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Modeling of the Multiphase Behavior of Nitrogen-Containing Systems at Low Temperatures with Equations of State[†]

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In this work, we present the modeling of the vapor−liquid−liquid equilibria (VLLE) for three ternary systems that are of interest in the natural gas and oil industry: nitrogen + methane + *n*-pentane, nitrogen + methane + *n*-hexane, and nitrogen + methane + *n*-heptane. The capabilities of the PC-SAFT and SRK equations of state to predict the complex phase behavior exhibited at low temperatures by the systems studied were compared and analyzed. The computer algorithm performing the isothermal multiphase flash calculations in the first case is based on the minimization of the Gibbs energy, while the second is based on the minimization of a modified tangent−plane distance function. The results obtained demonstrate that both equations of state predict with reasonable accuracy the experimentally observed phase behavior of the ternary systems considered.

Introduction

It is well-known that the addition of nitrogen to miscible liquefied natural gas (LNG) systems can induce immiscibility and that the presence of a third phase can cause problems in the natural gas industry. Therefore, because these mixtures are separated by low-temperature distillation in the recovery of natural gas, it is important to know the temperatures, pressures, and compositions at which immiscibilities appear. A detailed description of the occurrence of VLLE phenomena in well-defined prototype natural gas systems can be found elsewhere.[1,2]

Experimental VLLE data have been reported for the systems nitrogen + ethane,[3,4] nitrogen + propane,[4] and nitrogen + methane + ethane,[3−5] including an observation of four fluid phases (one vapor phase and three liquid phases) at $T = 112.2$ K and $p = 1.403$ MPa for this ternary system.[6] Stroud et al.[7] also reported VLLE data for a nitrogen-rich natural gas system from $T = (116 \text{ to } 130)$ K and pressures up to 3.447 MPa. Subsequently, data of the two coexisting liquid phases in binary and ternary mixtures of nitrogen with *n*-alkanes have been published by Kohn and co-workers.[8−12]

The success of the design and operation of separation processes in the oil and gas industry at low temperatures is critically dependent upon accurate descriptions of the thermodynamic properties and phase behavior of the concerned multicomponent hydrocarbon mixtures with inorganic gases. Thus, it is important to apply appropriate models within a thermodynamic modeling framework to predict, describe, and validate the complex phase behavior of LNG mixtures. In this case, equations of state (EoS) are usually the primary choice.

The aim of this work is to use two reliable techniques for multiphase flash calculations to calculate the phase behavior and calculate the components' distribution among the equilibrium phases for the ternary systems nitrogen + methane + *n*-pentane, nitrogen + methane + *n*-hexane, and nitrogen + methane + *n*-heptane to compare the capabilities of the SRK and PC-SAFT EoS for predicting the VLLE behavior that these ternary systems exhibit experimentally over certain temperature and pressure ranges. In this case, the first technique employs the PC-SAFT EoS[13] as the thermodynamic model, while the second employs the SRK EoS.[14] Here, it is worth mentioning that although there are other EoS published in the literature for hydrocarbons and nitrogen[15,16] and their mixtures,[17−19] the reason to select the SRK and the PC-SAFT EoS with the view to compare their performance in this work is that these equations are very widely used for phase equilibrium calculations for fluid mixtures, including those encountered in the natural gas and petroleum industries, and because, at present, most of the commercially available process simulators include these EoS in their models bank.

Solution Procedures

Computational Technique 1. This first technique uses an efficient computational procedure for solving the isothermal multiphase problem by assuming that the system is initially monophasic. A stability test allows verifying whether the system is stable or not. In the latter case, it provides an estimation of the composition of an additional phase. The number of phases is then increased by one, and equilibrium is achieved by minimizing the Gibbs energy. This approach, advocated as a stagewise procedure,[20,21] is continued until a stable solution is found.

In this technique, the stability analysis of a homogeneous system of composition z, based on the minimization of the distance separating the Gibbs energy surface from the tangent plane at z, is considered.[22,23] In terms of fugacity coefficients, φ_i, this criterion for stability can be written as[23]

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$$F(\xi) = 1 + \sum_{i=1}^{N} \xi_i[\ln \xi_i + \ln \varphi_i(\xi) - h_i - 1] \geq 0 \quad \forall \xi > 0 \tag{1}$$

where ξ_i are mole numbers with corresponding mole fractions as $y_i = \xi_i/\sum_{j=1}^{N}\xi_j$ and

$$h_i = \ln z_i + \ln \varphi_i(z) \quad i = 1, ..., N \tag{2}$$

Equation 1 requires that the tangent plane, at no point, lies above the Gibbs energy surface, and this is achieved when $F(\xi)$ is positive in all its minima. Consequently, a minimum of $F(\xi)$ should be considered in the interior of the permissible region $\sum_{i=1}^{N} y_i = 1$, $\forall y \geq 0$. Since testing condition 1 for all trial compositions is not physically possible, it is sufficient to test the stability at all stationary points of $F(\xi)$ since this function is not negative at all stationary points. Here, the quasi-Newton BFGS minimization method[24] was applied to eq 1 for determining the stability of a given system of composition z at specified temperature and pressure.

