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Modeling Phase Equilibria of Asymmetric Mixtures Using a Group-Contribution SAFT (GC-SAFT) with a k_{ij} Correlation Method Based on London's Theory. 2. Application to Binary Mixtures Containing Aromatic Hydrocarbons, *n*-Alkanes, CO₂, N₂, and H₂S

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A group-contribution statistical associating fluid theory equation of state (GC-SAFT EOS) that was proposed by Tamouza et al. [Tamouza et al. *Fluid Phase Equilib.* **2004**, *222–223*, 67–76], which was extended in the first part in this series of papers to the asymmetric systems CO₂ + *n*-alkane, methane + *n*-alkane, and ethane + *n*-alkane, is further tested here on binary mixtures that contain aromatic hydrocarbons, *n*-alkanes, CO₂, N₂, and H₂S. The method for correlating the binary interaction parameters (k_{ij}), which is inspired by London's theory of dispersive interactions, uses only pure compound adjustable parameters ("pseudo-ionization energies" of compounds *i* and *j*, denoted as J_i and J_j). A group contribution for the latter parameters also is used for *n*-alkane and alkyl benzene series. Numerous prediction tests on the aforementioned cited systems were performed in a systematic and comprehensive way. Predictions are both qualitatively and quantitatively satisfactory, within deviations (4%–5%) that are comparable to those obtained on previously investigated systems (*n*-alkane + *n*-alkane, *n*-alkane + aromatic, *n*-alkane + *n*-alkanol).

1. Introduction

Knowledge of the thermodynamics and especially the phase behavior of fluid systems is central to chemical process design, particularly in oil and petroleum industries (separation and refining process, natural gas processing, natural gas production, etc.), and it is now more crucial than several years ago, because, for many reasons (environmental, global competition, etc.) the plants should be designed more accurately. For this purpose, thermodynamic models are needed. However, the experimental information that is available for these systems and needed to develop the models for fluid-phase computations is not always plentiful. Measurements that are used to complete the database are time-consuming and expensive to perform. This is why, currently, it is important to have access to a reliable tool that can make realistic predictions to supply data that, at least partially, compensates for the lack of information. Efforts must be made in that direction, and this work is performed in that perspective.

In the first part of this work,[1] our research group extended a group contribution method, combined with the perturbed-chain statistical associating fluid theory equation of state (PC-SAFT EOS), to predict the fluid-phase equilibria of some asymmetric systems of interest in the petroleum industry. Contrary to more-symmetric systems, the vapor–liquid equilibria (VLE) and liquid–liquid equilibria (LLE) of these former systems are well-represented, provided that nonzero binary interaction parameters (k_{ij}) are used. A simple method was proposed earlier[1] to compute the corresponding k_{ij} parameters and was tested for some selected systems, namely, CO₂ + *n*-alkane, methane + *n*-alkane, and ethane + *n*-alkane. However, to be used as a reliable tool for prediction, this method should be evaluated on a broader variety of systems than those examined in the first part of this series of papers;[1] that is the goal of the work in this part of the series.

Here, to test our approach further, a decision was made to consider the phase equilibria of mixtures that contain methane (CH₄), ethane (C₂H₆), and other hydrocarbons, as well as carbon dioxide (CO₂), nitrogen gas (N₂), and hydrogen sulfide (H₂S), because they are major compounds that are involved in natural gas and petroleum, either as components or additives. For instance, for enhanced oil recovery, carbon dioxide, nitrogen, or natural gas is injected into the petroleum reservoir, to push additional oil toward the surface ground and to reduce its viscosity by dissolution, thus improving the oil flow rate.

Here again, the tests were conducted as comprehensively as possible.

2. Group-Contribution–Perturbed-Chain Statistical Associating Fluid Theory Equation of State (GC–PC-SAFT EOS)

As explained in the first paper in this series,[1] phase equilibria computations were made in this work using PC-SAFT EOS. The main reason for choosing PC-SAFT rather than variable-range statistical associating fluid theory (VR-SAFT) and the original version is that the former proved to be more accurate for treating systems that contain a species under supercritical conditions.[2,3]

The expressions of the PC-SAFT EOS are not recalled here, and the interested reader can refer directly to the original paper for more details.[4] However, when polar compounds are involved, such as CO₂ and N₂ (quadrupolar compounds), it was shown[1,5,6] that it is then preferable to use an extended EOS,

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$$a = a^{\text{nonpolar}} + a^{\text{QQ}} \tag{1}$$

to improve the representation of the phase diagram significantly. In eq 1, a^{nonpolar} refers to the original PC-SAFT EOS, whereas a^{QQ} is a term that accounts for quadrupole—quadrupole interactions (here, only quadrupolar species are considered). The a^{QQ} term used here is an extension of Gubbins and Twu's theory[7] to chain molecules, following the "segment-approach" that was proposed by Jog and Chapman.[8-10] In this approach, the polar moments are assumed to be well-localized on certain segments of the chain. The detailed expression for a^{QQ} can be found in the appendix given in the first paper in this series.[1] In addition to the quadrupole moment (Q), this extension involves the quadrupolar fraction x_p^Q, which is defined as the fraction of segments in the chain that carries quadrupoles.

