three sets are of similar consistency.

Notation

a = Peng and Robinson attraction parameter
a_{ij} = UNIQUAC interaction parameter, K
b = Peng and Robinson covolume parameter
B = 2nd virial coefficient in Virial EOS
f = fugacity
f^{0L} = standard state liquid fugacity
G = Gibbs free energy
K = equilibrium K values
n = number of moles
P = pressure
R = ideal gas constant
S = objective function
T = temperature
ν_j^i = number of groups j in molecule i (group contribution EOS)
V = molar volume
x = liquid phase mole fraction
y = vapor phase mole fraction

Greek letters

δ = Peng and Robinson interaction parameter
ϕ = fugacity coefficient
γ = activity coefficient

Superscripts

L = liquid phase
s = saturated
v = vapor phase
$\hat{}$ = quantity's value when component is part of a mixture

Subscripts

c = critical property

i, j = component identification
ij = interaction of component 1 and j
m = mixture

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