Once instability is detected with the solution at $p - 1$ phases, the equilibrium calculation at p phases is solved by minimizing the following function

$$\min_{n_i^{(\phi)}} \Delta g = \frac{(G - G^\circ)}{RT} = \sum_{\phi=1}^{p} \sum_{i=1}^{N} n_i^{(\phi)} \ln\left(\frac{x_i^{(\phi)} \varphi_i^{(\phi)} P}{P^\circ}\right) \tag{3}$$

subject to the inequality constraints given by

$$\sum_{\phi=1}^{p-1} n_i^{(\phi)} \leq z_i \quad i = 1, ..., N \tag{4}$$

and

$$n_i^{(\phi)} \geq 0 \quad i = 1, ..., N; \phi = 1, ..., p - 1 \tag{5}$$

where G is the molar Gibbs energy of the system; G° is the molar Gibbs energy of the system at the standard state; z_i is the mole fraction of the component i in the system; $n_i^{(\phi)}$ ($i = 1, ..., N$; $\phi = 1, ..., p - 1$) is the mole number of component i in phase ϕ per mole of feed; $x_i^{(\phi)}$ is the mole fraction of component i in phase ϕ; T is the temperature; P is the pressure; and P° is the pressure at the standard state of 1 atm (101.325 kPa). In eq 3, the variables $n_i^{(p)}$, $x_i^{(p)}$, and $\varphi_i^{(p)}$ are considered functions of $n_i^{(\phi)}$.

Equation 3 was solved using an unconstrained minimization algorithm by keeping the variables $n_i^{(\phi)}$ inside the convex constraint domain given by eqs 4 and 5 during the search for the solution. In this case, we used a hybrid approach to minimize eq 3 starting with the steepest-descent method in conjunction with a robust initialization supplied from the stability test to ensure a certain progress from initializations and ending with the quasi-Newton BFGS method which ensures the property of strict descent of the Gibbs energy surface. A detailed description of this approach for solving the isothermal multiphase problem can be found elsewhere.[25]

Computational Technique 2. The second approach to predict and calculate multiphase equilibria used here applies a rigorous thermodynamic stability analysis and a simple and effective method for identifying the phase configuration at equilibrium with the minimum Gibbs energy. The stability analysis is exercised once and on the initial system only. It is based on the well-known tangent plane criterion[22,23] but uses a different objective function.[26,27] The key point is to locate all zeros (y^*) of a function $\Phi(y)$ given as

$$\Phi(y) = \sum_{i=1}^{N} [k_{i+1}(y) - k_i(y)]^2 \tag{6}$$

where

$$k_i(y) = \ln \varphi_i(y) + \ln y_i - h_i \quad i = 1, ..., N \tag{7}$$

with h_i given by eq 2 and assuming $k_{N+1}(y) = k_1(y)$. From eqs 6 and 7, it follows that min $\Phi(y) = 0$ when $k_1(y^*) = k_2(y^*) = ... = k_N(y^*)$.

The zeros of $\Phi(y)$ conform to points on the Gibbs energy hypersurface, where the local tangent hyperplane is parallel to that at z. To each zero y^*, a number k^* (equal for each y_i^*, $i = 1, ..., N$ of a zero of the functional) corresponds, such that

$$k_i^* = \ln y_i^* + \ln \varphi(y^*) - h_i \quad i = 1, ..., N \tag{8}$$

Furthermore, the number k^*, which geometrically is the distance between two such hyperplanes, can be either positive or negative. A positive k^* corresponds to a zero, which represents a more stable state of the system, in comparison to the initial one; a negative k^*, a more unstable one. When all calculated k^* are positive, the initial system is stable; otherwise, it is unstable.

