Vapor−Liquid−Liquid Equilibria, Azeotropic, and Excess Enthalpy Data for the Binary System *n*-Undecane + Propionamide and Pure-Component Vapor Pressure and Density Data for Propionamide[†]

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Vapor−liquid−liquid equilibria (VLLE), azeotropic, and excess enthalpy (H^E) data for the binary system *n*-undecane + propionamide were measured at temperatures from 359.25 to 416.65 K. Additionally, pure-component vapor pressure and density data for propionamide were determined experimentally. The LLE and VLLE measurements were performed in a stirred glass cell and in a static equilibrium cell with a capability to take small samples from the different phases by using pneumatic micro samplers. For the H^E measurements, an isothermal flow calorimeter was used, and the azeotropic data were obtained from distillation experiments using a micro spinning band column. The pure-component vapor pressures and densities were measured with the help of the dynamic method (ebulliometer) and a vibrating tube densimeter, respectively. To the experimental mixture data from this work linear temperature-dependent interaction parameters for the NRTL model were fitted. They can be used to represent the phase equilibrium behavior and excess enthalpies of the investigated system.

Introduction

For the synthesis, design, and optimization of separation processes, thermodynamic models (G^E models, equations of state, group contribution methods) can be applied. For the development of group contributions, a reliable knowledge of the phase equilibrium behavior is required and, consequently, a systematic extension of the existing database is desired.

For the binary system *n*-undecane + propionamide, only limited experimental information are available in the literature. Azeotropic data for this system were measured by Bruner and Darden (1952).[1] They are also published in the data collection of Gmehling et al. (2004).[2] In this work, several thermodynamic properties (vapor−liquid−liquid equilibria, excess enthalpies, azeotropic data, pure-component vapor pressures, and densities) were measured using different experimental approaches. In addition to the VLLE or azeotropic data, excess enthalpy data are also important to describe the temperature dependence of the activity coefficients following the Gibbs−Helmholtz equation

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_{P,x} = \frac{\overline{H}_i^E}{R} \qquad (1)$$

The experimental data of this work are presented together with calculated results using the parameters for the nonrandom two-liquid (NRTL) model[3] obtained by correlating the experimental mixture data.

This system was studied as part of an ongoing investigation sponsored by Project 805(F)/01 of the Design Institute for Physical Property Data of the American Institute of Chemical Engineers.

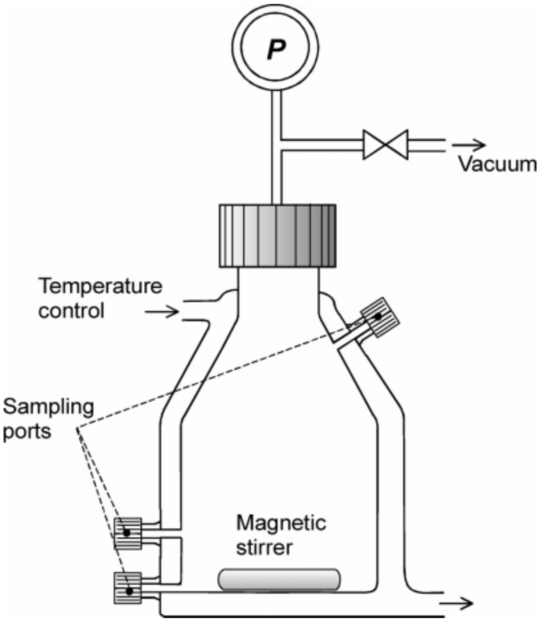

Figure 1. Schematic diagram of the glass LLE cell.

Experimental Section

Chemicals. The chemicals were purchased from commercial sources. They were used without further purification. The final purity and water content of the components were checked by gas chromatography and Karl Fischer titration, respectively (*n*-undecane, Aldrich, >99.9%, water content < 10 mass ppm; propionamide, ABCR, >99.9%).

