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Use of PC-SAFT for Global Phase Diagrams in Binary Mixtures Relevant to Natural Gases. 3. Alkane + Non-Hydrocarbons

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This work continues the systematic study of global phase diagrams in binary systems relevant for the description of natural gases using the perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state (EOS). Reservoirs frequently contain non-hydrocarbon compounds such as CO₂, N₂, or H₂S that have strong effects upon the thermodynamic properties of natural gases. Thus, we study the behavior of their binary mixtures with *n*-alkanes over wide pressure and temperature ranges to get a deeper insight into the intermolecular pair interactions reflected in the phase behavior of the mixtures. These systems show complex patterns within the van Konynenburg classification, and the theoretical model accurately reproduces them. In the case of H₂S containing mixtures (H₂S is a compound that has autoassociation hydrogen-bonding ability), we analyze several association models to obtain the most reliable approach by comparing the predicted association degree of H₂S to available experimental data. A conclusion from this series of papers is that PC-SAFT is a reliable and accurate model to predict the behavior of the different types of binary mixtures involved in complex multicomponent natural gases, with the ability to describe the different patterns of fluid-phase behavior presented by the studied systems over wide pressure and temperature ranges.

Introduction

Natural gases are mainly hydrocarbon molecules, but they also contain some light non-hydrocarbon compounds in significant proportions.^{1,2} The presence of these non-hydrocarbon molecules increases the structural complexity of natural gas multicomponent mixtures, because their sizes and shapes are very different from the hydrocarbons and because they give rise to stronger intermolecular forces in the mixtures because of their polar character or hydrogen bonding. This complexity appears in the strong effect of these compounds upon the phase behavior of natural gases;³ thus, the knowledge and systematic analysis of the phase-equilibria patterns of the binary systems *n*-alkane + non-hydrocarbon is a valuable tool to analyze the characteristics of molecular-level binary structural effects, which are useful for understanding the properties of the more-complex multicomponent mixtures, and to test the abilities of theoretical models to reproduce the intermolecular pair interactions in the binary systems reflected by the phase behavior of the mixtures.

Although the composition of natural gases is a function of the reservoir from which they come,¹ the most frequently found non-hydrocarbon molecules in natural gas reservoirs are CO₂, N₂, or H₂S.² N₂ and CO₂ systems are important, even though commercial natural gases must contain small quantities of these compounds. A significant proportion of natural gas reservoirs contain high levels of nitrogen, which decreases the quality of the gas and must be reduced before entering pipeline transportation systems. This is frequently an expensive operation that can cause uneconomic scenarios for the development of new fields. Accurate knowledge of phase equilibria may help in the development of more-efficient removal procedures. It is also important to remark that N₂, like methane, is always supercritical under reservoir conditions.^{2,3} Thus, its behavior must be described accurately by any model to give good predictions for the multicomponent natural gas mixtures.

Carbon dioxide binary systems are interesting both from academic and industrial viewpoints.⁴ CO₂ has no permanent dipole moment, but its large quadrupole⁵ moment gives rise to complex interactions with hydrocarbons that are difficult to predict theoretically and that result in complex phase behaviors, with the appearance of azeotropy in some systems such as ethane + CO₂. Use of CO₂ rich natural gas reservoirs has increased recently because of the rising demand for natural gas, and knowledge of their phase behavior is necessary for adequate development.

Hydrogen sulfide is generally an undesirable component of natural gases, but it may be present up to relatively high percentages, making the gas sour. When present, H₂S not only can affect the economic proportion of hydrocarbon gas in the reservoir, but it is highly toxic and corrosive for production equipment and for the environment. Thus, it should be eliminated or reduced before most uses by means of suitable technologies. As with CO₂, the need for greater natural gas production has increased the production of acid reservoirs, and removal of hydrogen sulfide has become increasingly important. The procedures for gas sweetening require accurate knowledge of complex mixtures phase behavior,^{6,7} which is affected by the hydrogen-bonding ability of H₂S.