It is widely acknowledged that the task to locate all zeros of the tangent−plane distance function (TPDF), $\Phi(y)$ in this particular case, is extremely challenging because a search over the entire composition space is required. The search is further complicated by the existence of a number of trivial solutions, corresponding with the number of equilibrium phases present. The specific form of $\Phi(y)$ (its zeros are its minima) and the fact that it is easily differentiated analytically allows the application of a nonlinear minimization technique for locating its stationary points, and in their works, Stateva and Tsvetkov[26,27] and Wakeham and Stateva[28] used the BFGS method with a line-search.[24] The implementation of any nonlinear minimization technique requires a set of "good" initial estimates, and the BFGS method is no exception. All details of the organization and implementation of the initialization strategy employed by the stability analysis procedure are given elsewhere[26,27] and will not be discussed here.

Thus, as discussed by Wakeham and Stateva,[28] a method has been created which leads, in practice, to an "extensive" search in the multidimensional composition space. It has proved to be extremely reliable in locating *almost all* zeros of $\Phi(y)$ at a reasonable computational cost. The term "almost all" zeros is used because there is no theoretically based guarantee that the scheme will always find them all. If, however, a zero is missed, the method is self-recovering. Furthermore, the TPDF is minimized *once only*, which is a distinct difference from the approach that stagewise methods generally adopt. Since stability analysis on its own cannot determine unequivocally which is the stable phase configuration of a system (identified as unstable at the given temperature and pressure), it is suggested to run a sequence of two-phase flash calculations to determine the correct number of the phases at equilibrium and the distribution of the components among the phases.

Results and Discussion

Experimental data reported by Merrill et al.[11] for the systems nitrogen + methane + *n*-pentane and nitrogen + methane + *n*-hexane and by Chen et al.[12] for the system nitrogen + methane + *n*-heptane were used to test the robustness, efficiency, and reliability of the two computational techniques employed and to compare the PC-SAFT and SRK EoS modeling results. The binary interaction parameters used with the PC-SAFT equation