Apparatus and Procedure. The LLE measurements (x', x'', T data) were performed in a stirred glass cell. The

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[†] This will be part of a special print edition containing papers reporting experimental results from the various projects of the Design Institute for Physical Properties of the American Institute of Chemical Engineers.

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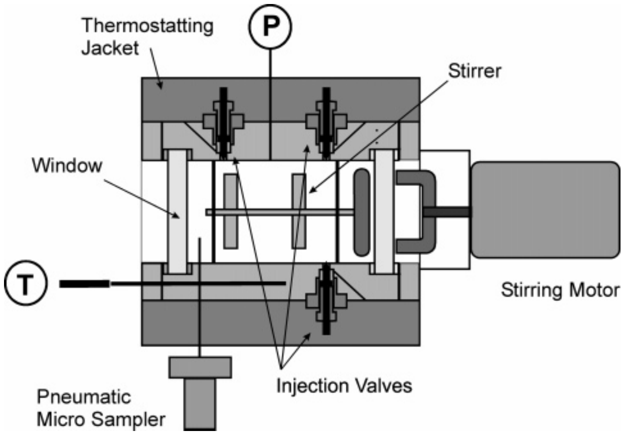

Figure 2. Schematic diagram of the static high-pressure cell.

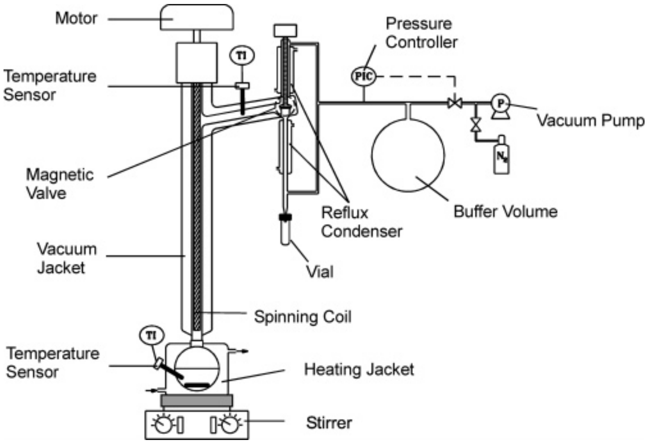

Figure 3. Schematic diagram of the spinning band column.

thermoregulated glass apparatus (Figure 1) allows measurements at pressures up to 2 bar. The cell can be filled with the desired mixture, and after equilibration and phase settling, samples can be taken from both phases. In this project, the samples were homogenized with ethylene glycol monobutyl ether and then analyzed by gas chromatography. At high temperatures and especially in the propionamide-rich phase, it was not possible to enable a proper sampling and, thus, another experimental technique was applied. The static equilibrium cell (Figure 2) can be used for the measurement of VLLE data (x', x'', y, T, P) at temperatures between (250 and 500) K and at pressures up to 100 bar. It is equipped with glass or sapphire windows. From this cell, small amounts of the substances can directly be injected into the carrier gas stream using pneumatic driven micro samplers (Guilbot et al.).[4] Turning the cell, the samples can be taken from the different phases. For this approach, a system pressure larger than the pressure of the carrier gas stream is required. Therefore an inert component (helium) was added to the mixture in order to increase the pressure to about 5 bar. Because of the high boiling points of both components and corresponding difficulties in gas chromatographic analysis, also a synthetic method for LLE measurements was applied in order to validate the reliability of the other methods. Known amounts of the substances were charged into the glass cell described above. Then, by temperature variation, the cloud point was visually detected.