Mixtures such as *n*-alkane + CO₂, +N₂, or +H₂S considered in this work are difficult tests for theoretical models because the complex intermolecular effects⁸ rising from the quadrupolar character of the molecules or from the existence of autoassociative hydrogen bonding, together with size and shape effects, cause complex phase-equilibria patterns. In this work, we apply the perturbed-chain statistical associating fluid theory (PC-SAFT)⁹ equation of state (EOS) to predict phase equilibria for mixtures over wide temperature and pressure ranges and to test the model capabilities. Although the most frequently used EOSs for design purposes are cubic,¹⁰ it is obvious that these EOSs are not reliable for prediction of phase equilibria in complex systems¹¹ such as the ones studied in this work. PC-SAFT, which has stronger molecular foundations and contains associative terms in the EOS, should produce more accurate predictions

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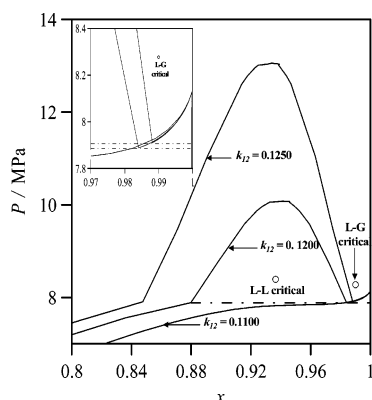


Figure 1. P -composition isothermal diagram for the $x\text{CO}_2 + (1-x)n$ -tridecane binary mixture at 310.80 K. (—) PC-SAFT diagram for different values of binary interaction parameter k_{12} , (---) PC-SAFT vapor-liquid-liquid three-phase line, (○) experimental gas-liquid and liquid-liquid critical points.²⁴

than a cubic EOS, representing a valuable alternative because it has only slightly greater computational complexity.

As in the previous papers in this series,^{12,13} the phase-equilibria patterns of the studied systems are classified and analyzed within the van Konynenburg and Scott classification,¹⁴ which, in spite of the existence of alternative and possibly more rigorous methods,¹⁵ is the most common and useful way to describe fluid-phase behavior.¹⁶

Methods

We apply the PC-SAFT EOS developed by Gross and Sadowski⁹ in this work. For associative compounds such as H_2S , the calculation of the additional associative term to the residual Helmholtz free energy requires two additional parameters: the association volume, κ^{AB} , and the association energy, ϵ^{AB} , between sites A and B¹⁷ together with an a priori definition of an association model according to the SAFT structure.¹⁸ Pure-component parameters, when not available in the literature, result from fitting literature vapor pressures and saturation liquid densities with a least-squares procedure. For binary mixtures, we use a simple monoparametric mixing rule for calculating cross parameters. We do not consider cross-association for n -alkane + H_2S binary systems. Hence, only one additional temperature-independent parameter, k_{ij} , is required from regression of isothermal vapor-liquid equilibrium data over wide temperature ranges. A detailed description of the model appears in the original model paper^{9,17} and in the first paper of this series.¹²

Results and Discussion

n -Alkane + CO_2 Binary Systems. This homologous series has received considerable attention in the literature, and reliable and accurate experimental data are available for most of the mixtures,¹⁹ because this system probes continuity in fluid-phase behavior for binary mixtures and because four of the six fluid-phase behavior patterns according to the van Konynenburg and Scott classification¹⁴ appear.^{4,19} Several models have been used to study phase equilibria in these systems,^{20,21} including molecular-based EOSs such as SAFT-variable range (SAFT-VR)¹⁹ and PC-SAFT.^{20,22} The literature contains reports of transitions from Type I to Type II on to the transition from Type IV to Type III as the n -alkane chain length increases. Mixtures up to n -hexane have Type I behavior. Type II low-temperature immiscibility appears for n -heptane and lasts until

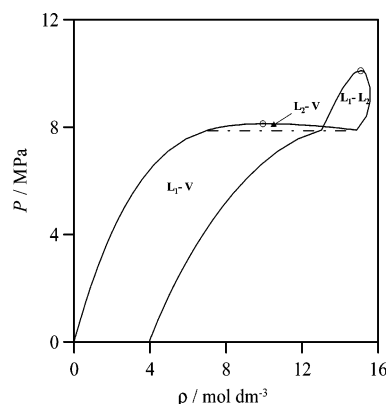


Figure 2. P - ρ isothermal diagram for $\text{CO}_2 + n$ -tridecane binary mixture at 310.80 K, calculated with PC-SAFT and $k_{12} = 0.1200$. (---) PC-SAFT vapor-liquid-liquid three-phase line, (○) experimental gas-liquid and liquid-liquid critical points.²⁴