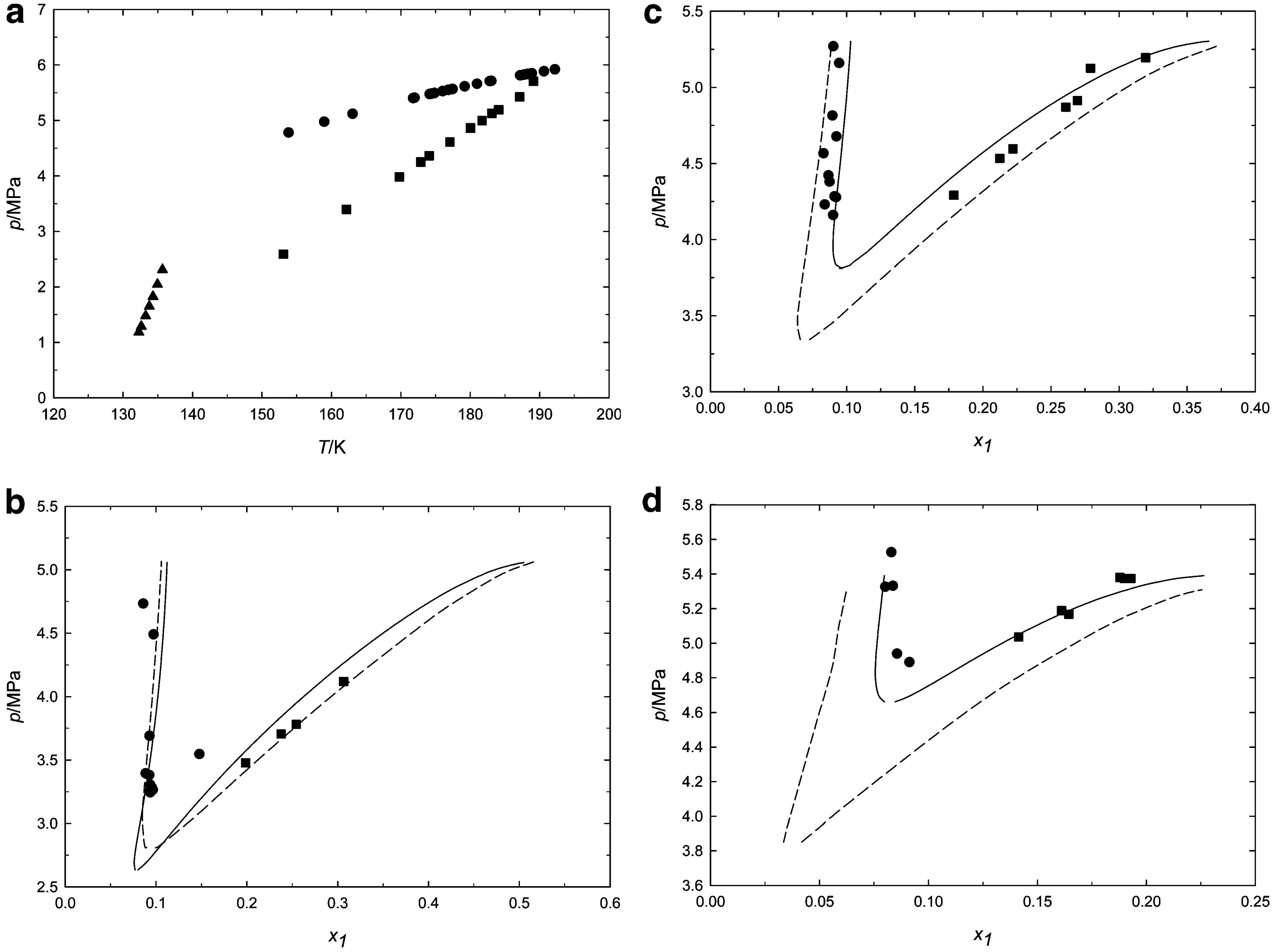

Figure 1. (a) Boundaries of the L_1-L_2-V immiscibility region for the system nitrogen + methane + *n*-pentane. Experimental data. Ref 11: ●, K points ($L_1-L_2{=}V$); ■, LCST points ($L_1{=}L_2-V$); ▲, Q points ($S-L_1-L_2-V$). (b) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-pentane (3) system at $T = 160$ K. Experimental data:[11] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1 (PC-SAFT EoS with computational technique 1); - - -, Method 2 (SRK EoS with computational technique 2). (c) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-pentane (3) system at 170 K. Experimental data:[11] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1; - - -, Method 2. (d) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-pentane (3) system at 180 K. Experimental data:[11] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1; - - -, Method 2.

were taken from García-Sánchez et al.[29] and from Justo-García et al.,[30] while those used with the SRK EoS were from Knapp et al.[31] and from Nagy and Shirkovskiy,[32] respectively. The binary interaction parameters used in this work are: $k_{N_2-C_1} = 0.0278$, $k_{N_2-C_5} = 0.0878$, $k_{N_2-C_6} = 0.11$, $k_{N_2-C_7} = 0.115$, $k_{C_1-C_5} = 0.0191$, $k_{C_1-C_6} = 0.02398$, and $k_{C_1-C_7} = 0.0307$ (for the SRK equation) and $k_{N_2-C_1} = 0.0307$, $k_{N_2-C_5} = 0.0697$, $k_{N_2-C_6} = 0.0767$, $k_{N_2-C_7} = 0.0910$, $k_{C_1-C_5} = 0.0213$, $k_{C_1-C_6} = 0.0220$, and $k_{C_1-C_7} = 0.0229$ (for the PC-SAFT equation). The components' physical properties required for the calculations performed with the SRK EoS were taken from DIPPR,[33] while the three pure-component parameters (i.e., temperature-independent segment diameter σ, depth of the potential ε, and number of segments per chain m) of these compounds for the PC-SAFT equation of state were taken from Gross and Sadowski.[13]

Nitrogen + Methane + n-Pentane System. The three-phase VLL region displayed by this ternary system (a surface in the thermodynamic phase space with two degrees of freedom) is bounded from above by a K-point locus ($L-L{=}V$), from below by a lower critical solution temperature LCST locus ($L{=}L-V$), and at low temperatures by a Q-point locus ($S-L-L-V$). For the three components in this system, there is no binary immiscibility. The topographical nature of the regions of immiscibility for the system nitrogen + methane + *n*-pentane is shown in Figure 1a, where symbols are the experimental data given by Merrill et al.[11] identifying the boundaries of the three-phase VLL region for this ternary system. This figure shows also that the $L-L{=}V$ and $L{=}L-V$ critical end-point loci intersect at a tricritical point ($L{=}L{=}V$) at the upper temperature limit.

Following the immiscibility region (Figure 1a), three different temperatures were chosen to test the capabilities of the PC-SAFT with computational technique 1 and the SRK EoS with computational technique 2, to predict the phase behavior for the system nitrogen + methane + *n*-pentane. Figures 1b to 1d compare the performance of the two methods at $T =$ (160, 170, and 180) K, respectively, and at different pressures on the basis of the experimentally measured and calculated nitrogen mole fractions for the liquid L_1 and L_2 phases by the two thermodynamic models employed. In this case, the predictions of the PC-SAFT model are closer to the experimental values than those of the SRK model at (170 and 180) K; however, the SRK model is superior to the PC-SAFT model in predicting the nitrogen mole fractions for liquid L_1 and L_2 phases at 160 K. An