The measurements of the heterogeneous azeotropic data (y_{az}, P, T) were carried out by distillation. They were measured at different pressures by using a micro spinning band column (NORMAG, see Figure 3). In this method, a mixture of the desired compounds is distilled with a high reflux ratio until the composition of the head product is constant. Since the reflux is realized on the basis of a vapor-dividing principle, not only homogeneous but also heterogeneous pressure maximum azeotropes can be determined. The determination of the composition of the homogenized distillate was again performed by gas chromatographic analysis. The equipment can be employed up to pressures of 3.5 bar. Details about this apparatus and the measurement procedure are described by Gmehling and Bölts.[5]

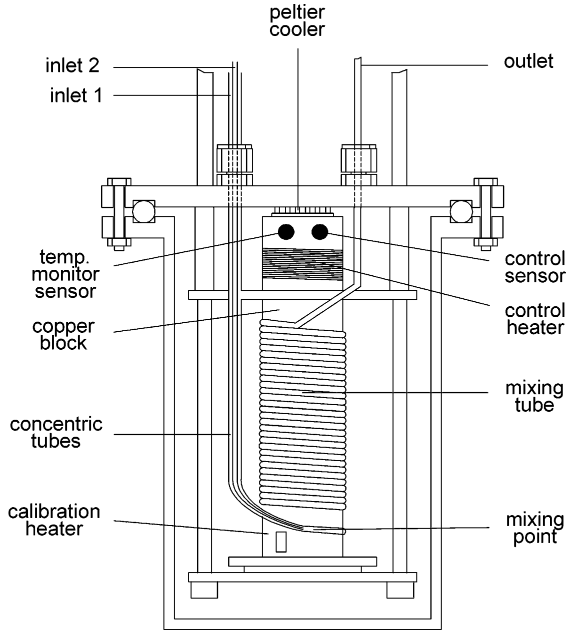

Figure 4. Schematic diagram of the calorimeter cell.

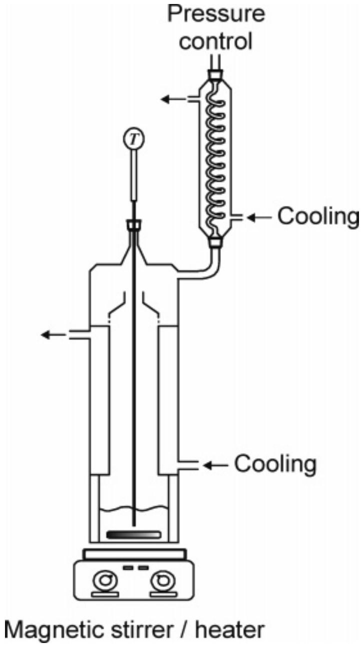

Figure 5. Schematic diagram of the ebulliometer.

The commercial isothermal flow calorimeter (Model 7501, Hart Scientific) used for the determination of the excess enthalpy data was described previously by Gmehling.[6] In this apparatus, two syringe pumps (Model LC-2600, ISCO) provide a flow of constant composition through a thermostated calorimeter cell (Figure 4) equipped