Table 1. Experimental and PC-SAFT Upper Critical Endpoints (UCEP) for Nitrogen + n -Alkane Binary Mixtures^a

	k_{12}	experimental ^b		PC-SAFT	
		T , K	P , MPa	T , K	P , MPa
ethane	0.0418	132.38	4.072	129.92	3.756
propane	0.0719	126.62	3.478	126.95	3.466
n -butane	0.0941			126.88	3.466
n -pentane	0.0992			126.87	3.465
n -hexane	0.1168			126.87	3.465
n -heptane	0.1176			126.87	3.465

^a k_{12} = Binary interaction parameters used in PC-SAFT calculation.

^b Reference 28.

Table 2. PC-SAFT Parameters for H_2S and Results for the Correlation of Saturated Pressure and Saturated Liquid Density Data with Different Association Models^a

	two sites (2B)	three sites (3B)	four sites (4C)
ϵ/k , K	227.34	231.46	241.57
σ , Å	3.0737	3.1373	3.3015
m	1.6517	1.5725	1.3935
ϵ^{AB}/k , K	426.03	425.22	424.70
κ^{AB}	0.009 952	0.009 910	0.009 915
AAD P^{sat}	1.88	1.98	2.34
AAD ρ^{sat}	1.77	1.85	1.94
ΔT_c , K	0.82	0.84	0.81
ΔP_c , MPa	0.26	0.26	0.29
$-\Delta h^{\text{HB}}$, kJ mol ⁻¹	3.5	3.5	3.5
$-\Delta s^{\text{HB}}$, J mol ⁻¹ K ⁻¹	38.3	38.4	38.4

^a Reduced temperature range for parameter optimization = 0.570–0.998. Experimental data from ref 43.

n -dodecane. N -tridecane has Type IV behavior, and higher hydrocarbons have Type III patterns. The transition II/IV occurs with the presence of a tricritical point ($n = 12.33$ and $T = 317.5$ K),²³ and that of IV/III occurs with a double critical point ($n = 13.55$ and $T = 296.0$ K).²³ Thus, the transitional Type IV zone extends over a very narrow range. For mixtures with long-chain n -alkanes, solid phases interfere with the three-phase liquid-liquid-vapor region, and quadruple points appear. So, for n -dodecane and higher n -alkanes, solid phases obscure the three-phase region. The different sizes and shapes of the involved molecules, which give rise to asymmetric mixtures, and the quadrupolar character of carbon dioxide produce strong non-ideality with positive deviations from Raoult's law.¹⁶

García et al.⁴ have reported a complete study of global phase diagrams for this homologous series using PC-SAFT, showing that the model accurately reproduces the complex phase-equilibria patterns together with the transitions between the different types; thus, we only note additional features of the