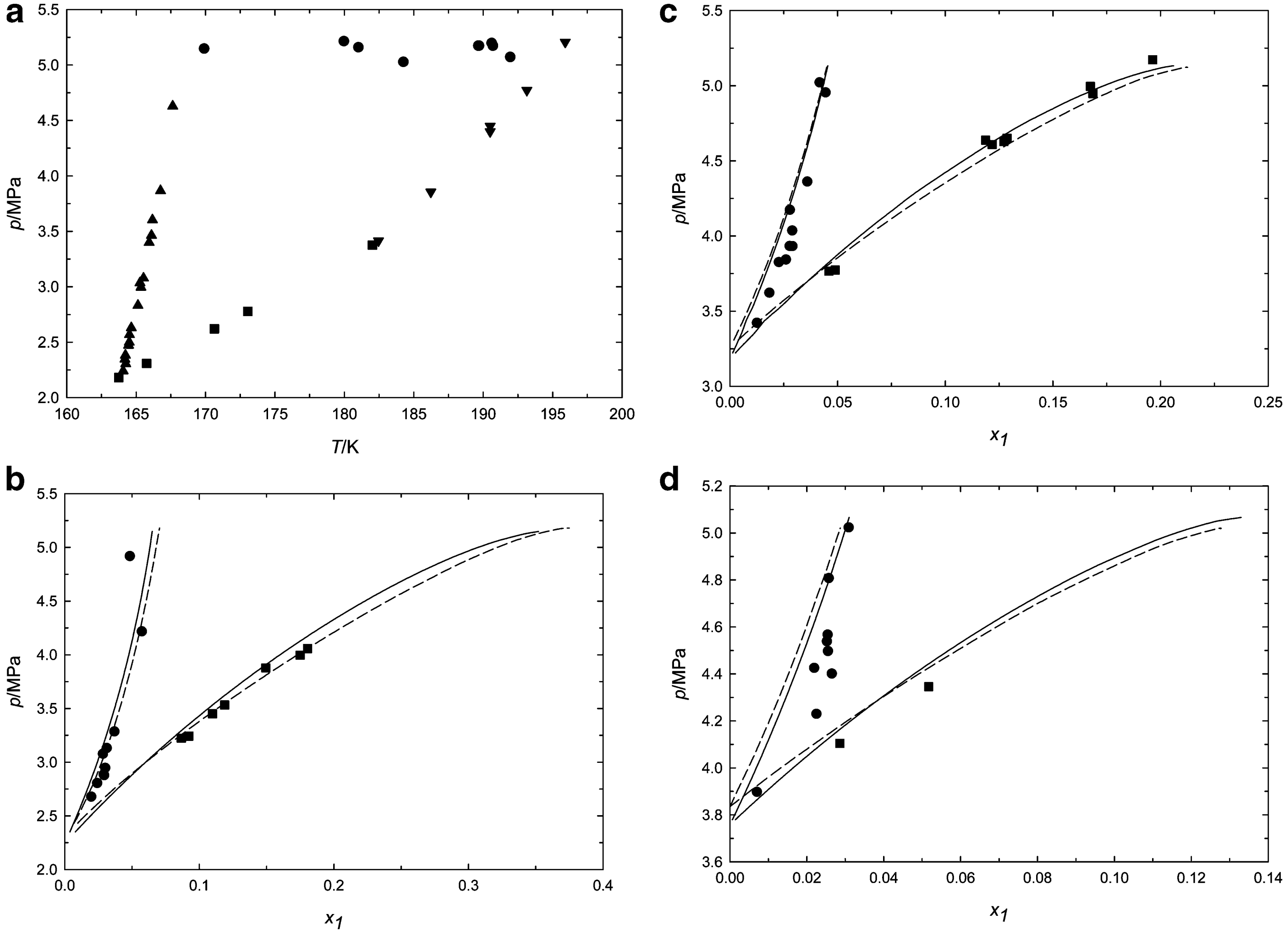

Figure 2. (a) Boundaries of the L_1-L_2-V immiscibility region for the system nitrogen + methane + *n*-hexane. Experimental data. Ref 11: ●, K points ($L_1-L_2=V$); ■, LCST points ($L_1=L_2-V$); ▲, Q points ($S-L_1-L_2-V$). Ref 34: ▼, binary methane + *n*-hexane L_1-L_2-V points. (b) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-hexane (3) system at 170 K. Experimental data:[11] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1; - - -, Method 2. (c) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-hexane (3) system at 180 K. Experimental data:[11] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1; - - -, Method 2. (d) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-hexane (3) system at 185 K. Experimental data:[11] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1; - - -, Method 2.

inspection of these figures shows that the predictions of both EoS follow closely the almost linear behavior of the liquid phase L_1 as well as the variation of the liquid phase L_2 as pressure decreases. It is interesting to note that although there is not a true experimental value of the LCST at the three temperatures considered Figures 1c and 1d indicate that the estimated LCST point with the PC-SAFT model is closer to the "experimental" ones (4.0 MPa at 170 K and 4.85 at 180 K) than those obtained with the SRK model, whereas Figure 1b indicates that the estimated LCST point with the SRK model is closer to the "experimental" one (3.19 MPa at 160 K) than that obtained with the PC-SAFT model.