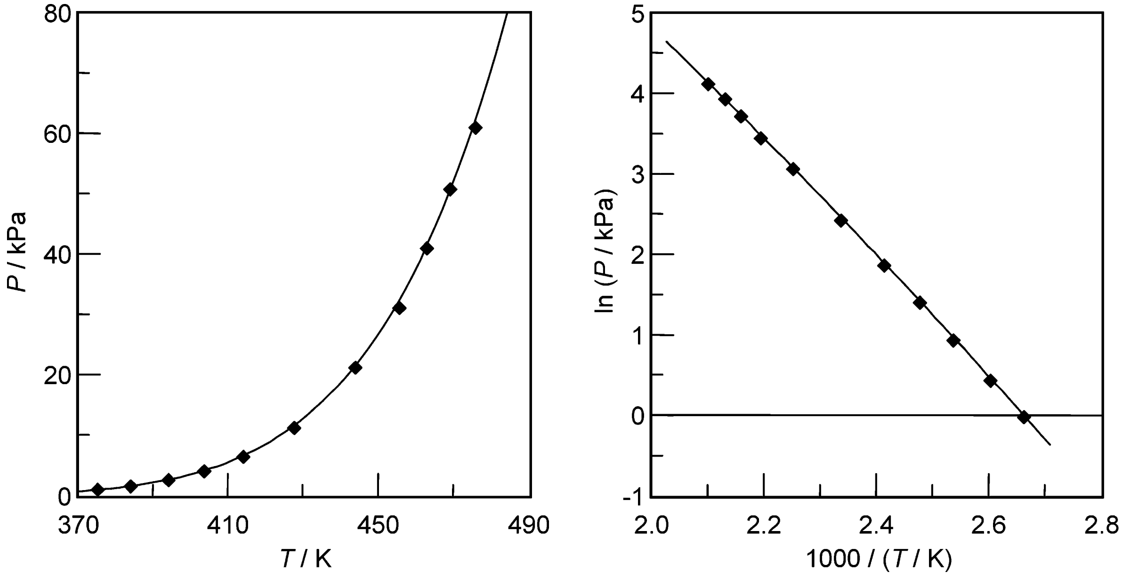

Figure 6. Experimental and calculated vapor pressure data for propionamide: ◆, experimental data, this work; solid line, Antoine.

Table 1. Experimental Vapor Pressures for Propionamide

T/K	P/kPa
375.45	0.97
384.15	1.53
394.15	2.52
403.65	4.02
414.05	6.40
427.65	11.22
443.85	21.16
455.55	31.04
462.95	40.87
469.05	50.69
475.85	60.86

Table 2. Experimental Densities at Atmospheric Pressure for Propionamide

T/K	ρ/kg·m^{-3}
355.65	963.2
358.15	961.2
363.15	957.2

Table 3. Experimental VLLE Data for the System *n*-Undecane (1) + Propionamide (2)

T/K	P/kPa	x_1'	x_1''	$y_1{}^a$	method
359.25			0.9932		glass cell (analytic method)
373.15			0.9867		glass cell (analytic method)
393.15		0.0173	0.9795		glass cell (analytic method)
342.65			0.9940		glass cell (synthetic method)
376.15			0.9910		glass cell (synthetic method)
359.15		0.0066			static cell (analytic method)
372.65		0.0113		0.8216	static cell (analytic method)
393.75		0.0138			static cell (analytic method)
415.15		0.0189	0.9492	0.7625	static cell (analytic method)
413.15		0.016			H^E measurements
380.20	7.23			0.7877	spinning band column
391.95	11.89			0.7621	spinning band column
416.65	29.99			0.7343	spinning band column

[a] Azeotropic composition.

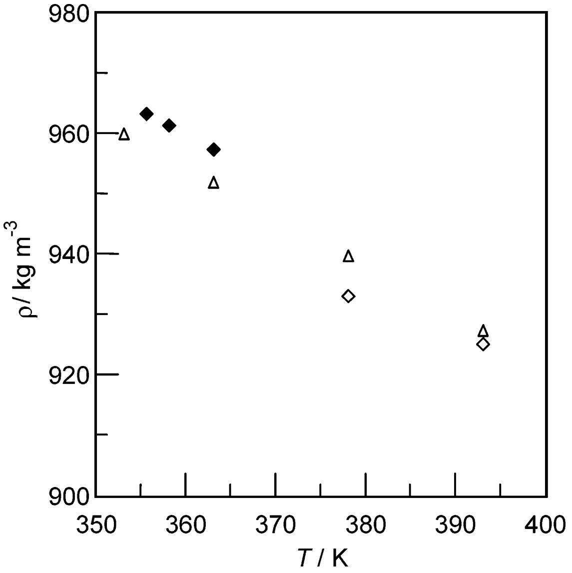

Figure 7. Experimental density data for propionamide: ◆, this work; ◇, Dunstan and Mussel;[7] △, Turner and Merry.[8]

Table 4. Experimental H^E Data for the System *n*-Undecane (1) + Propionamide (2) at 413.15 K and 1.62 MPa

x_1	H^E/J·mol^{-1}
0.0092	139
0.0284	241
0.0490	254
0.1074	280
0.7646	556
0.9337	628
0.9661	644