For predictive purposes, a group contribution method is incorporated to evaluate the equation of state (EOS) parameters. Segment parameters (such as energy (ε) and diameter (σ)) and the chain parameter (m) of the molecule are calculated using group contribution relations that were inspired by the Lorentz—Berthelot combining rules,[2,11] and these expressions are written as follows:

$$\varepsilon = \sqrt[n_{\text{G}}]{\left(\prod_{k=1}^{n_{\text{groups}}} \varepsilon_k^{n_k}\right)} \tag{2}$$

$$\sigma = \sum_{k=1}^{n_{\text{groups}}} \left(\frac{n_k \sigma_k}{n_{\text{G}}}\right) \tag{3}$$

$$m = \sum_{k=1}^{n_{\text{groups}}} n_k R_k \tag{4}$$

ε_k, σ_k, and R_k are parameters of the chemical group k; n_k is the number of groups k in the molecule that is composed of a number n_{groups} of different groups. The total number of groups in the molecule is denoted n_{G} and is simply given by

$$n_{\text{G}} = \sum_{k=1}^{n_{\text{groups}}} n_k$$

These relations may be used for compounds that belong to a well-defined chemical family (n-alkane, 1-alkanol, etc.), with the exception of the first or sometimes the first two member(s) (methane, ethane, methanol, etc.), which should be treated specifically.

3. Extension to Asymmetric Mixtures: A Description of the k_{ij} Correlation Method

PC-SAFT is extended to mixtures using the Van der Waals one-fluid model and the Lorentz—Berthelot combining rules, modified to introduce empirical binary interaction parameters k_{ij} and l_{ij}:

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{5}$$

$$\sigma_{ij} = (1 - l_{ij})\left(\frac{\sigma_{ii} + \sigma_{jj}}{2}\right) \tag{6}$$

By setting $k_{ij} = l_{ij} = 0$, one recovers the original combination rules, which allow for pure prediction. This hypothesis was found out to be suitable for some systems, rather symmetric, as noticed from earlier works,[2,12-15] and containing species following the group contribution approach defined by eqs 2—4. However, for systems that contain small species, such as CO_2, methane, and ethane, nonzero binary interaction parameters were needed to obtain a realistic prediction of the corresponding phase

Table 1. Parameters for Small Species Considered in This Study (PC-SAFT Model)

	ε/k (K)	σ (Å)	m	κ^{AB}	ε^{AB}	quadrupole moment, Q (B)[a]	$x_p m$
CH_4	147.42	3.66	1.03				
C_2H_6	189.00	3.51	1.64				
H_2S	225.05	3.42	1.30	0.0947	449.7061		
N_2	98.70	3.72	0.93			1.8	1.00
CO_2	139.99	2.98	1.84			4.3	0.52

[a] The unit B represents Buckinghams; 1 Buckingham = 3.335641 × 10^{-40} C m².

envelopes. In our previous study,[1] only one binary parameter—namely, k_{ij}—necessary for this purpose. This hypothesis was followed here, and l_{ij} was then set to zero again.

The classical evaluation method of k_{ij} involves data regression for each considered mixture. However, as shown earlier[1] for some binary systems (CO_2 + n-alkane, methane + n-alkane, and ethane + n-alkane), the total number of adjustable parameters could be dramatically reduced using a correlation inspired by London's dispersive interaction theory.[12,13] This correlation method has an advantage over other correlation methods in that it incorporates only pure compound parameters (see Part 1[1] for a full discussion). One reads:

$$1 - k_{ij} = \frac{2\sqrt{(J_i J_j)}}{J_i + J_j} \tag{7}$$

where J_i and J_j represent the "pseudo-ionization energy" of the segments in chain molecules i and j. Notice that J_i and J_j are treated as adjustable parameters and are not a priori expected to be equal to experimental values of the true ionization energy. In this work, J is also described by a group contribution method,

$$J = \sqrt[n_{\text{G}}]{\left(\prod_{k=1}^{n_{\text{groups}}} J_k^{n_k}\right)} \tag{8}$$

that applies to series of chemical compounds.