The predictions of the two thermodynamic models for the $V-L_1-L_2$ region (in terms of L_1-L_2 nitrogen mole fraction data) at pressures above (3.3 and 4.1) MPa for the isotherms of (160 and 170) K almost do not differ from the experimentally measured one (Figures 1b and 1c). However, at $T = 180$ K, the $V-L_1-L_2$ region calculated with the SRK model deviates considerably from the experimental one, while the PC-SAFT model predictions are quite good (Figure 1d). Since the interaction parameters for the PC-SAFT and SRK models were determined from binary vapor−liquid equilibrium data, the rather poor fit in this region with either model is not unexpected.

Nitrogen + Methane + n-Hexane System. In the nitrogen + methane + *n*-hexane system, the binary methane + *n*-hexane displays immiscibility,[34] the locus of which truncates the usual "triangular" VLL region at the high temperature side, yielding a four-sided space without a tricritical point. Thus, the system's three-phase region is bounded above by a K-point locus, from below by a lower critical solution temperature LCST locus, and at low temperatures by a Q-point locus. As pointed out above, the partially miscible pair methane + *n*-hexane spans the VLL space from a position of the LCST locus to a position on the K-point space, while the addition of nitrogen to the binary extends the three-phase region downward in temperature and pressure from the binary LLV locus (Figure 2a).

Figures 2b, 2c, and 2d present the experimental and calculated $V-L_1-L_2$ phase behavior (in terms of L_1-L_2 nitrogen mole fraction data) for this system at (170, 180, and 185) K, respectively, and different pressures. For the three temperatures examined, both models agree closely with each other in their representation of the experimental data. At $T = (170$ and $180)$ K, a very good agreement between the experimental values and those calculated with both models is achieved, while at $T = 185$ K, both models fail to represent the L_1 experimental data but do well for the L_2 data.