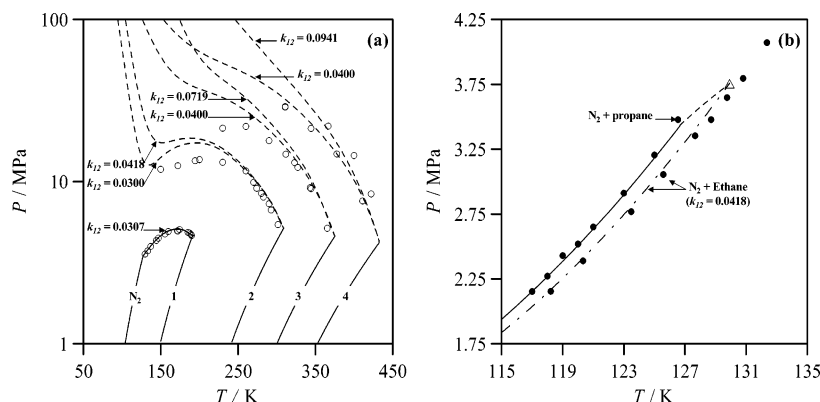


Figure 3. P – T projection of the global phase diagram for nitrogen + n -alkane binary mixtures. (—) PC-SAFT pure-compound vapor pressures, (○) experimental gas–liquid critical points,^{28,30–41} (---) PC-SAFT critical loci for different values of binary interaction parameter k_{12} , (●) experimental vapor–liquid–liquid equilibria, (– · –) PC-SAFT vapor–liquid–liquid equilibria curve, (△) PC-SAFT upper critical endpoint. The highest experimental vapor–liquid–liquid equilibrium corresponds to the experimental upper critical endpoint. The numbers in the plot indicate the number of carbon atoms for each compound.

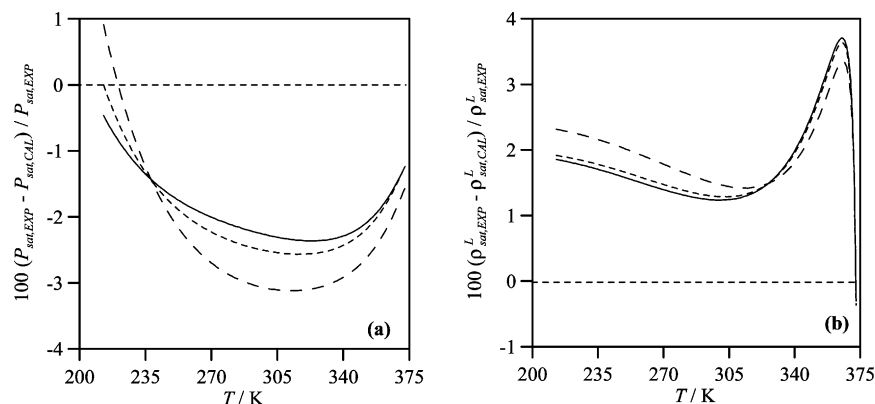


Figure 4. Percentage deviation between experimental⁴³ and calculated (a) saturated pressure and (b) saturated liquid density for H_2S with PC-SAFT model and different association models: (—) 2B, (---) 3B, and (– · –) 4C. Model parameters are from Table 2.

model for these systems. The transition between the different patterns along a homologous series is a delicate phenomenon and a strong test for any theoretical model. Thus, in Figure 1, we report the PC-SAFT pressure–composition isothermal diagram for CO_2 + n -tridecane in the three-phase region. This mixture has the complicated Type IV behavior^{24,25} and produces two separate miscibility zones. García et al.⁴ have considered a transferable parameter $k_{12} = 0.1200$ like Galindo and Blas¹⁹ using SAFT-VR. Figure 1 demonstrates how the behavior of this system in that region is sensitive to small changes in the binary interaction parameter. Although the model overestimates the size of the liquid–liquid zone giving critical values over 2 MPa above the experimental ones, the transferable parameter proposed produces the best results, reproducing the behavior of the mixture. Figure 2 contains the pressure–density isothermal diagram in the three-phase region. PC-SAFT reproduces properly the patterns in the different regions of the diagram, predicting the small L_2 –V region that collapses into a final point that denotes the end of the liquid–liquid–vapor coexistence curve. Thus, although some authors²⁵ have reported the need of more than one binary interaction parameter to describe the broad range of phase equilibria for CO_2 + n -tridecane mixtures with simple cubic EOSs, with PC-SAFT, a single transferable parameter describes the whole phenomenon along the homologous series.

n -Alkane + N_2 Binary Systems. Nitrogen is a common compound in natural gases and plays an important role in the design of several processes, such as liquefied natural gas. The interactions between nitrogen molecules are much weaker than those of hydrocarbons, as is apparent from comparison of the