Table 5. Antoine Coefficients A_i, B_i, and C_i for the Pure Components

component	A_i	B_i/K	C_i/K
n-undecane	6.09710	1569.57	−85.450
propionamide	6.86665	1945.10	−92.360

with a pulsed heater and a Peltier cooler. The Peltier cooler is working at constant power producing a constant heat loss from the calorimeter cell. This allows the measurement of endothermal as well as exothermal heat effects. A back-pressure regulator serves to keep the pressure at a level at which evaporation and degassing effects can be prevented. For high melting substances as in this case, the syringe pumps were thermostated above the melting point of propionamide at 90 °C. The experimental uncertainties of this device are as follows: $\sigma(T) = 0.03$ K; $\sigma(H^E) = 2$ J mol^{-1}+ 0.01 (H^E/J mol^{-1}); $\sigma(x_i) = 0.0001$. From the experimental H^E data of the investigated system, LLE data were also derived graphically.

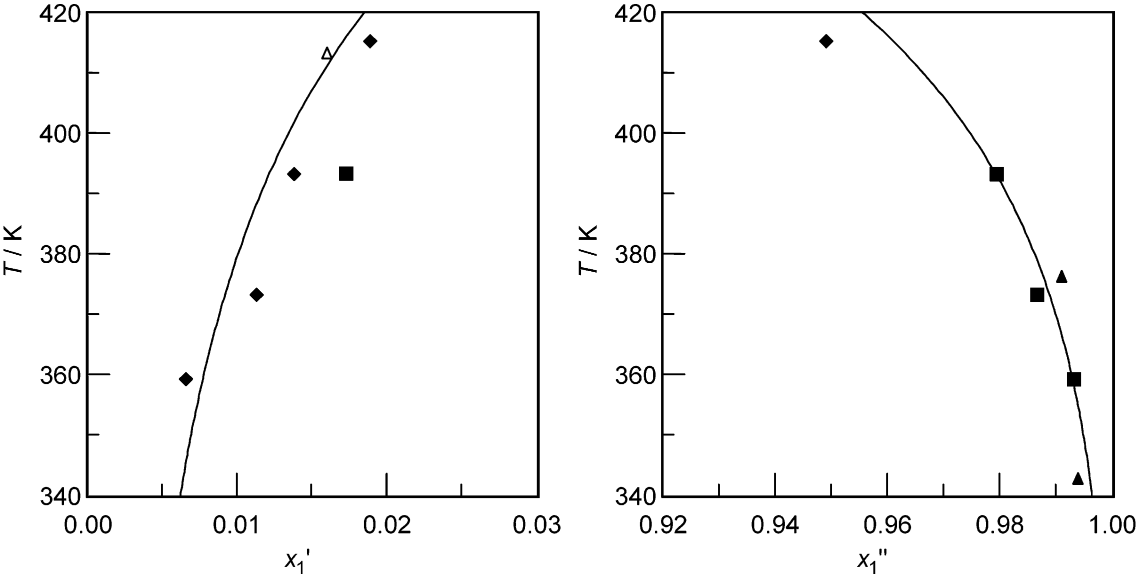

Figure 8. Experimental and calculated LLE data for the system *n*-undecane (1) + propionamide (2): ◆, static cell (analytic method); ■, glass cell (analytic method); ▲, glass cell (synthetic method); △, H^E measurements; solid line, NRTL.