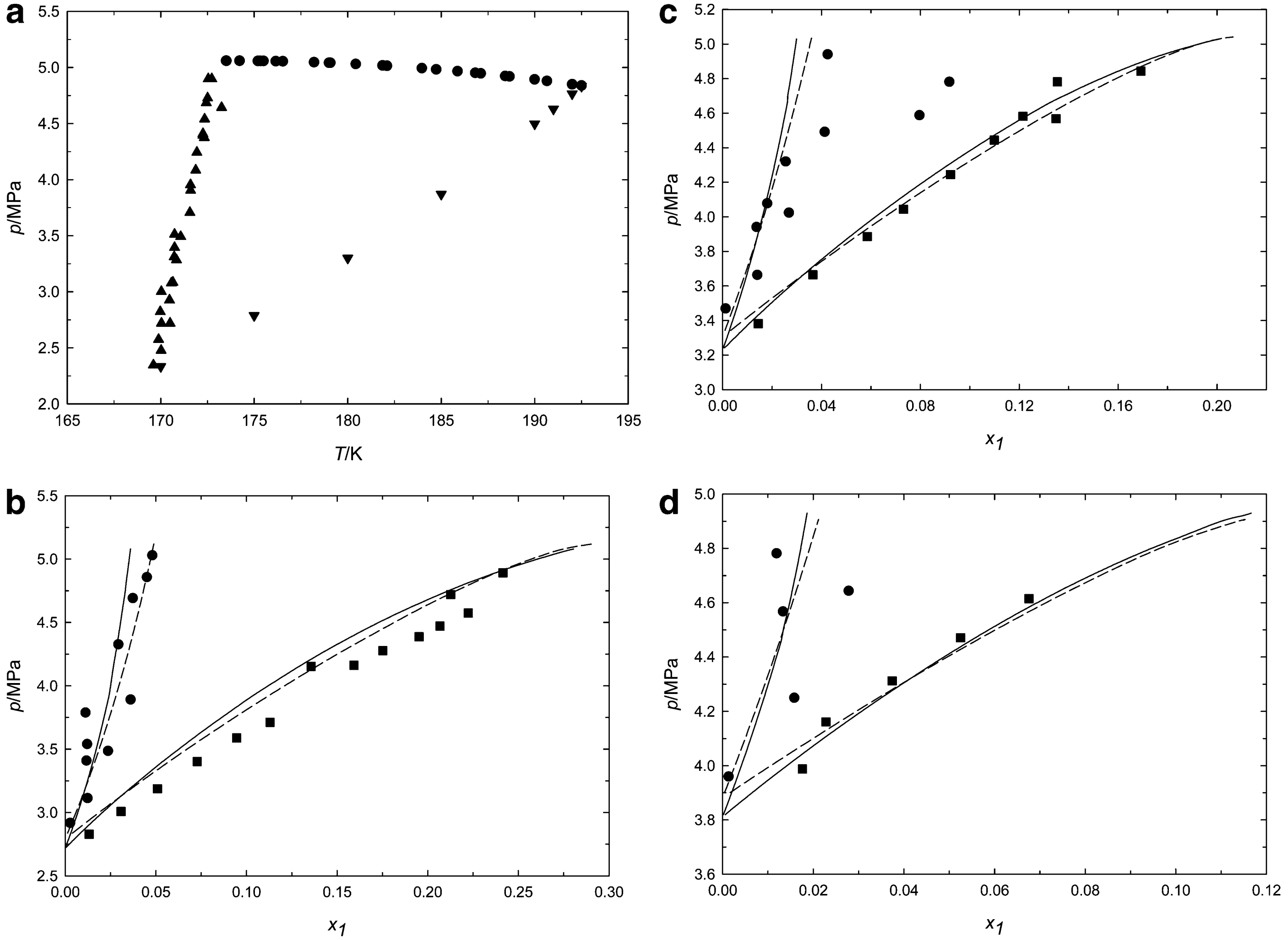

Figure 3. (a) Boundaries of the L_1-L_2-V immiscibility region for the system nitrogen + methane + *n*-heptane. Experimental data. Ref 12: ●, K points ($L_1-L_2=V$); ▲, Q points ($S-L_1-L_2-V$). Ref 35: ▼, binary methane + *n*-heptane L_1-L_2-V points. (b) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-heptane (3) system at 175 K. Experimental data:[12] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1; - - -, Method 2. (c) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-heptane (3) system at 180 K. Experimental data:[12] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1; - - -, Method 2. (d) Experimental and calculated N_2 mole fractions for the coexisting L_1 and L_2 phases of the nitrogen (1) + methane (2) + *n*-heptane (3) system at 185 K. Experimental data:[12] ●, L_1 phase; ■, L_2 phase. Calculated: —, Method 1; - - -, Method 2.

Since there are no experimental data below (2.7, 3.4, and 3.9) MPa for the three isotherms, a direct comparison with the experiment in the region of the LCST at (170 and 180) K and in the region of the methane + *n*-hexane binary $V-L_1-L_2$ behavior cannot be realized. However, according to our predictions, the respective LCST points estimated with both models are in good agreement with the "hypothetical" experimental LCST points (2.58 MPa at 170 K and 3.24 MPa at 180 K) and the "hypothetical" experimental binary methane + *n*-hexane $V-L_1-L_2$ point (3.69 MPa at 185 K). Once again, these slight discrepancies between experimental and calculated values with both models can be attributed to the fact that binary interaction parameters, determined from binary vapor−liquid equilibrium data, were used. Nevertheless, it can be said that, on the whole, both models give a satisfactory representation of the VLL phase behavior for this system and can be used with confidence to predict the K-point, Q-point, LCST, and binary VLL loci for this ternary system applying appropriate numerical algorithms. These calculations are currently in progress and will be presented in a future publication for a series of nitrogen-containing ternary systems.

Nitrogen + Methane + n-Heptane System. As mentioned above, the type of the VLL region displayed by a ternary system depends on whether it contains an immiscible pair or not.[1,2] In this context, the system nitrogen + methane + *n*-heptane exhibits immiscibility in the methane + *n*-heptane binary pair, thus its three-phase region is similar to that exhibited by the system nitrogen + methane + *n*-pentane. Therefore, the VLL region is "triangular" and is bounded from above by a K-point locus ($L-L=V$), at low temperatures by a Q-point locus ($S-L-L-V$), and, from a position of the Q-point locus to a position on the K-point space, by a binary methane + *n*-heptane VLL locus. Figure 3a presents the experimental pressure−temperature diagram of the VLL space developed by this ternary system.[12,35] An examination of the figure shows that this system does not exhibit a LCST ($L=L-V$) locus and that the Q-point locus terminates at an invariant point of the type $S-L-L=V$. Thus, due to the fact that the nitrogen + methane+ *n*-heptane system contains a binary pair (methane + *n*-heptane) exhibiting VLL behavior, its "triangular" VLL region is a three-sided space without a tricritical point.