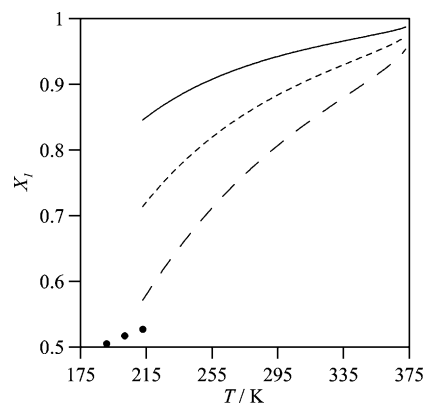


Figure 5. Monomer fraction in H_2S at saturation for different temperatures with PC-SAFT and different association models. Model parameters are from Table 2. Symbols are as in Figure 4. (●) QCE/B3LYP/6-311G** quantum calculations are from ref 46.

critical temperature of nitrogen, 126.2 K, to that of ethane, 304.1 K. Interactions between nitrogen and hydrocarbons should be weak, with positive deviations from Raoult's law. Thus, N_2 is a poor solvent for long-chain n -alkanes. In the homologous series n -alkane + nitrogen, immiscibility starts with ethane. Thus, the mixture methane + N_2 has Type I behavior,²⁶ whereas the rest of the n -alkanes have Type III patterns.^{27,28}

The binary interaction parameters required for PC-SAFT calculations come from García-Sánchez et al.²⁹ Figure 3 shows the PC-SAFT predictions for the first members of the homologous series, illustrating the effect of the binary interaction parameter on the predictions. PC-SAFT correctly predicts the

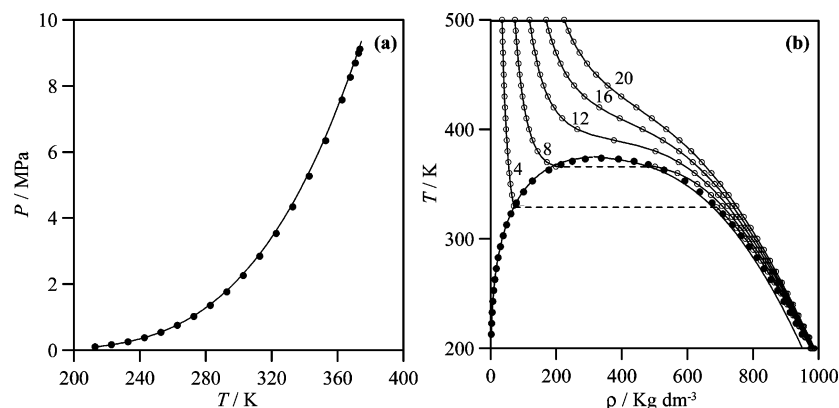


Figure 6. (a) Vapor pressure and (b) densities at saturation, subcritical, and supercritical conditions for H_2S : (●,○) Experimental⁴³ and (—) 4C/PC-SAFT values. Model parameters are from Table 2.

phase-behavior pattern. Methane + N_2 demonstrates total miscibility, Type I. The model predicts the appearance of immiscibility for ethane, as found experimentally. The critical locus for this system passes through a maximum and a minimum in pressure. Using García-Sánchez et al.²⁹ parameters results in overprediction of the critical loci for other members of the series, as shown in Figure 3. This may be a result of the parameter fitting procedure that does not consider experimental critical data.²⁹ Thus, although the subcritical vapor–liquid equilibria are reproduced well, the quality of predictions in the vicinity of the critical points is worse. The best predictions result from lower parameters. The model predicts the three-phase liquid–liquid–vapor region well, although it overestimates the UCEP (Figure 3b). Table 1 reports the calculated UCEP and compares them to the experimental values. It is apparent that, for n -alkanes above ethane, the predicted UCEP remains almost constant. From the results, it is clear that the phase behavior in this homologous series cannot be reproduced by a single transferable parameter; the weak N_2/n -alkane interactions together with the very different properties of the involved molecules require use of compound-dependent parameters to obtain accurate predictions. PC-SAFT can reproduce the subtle molecular effects of these mixtures reflected in their phase-equilibria patterns.

n -Alkane + H_2S Binary Systems. Hydrogen sulfide exists in many natural gas reservoirs. This acid gas must be removed to sweeten the gas, and accurate knowledge of phase-equilibria behavior of hydrocarbon + H_2S binary pairs is important for industrial purposes. Some of these systems have complex phase behavior, such as those containing ethane⁴² or propane⁷ that have positive azeotropic behavior.