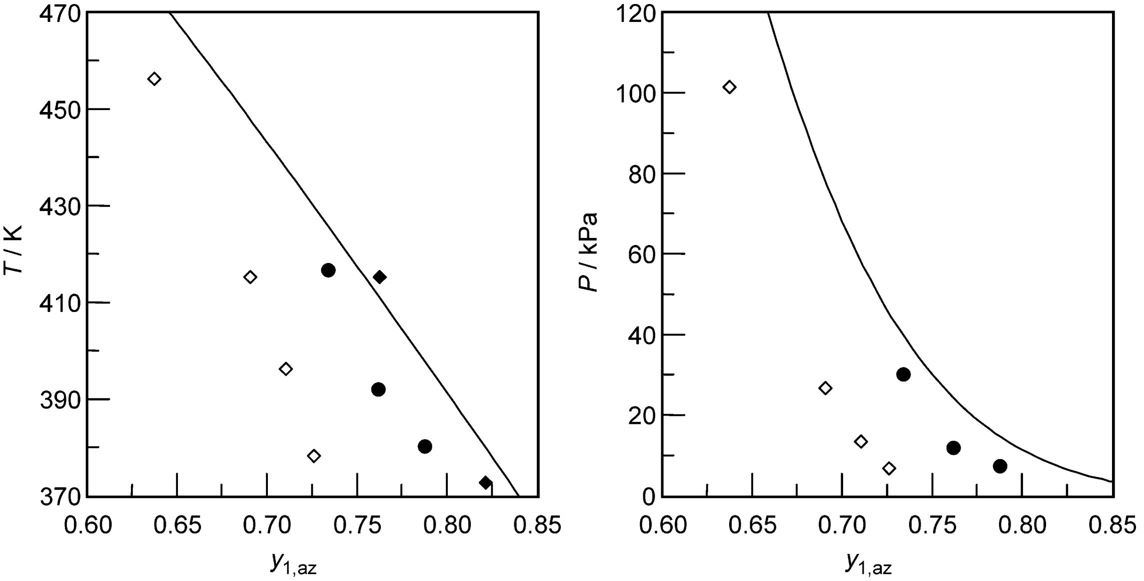

Figure 9. Experimental and calculated azeotropic behavior of the system n-undecane (1) + propionamide (2): ◆, static cell (analytic method); ●, spinning band column; ◇, experimental data, Bruner and Draden;[1] solid line, NRTL.

Table 6. NRTL Interaction Parameters for the System *n*-Undecane (1) + Propionamide (2)

a_{12}/J·mol^{-1}	a_{21}/J·mol^{-1}	b_{12}/J·mol^{-1}·K^{-1}	b_{21}/J·mol^{-1}·K^{-1}	α_{12}
33159.37	6452.38	−64.3511	9.0526	0.200

Additionally, pure-component properties for propionamide were determined experimentally. The vapor pressure data for propionamide were measured by means of a dynamic method using an ebulliometer (Figure 5). With this glass equipment, vapor pressures of pure components can be experimentally determined in a temperature range from approximately 270 to 620 K and at pressures from about 2 mbar up to 1 bar. At a given pressure (regulated by an electronic pressure control), the boiling temperatures of a component are measured. Because of the volume of the equipment, only small amounts of the substances (about 20 mL) are needed. The pure-component density data for propionamide required for the H^E measurements were measured with a commercial vibrating tube densimeter (Model DMA 4500, Anton Paar). These data were measured because only very old data are available in the literature.[7,8]

Results

The experimental pure component and mixture data for the investigated system are listed in Tables 1−4.

The required constants of the Antoine equation for vapor pressures

$$\log(P_i^s/\text{kPa}) = A_i - \frac{B_i}{C_i + T/\text{K}} \qquad (2)$$

are listed in Table 5. For *n*-undecane, they were fitted to the vapor pressure data of several authors stored in the Dortmund Data Bank (DDB 2004).[9] Since for propionamide no experimental data were available, experiments were carried out in this project. The results are shown together with the Antoine calculations in Figure 6. In Figure 7, the experimental density data from this work are compared to the data from literature.