Three temperatures [(175, 180, and 185) K] were chosen, and the results obtained are presented in Figures 3b, 3c, and 3d, respectively. These figures show that both thermodynamic models predict well the experimental nitrogen compositions of the liquid L_2 phase up to the lowest measured pressures of

(2.829, 3.382, and 3.988) MPa for the isotherms of (175, 180, and 185) K, respectively.

On the other hand, both models predict similar nitrogen compositions of the liquid L_1 phase, but these compositions differ, in many cases, considerably from the experimental data. The latter seem (even to superficial examination) to be not internally consistent; i.e., there is a great deal of scatter among the experimental points. Nonetheless, for the three temperatures examined, the predicted VLL regions show a satisfactory representation of the experimental data.

Furthermore, the compositions for the L_1 and L_2 phases calculated with the two models up to the binary methane + *n*-heptane VLL boundary, where the nitrogen mole fractions are zero in all three phases, agree closely with the experimental values of (2.786, 3.313, and 3.867) MPa at the temperatures of (175, 180, and 185) K, respectively, as reported by Chen et al.[12] The predicted pressures for the temperatures examined are, respectively, the following: (2.837, 3.343, and 3.901) MPa for the SRK model and (2.726, 3.242, and 3.820) MPa for the PC-SAFT model. The pressure differences between the experimental data and the calculated values show that the SRK model underpredicts the position of the binary VLL boundary, whereas the PC-SAFT model overpredicts this position for the three isotherms studied.

Regarding the error between the experimental nitrogen compositions (maximum error of 8.85 % in the L_1 phase and 2.93 % in the L_2 phase for the two ternary systems containing *n*-pentane and *n*-hexane as solutes,[11] and accuracy of 15.2 % in the L_1 phase and 0.6 % in the L_2 phase for the nitrogen + methane + *n*-heptane system[12]) and those compositions predicted with the SRK and PC-SAFT models, it can be said that both models are able to predict phase compositions within the experimental error, especially for the L_1 phase, demonstrating thus the capacity of these models in predicting experimentally VLLE phase behavior exhibited by the three ternary systems studied.

On the other hand, it is worthwhile mentioning that both EoS were interwoven into each of the computational procedures and that a series of multiphase flash calculations were carried out at different temperatures and pressures for the three ternary systems studied obtaining the same results for the specific EoS, irrespective of the computational procedure utilized. The results obtained showed that there are not any essential differences between, or particular advantages of, any of two computational procedures, either in their efficiency, effectiveness, robustness or in their convergence behavior. Thus, it can be said that both computational procedures can be used with complete confidence to predict the experimentally complex phase behavior that certain fluid systems exhibit experimentally over different conditions of temperature and pressure.

Finally, to investigate whether the PC-SAFT EoS provides good accuracy for multicomponent systems with only binary information, this model was applied to the modeling of the vapor−liquid equilibrium data for 43 multicomponent mixtures containing hydrocarbon (methane, ethane, propane, *n*-pentane, *n*-heptane, and *n*-decane) and nonhydrocarbon (nitrogen, carbon dioxide, and hydrogen sulfide) components, studied experimentally by Yarborough,[36] and the three-phase vapor−liquid−liquid equilibrium data of a natural gas system rich in nitrogen, reported by Stroud et al.[7] The results of the modeling obtained for these systems indicate that the PC-SAFT EoS can be used with confidence to predict the phase behavior of multicomponent systems by using interaction parameters obtained only from experimental binary vapor−liquid equilibrium data.

Conclusions

The capabilities of two thermodynamic models, the PC-SAFT and SRK EoS, to predict the complex phase behavior exhibited at low temperatures by three nitrogen-containing systems (nitrogen + methane + *n*-pentane, nitrogen + methane + *n*-hexane, and nitrogen + methane + *n*-heptane) that are of interest in the natural gas and oil industry were compared and analyzed. In the first case, the numerical technique performing the isothermal multiphase flash calculations is based on the minimization of the Gibbs energy, while the second case is based on the minimization of a modified TPDF and a simple phase identification procedure. Both techniques demonstrate robustness and a steady and nonoscillatory convergence of the flash calculations, with no tendency toward a strong attraction to the trivial solution. The results obtained demonstrate that both thermodynamic models predict with reasonable accuracy the experimentally observed phase behavior of the nitrogen-containing ternary systems considered in this work.

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