PC-SAFT parameters for pure H_2S are not available in the literature, so we have produced them from regression of saturation pressures and densities. H_2S is a self-associating compound, so the associative term is necessary for calculating the total Helmholtz energy. The selection of the association model must precede application of the model to obtain explicit expressions to determine the monomer fraction in the fluid (fraction of molecules nonassociated through hydrogen bonding). Huang and Radosz¹⁸ suggested a 3B, three-sites model, association scheme for the original SAFT model, but in this work, we have tested the results obtained with a 2B model, two-sites simplified association scheme, 3B and 4C, four-sites rigorous association type. In Figure 4 and Table 2, we report the results obtained with the three considered association models for the correlation of experimental saturation properties. The correlation results obtained with the different models are similar with slightly greater deviations for the 4C association scheme. From the results of Table 2, we conclude that, although the critical

Table 3. Correlation Results for Binary Vapor–Liquid Equilibria with PC-SAFT^a

	k_{12}	AAD, %		T , K	N	ref
		x	y			
H_2S + methane	0.0401	5.14	2.70	277.59–344.26	62	6
H_2S + ethane	0.0598	4.44	4.97	199.93–283.15	45	47
H_2S + n -propane	0.0850	11.61	3.39	243.15–288.15	27	48
H_2S + n -butane	0.0469	7.85	5.81	366.45–418.15	63	49
H_2S + n -pentane	0.0753	4.04	6.26	277.59–444.26	71	50

^a k_{12} = Binary interaction parameter, N = number of experimental data points, and AAD (%) is the percentage absolute average deviation in liquid and vapor compositions.

properties are overpredicted by the model, the differences from experimental values are small compared to those of other models. For the selection of the correct association model, we must consider that one of the main advantages of the SAFT family EOS is the clear physical meaning of the model parameters. For associative compounds, the κ^{AB} and ϵ^{AB} parameters can be related to the enthalpy, Δh^{HB} , and entropy, Δs^{HB} , of association (hydrogen bonding) using the quasi-chemical theory.^{44,45} The values of Δh^{HB} and Δs^{HB} are independent of the selected association model, but they are physically reasonable considering that weak hydrogen bonding occurs between hydrogen sulfide molecules. Ludwig⁴⁶ has reported a theoretical study at the B3LYP/6-311G** level on the energetics of hydrogen bonding of hydrogen sulfide, reporting a value of 4.274 kJ mol^{−1} for the dimer. This value is close to the 3.5 kJ mol^{−1} reported in Table 2 and shows the weak character of the hydrogen bonding for this molecule. Another test of the model can be done through analysis of monomer fraction, X_1 , in the fluid. Ludwig⁴⁶ reports an analysis of cluster populations, giving a value of $X_1 = 0.505$ at the melting point. In Figure 5, the monomer fraction calculated with PC-SAFT and different association models is compared to the values reported from Ludwig.⁴⁶ X_1 is overpredicted by the three association schemes, as we might expect given the lower association enthalpies reported in Table 2, but closer results are obtained with the four-sites association scheme. Thus, considering the similar correlative ability of the three association models, but taking into account the physical meaning of the association parameters, a four-sites rigorous model, with the parameters reported in Table 2, is chosen for the phase-equilibria calculations for pure H_2S and for the binary mixtures. In Figure 6, we see how PC-SAFT demonstrates good correlative ability, both for the saturation dome and the supercritical regions.

The binary interaction parameters for n -alkane + H_2S are not available in the literature, so we have regressed experimental vapor–liquid equilibrium data (Table 3). Figure 7 compares