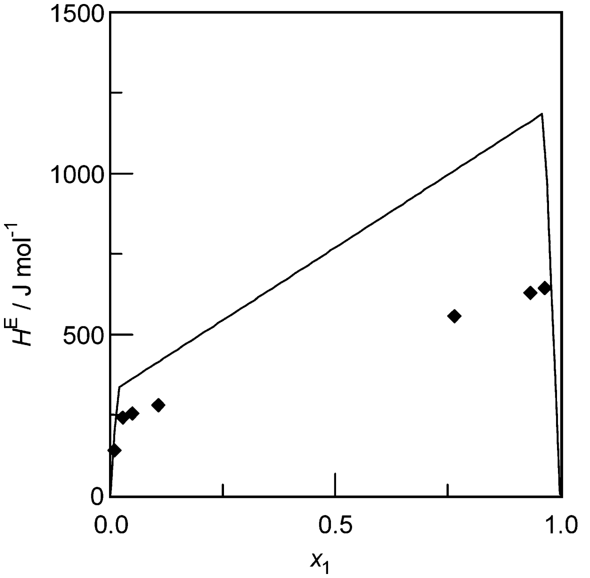

Figure 10. Experimental and calculated excess enthalpy data for the system n-undecane (1) + propionamide (2) at 413.15 K: ◆, experimental data, this work; solid line, NRTL.

To the experimental mixture data of the system *n*-undecance + propionamide, temperature-dependent NRTL parameters were fitted. To describe the temperature dependence of the interaction parameters the following expression was used

$$\Delta g_{ij}/\text{J·mol}^{-1} = a_{ij} + b_{ij}(T/\text{K}) \tag{3}$$

The obtained parameters are given in Table 6.

A graphical representation of the experimental LLE, azeotropic, and H^E data is given in Figures 8−10 together with the values calculated with the NRTL equation. As can be seen, the temperature dependence of the LLE behavior (Figure 8) can be reliably described. The agreement between the obtained liquid phases from the different experimental techniques is better than ±0.005 in terms of mole fraction. Also, the temperature and pressure dependence of the experimental azeotropic data can be well described, although the data of Bruner and Darden,[1] for which only approximate mole fractions are given, show small deviations to our data. Finally, the shape of the H^E data, which also indicate a large miscibility gap of this system, can be described. The difference in the magnitude is resulting from the slope of the H^E curve in the homogeneous range, so that small deviations in the LLE behavior have a big influence on the description of the excess enthalpy behavior. The resulting VLE behavior at 413.15 K is shown in Figure 11.

Conclusions

Several thermodynamic data (VLLE, azeotropic, and H^E data, vapor pressures, and densities) were measured for the system *n*-undecane + propionamide using diverse experimental equipments. From these data, temperature-dependent NTRL parameters were fitted, which are able to describe to behavior of the studied system, as can be seen from the different diagrams. Because of these results, the NRTL parameters given in Table 6 can be recommended for the investigated systems in a temperature range from about (350 to 470) K.

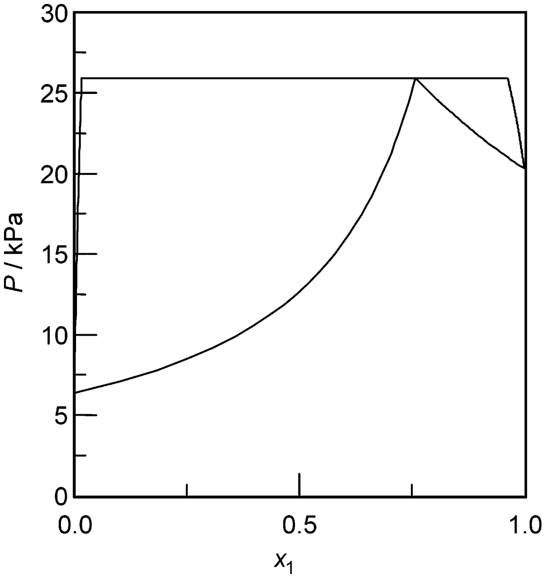

Figure 11. Calculated (NRTL) VLE behavior for the system *n*-undecane (1) + propionamide (2) at 413.15 K.

Acknowledgment

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