Relations 7 and 8 represent the basis of our method that is tested further on various systems that were quoted in the Introduction of the present publication.

4. Determination of Parameters

Phase equilibria computations and the regression procedure were performed in the same manner as that described in the first paper in this series. (For more details, refer to Part 1 of this series of papers.[1])

4.1. EOS Parameters. 4.1.1. n-Alkane Series. All these species have been already considered in previous works.[2] For the sake of completeness, the parameters and the hypotheses used to obtain them are very briefly recalled here.

Methane and ethane were treated as specific nonpolar, non-associative compounds, possessing their own parameters (see Table 1). All the remaining n-alkanes were modeled using the group contribution relations described by eqs 2—4). Two groups ((CH_2) and (CH_3)) are needed for their description (see Table 2).

4.1.2. Methyl Branched Alkanes. As was already presented elsewhere,[2,14] the branched alkanes are described using the following hypothesis, which is similar to that used for alkyl esters. They are decomposed into four groups: (CH_2), (CH_3) at the chain end, (CH) in the linear chain, and a substituted group (CH_3). The parameters of the groups (CH_2) and (CH_3) at the chain end were reused from n-alkanes. (CH) parameters were

Table 2. Group Contribution Parameters for Alkane Series (GC−PC-SAFT EOS)

group	ε/k (K)	σ (Å)	R
		n-Alkane	
CH_2	261.0866	3.9308	0.3821
		Branched Alkanes	
$>CH-$	402.0232	4.9252	0.2000
$(-CH_3)_1$	189.9628	3.4873	0.7866
$(-CH_3)_2$	189.9628	3.4873	0.5527
$(-CH_3)_3$	189.9628	3.4873	0.3424
$(-CH_3)_4$	189.9628	3.4873	0.3029
$(-CH_3)_5$	189.9628	3.4873	0.2741

Table 3. Relative Deviations of Vapor Pressures and Saturated Liquid Volumes of the Regression Database of Branched Alkanes with the GC−PC-SAFT

compound	Npt^a	temperature, T (K)	average absolute deviation (AAD) for P^{vap} (%)	Npt	temperature, T (K)	average absolute deviation (AAD) for ρ^{liq} (%)
2-methyl butane	24	217−460	1.62	26	190−455	0.32
2-methyl pentane	25	241−498	0.97	8	258−333	0.46
2-methyl hexane	27	271−530	1.05	24	272−523	1.63
2-methyl heptane	35	222−560	0.92	29	263−543	1.36
2-methyl octane	16	313−571	1.47	5	283−313	1.09
2-methyl nonane	15	325−469	1.37	4	273−313	1.26
3-methyl pentane	27	243−504	4.52	10	266−339	2.26
3-methyl hexane	26	272−535	0.78	29	233−523	2.19
3-methyl heptane	36	223−564	1.35	31	263−558	1.29
3-methyl octane	14	306−445	2.68	5	283−313	0.42
3-methyl nonane	17	325−470	2.67	4	273−313	0.15
4-methyl heptane	28	293−562	2.06	28	263−533	0.32
4-methyl octane	15	305−443	1.38	5	283−313	0.52
4-methyl nonane	15	323−467	3.06	4	273−313	0.89
5-methyl nonane	15	323−467	0.80	4	273−313	1.42
overall			1.72			1.16

^{a} NPT = number of points.

adjusted using the pure vapor pressure and liquid-phase saturated densities for the entire series of methyl branched alkanes (see Tables 2 and 3). Concerning the substituted (CH_3) group, the energy and the diameter were assumed to be equal to those of (CH_3) at the chain end. However, the chain contribution R_{CH_3} for this substituted group was assumed to be position-dependent and different values were regressed for different positions in the chain.

All the parameter values are given in Table 2. The results obtained are detailed in Table 3. These hypotheses allow a good description of the pure VLE of methyl branched alkanes.

4.1.3. Pure Alkyl Benzenes and Xylenes. These compounds were already considered in earlier work.[15]

Alkyl benzenes are composed of four different chemical groups: (CH_2) and (CH_3), whose parameters are already known from *n*-alkane study; $(CH)_{BR}$ in a benzene ring; and $(C)_{AB}$, the condensed carbon in alkyl benzene. The latter parameters were adjusted on the VLE data alkyl benzene series.