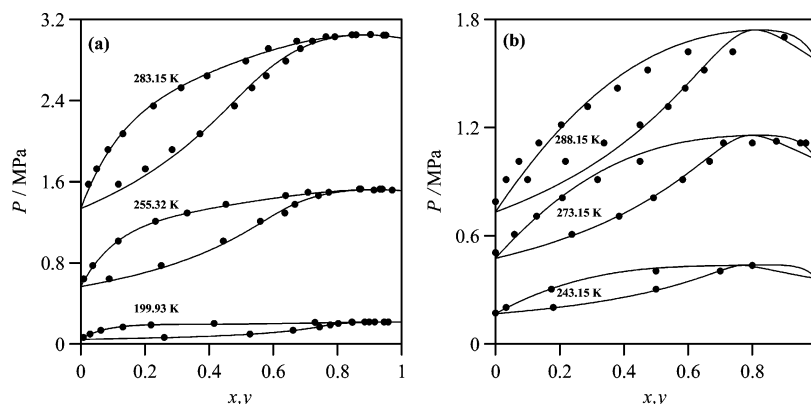


Figure 7. Isothermal vapor–liquid equilibria for (a) (x)ethane + (1 - x)H₂S and (b) (x)propane + (1 - x)H₂S: (●) experimental^{47,48} and (—) PC-SAFT ($k_{12} = 0.0598$, ethane, and $k_{12} = 0.0850$, propane) values.

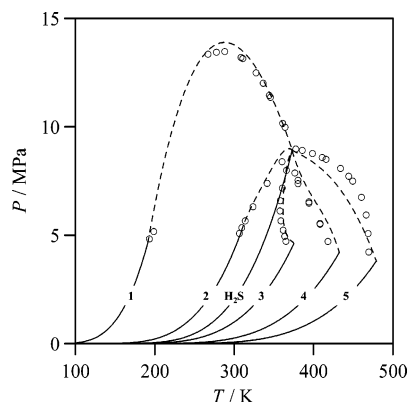


Figure 8. P – T projection of the global phase diagram for n -alkane + H₂S binary mixtures: (○) experimental gas–liquid critical points,^{6,49,50,51–55} (—) PC-SAFT pure-compound vapor pressures, (---) PC-SAFT critical loci ($k_{12} = 0.0401$, methane; $k_{12} = 0.0598$, ethane; $k_{12} = 0.0850$, propane; $k_{12} = 0.0469$, n -butane; and $k_{12} = 0.0753$, n -pentane). The numbers in the plot indicate the number of carbon atoms of each compound.

experimental and PC-SAFT vapor–liquid equilibria at different temperatures for ethane or propane + H₂S binary systems. PC-SAFT correlates well the complex azeotropic behavior of these mixtures with just a single binary interaction parameter over wide temperature ranges. The model predicts the location of the azeotrope well at the different temperatures studied.

The P – T projection of the global phase diagram for the first members of the series appears in Figure 8. All the systems show Type I behavior (or Type II with the immiscibility region at low temperatures hidden by solidification). The model predicts the values and shapes of the critical loci well, and greater deviations appear only for the longest n -alkanes. The methane + H₂S system has a critical locus with a well-defined maximum in pressure. The systems with ethane and propane have more-complex trends because of azeotropy (Figure 7). The ethane binary system has azeotropic behavior without a minimum temperature on the critical locus.⁵² PC-SAFT correctly predicts this behavior also. For n -alkanes longer than propane, PC-SAFT does not predict an azeotrope, and with the increasing chain length, the curvature of the critical loci increases with the appearance of pressure maxima. The complex behavior of this homologous series does not allow use of transferable parameters, so compound-dependent binary interaction parameters are required.

Concluding Remarks

PC-SAFT accurately predicts complex fluid-phase behavior for n -alkane + CO₂, + N₂, and + H₂S. The model predicts the

evolution of fluid-phase behavior patterns along homologous series along with the transitions between the different types. For the homologous series, the phase behavior is reproduced with a single transferable parameter for all the mixtures, and the characteristics of the complex transitional Type IV pattern for the n -tridecane system are correctly predicted. The homologous N₂ containing series does not allow the use of transferable parameters, but their phase-equilibria patterns are reproduced well with compound-dependent parameters in spite of the weak interactions between nitrogen and n -alkanes. For H₂S, the hydrogen-bonding ability of the compound requires adequate associative parameters that are physically meaningful, but despite these difficulties and the complex phase patterns of binary mixtures with n -alkanes, the model produces accurate predictions along the homologous series, even predicting the appearance of azeotropy with some of the smallest n -alkanes of the homologous series.

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