These compounds were considered to be quadrupolar. With regard to the quadrupole moments, note that, strictly speaking, they are tensors and only in the case of a highly symmetrical molecule (such as benzene) does the quadrupole tensor reduce to a scalar quantity, which allows the use of relations A1−A4 in the appendix given in Part 1[1] for computations. In the other cases, more-general (but also more-complex) expressions should be used, but they require physical parameters that are often unavailable.[16] For engineering applications, a simple approximation can be made, assuming an effective scalar quad-

rupole moment $\langle Q \rangle$. The conditions of validity for this approach have been discussed by Gubbins et al.[16] This approximation will be made here.

Experimental or estimated (e.g., using ab initio calculations)[17] values of the effective quadrupole moments $\langle Q \rangle$ are only available for some compounds (such as benzene, toluene, and *para*-xylene[17,18]) and may vary considerably from one author to another.[18] In the case of benzene, for instance, most of the experimental absolute values are in the range of 8.5−9.98 B,[18] and Stogryn and Stogryn[19] even reported a value of 3.6 B. [Note that the unit B denote a Buckingham; 1 Buckingham = 3.335641 × 10^{-40} C m².] In the case of toluene and *para*-xylene, the quadrupole moment is not scalar, and, to the best of our knowledge, only $\langle Q \rangle$ values that have been estimated via ab initio techniques are provided.[17] However, one must use these values with care, because when comparison is possible, significant deviations between estimates and experimental data are sometimes observed (see Table 2 in the article of Reynolds et al.[17])

Unfortunately, quadrupole moments are unavailable for the other aromatic compounds that have been considered here. To treat the entire series of alkyl benzenes, one must make some additional hypotheses, such as assuming, as did Karakatsani and Economou,[20] for instance, that all alkyl benzenes have the same effective quadrupole moment as toluene (7.92 B, from Reynolds et al.[17]).

For all the reasons cited above, we have considered the quadrupole moments to be adjustable parameters but we have allowed them to vary in bounded limits, to preserve some physical meaning. Preliminary calculations showed us that it was necessary to set specific values of quadrupole moments for benzene (BZ), toluene (C_1BZ), and ethyl benzene (C_2BZ). For all the other alkyl benzenes that have been considered here, a single common quadrupole moment value was determined to be sufficient.

The quadrupolar fraction is defined as

$$x_P^Q = \frac{b}{m} \tag{9}$$

where the parameter b was adjusted as proposed by Chapman and co-workers[10,21] to obtain better results. Theoretically, b should be an integer, so the choice to adjust this parameter may be surprising and questionable initially. But remember that the SAFT EOSs rely on a very simplified description of the molecular structure: molecules are viewed as tangentially bonded equally sized hard spheres. As a consequence of this simplification, the total number of segments (m) is generally not an integer[4,22,23] and is frequently adjusted. Moreover, segments are not identified stricto sensu to the chemical groups. Thus, an integer number of polar groups does not result in an integer number b. Finally, the polar moments are defined in principle for the entire molecule, so that the assumption (which is made with the segment approach) that they are localized on certain chemical groups of the molecule may not be fully justified in all cases. For all these reasons, it is acceptable that the number of polar segments $x_P m$ is not an integer. The optimal value is then obtained by regression.

The xylenes considered here are *meta*-xylene, *ortho*-xylene, and *para*-xylene. The chemical groups that are involved are the same as those in alkyl benzenes, but in different numbers: two $(C)_{AB}$, two substituted (CH_3), and four $(CH)_{BR}$. However, the distinction between the three isomers is made as follows. The parameters of $(CH)_{BR}$ and $(C)_{AB}$ groups are those from alkyl benzenes. The energy (ε_{CH_3}) and diameter (σ_{CH_3}) values of the two (CH_3) groups were set to values that have been used for

Table 4. (a) Group Contribution Parameters for Alkyl Benzene Series and Xylenes (Polar GC−PC-SAFT EOS) and (b) Polar Parameters for Aromatic Compounds

compound	ε/k (K)	σ (Å)	R	quadrupole moment, Q (B)[a]	$x_p m$
(a) Group Contribution Parameters					
alkyl benzene					
(C)$_{AB}$ group	391.5410	4.2783	0.0016		
(C)$_{BR}$ group	294.2235	3.7572	0.3805		
xylene					
CH$_3$ para group	189.9628	3.4873	0.7866		
CH$_3$ ortho group	189.9628	3.4873	0.8593		
CH$_3$ meta group	189.9628	3.4873	0.7796		
Polar Parameters					
benzene				8.52	0.250
toluene				9.17	0.250
ethyl benzene				8.78	0.250
alkyl benzene series, starting from propyl benzene				7.00	0.250
ortho-xylene				7.12	0.250
meta-xylene				8.55	0.250
para-xylene				9.52	0.250

[a] The unit B represents Buckinghams; 1 Buckingham = 3.335641 × 10^{-40} C m^2.

n-alkanes. The chain contribution (R_{CH_3}) of one substituted (CH$_3$) group was set to the value of *n*-alkanes, and the other RCH$_3$ was considered to be dependent on the relative position (ortho, meta, and para) and was determined using data regression.

The quadrupolar fraction for xylenes was reused from alkylbenzenes. Specific quadrupole moments were assigned to each xylene and adjusted.

All the pure parameters of the different groups are given in Table 4.

4.1.4. Pure N$_2$ and CO$_2$. These two compounds are treated specifically in a manner similar to that considered earlier for CO$_2$.[1] They are quadrupolar compounds whose quadrupole moments were set to their respective experimental values (1.8 B for N$_2$ and 4.3 B for CO$_2$).[18,19] The polar fractions were adjusted for the same reasons as those explained above in the case of aromatic compounds.

As noticed from earlier works[1,9] on polar systems and by our own observations, the EOS parameters (and especially the energy parameter ε) often seem to be strongly correlated to the quadrupolar parameters Q and x_p^Q. As a consequence, numerous sets of parameters allow for a good representation of the pure compound VLE but only some of them may also provide a good prediction of the phase equilibria of the mixtures.

The values of these parameters were then determined by regression of the corresponding pure vapor pressure and saturated liquid density data and some mixture data of a "key binary mixture". Here, CO$_2$ + propane and N$_2$ + propane were selected as key mixtures, because numerous and reliable data are available for these systems. A zero value could be set to $k_{CO_2,propane}$ to determine the CO$_2$ EOS parameters, whereas from preliminary calculations, a similar assumption did not seem to hold in the case of the N$_2$ + propane system. Even when setting J_{N_2} to the experimental value of the corresponding true ionization energy ($k_{N_2,propane}$, estimated using relation 7), a systematic and significant overestimation of bubble pressure was observed. It was thus decided to adjust $k_{N_2,propane}$, together with the other N$_2$ EOS parameters.

Pure vapor pressures and saturated liquid densities for N$_2$ were taken from DIPPR.[24] Polar PC-SAFT parameters for nitrogen, and the deviations obtained on vapor pressure and liquid density, are reported in Tables 1 and 5, respectively.

Table 5. Deviation on Vapor Pressure and Liquid Density (PC-SAFT)

Compound	temperature, T (K)	Npt	average absolute deviation (AAD) for P^{vap} (%)	temperature, T (K)	Npt	average absolute deviation (AAD) for ρ^{liq} (%)
CH$_4$	91−191	21	0.49	91−191	21	1.06
C$_2$H$_6$	90−305	44	0.67	90−305	44	0.80
N$_2$	63−126	64	0.13	63−126	64	0.58
H$_2$S	187−373	38	1.55	187−373	38	2.92
CO$_2$	216−304	19	0.55	216−302	18	1.21

Table 6. Pseudo-ionization Energies of a Series of *n*-Alkanes and Alkyl Benzenes

chemical group	pseudo-ionization energy, J (eV)
n-Alkane Series (Starting with *n*-Propane)	
CH$_2$	7.35
CH$_3$	12.99
Alkyl Benzene Series (Starting with Propyl Benzene)	
(C)$_{AB}$	3.88
(CH)$_{BR}$	8.45

4.1.5. Pure H$_2$S. Here, pure hydrogen sulfide (H$_2$S) is considered to be an associative compound but nonpolar. Following the suggestions of several researchers,[23,25] here, the selected association model is 3B in Huang and Radosz's notation.[23] The parameters were determined via the simultaneous regression of pure compound data (saturation pressure and saturated liquid-phase volume) and VLE data of a hydrogen sulfide + propane mixture as the key mixture (as defined above). As a first approximation (as in the case of methane and ethane), the pseudo-ionization energy of H$_2$S was set to its experimental value (that is 10.45 eV[26]) to allow calculation of the value of $k_{H_2S,propane}$ from eq 7.

The PC-SAFT pure compound parameters and the deviations obtained on vapor pressure and liquid density at saturation are reported in Tables 1 and 5, respectively.

4.2. Pseudo-ionization Energy. 4.2.1. Nonaromatic and Aromatic Hydrocarbons. The pseudo-ionization energies (J) of the *n*-alkane series (starting from propane) and the values of J_{CH_3} and J_{CH_2} were determined in the first paper of this series[1] by considering CO$_2$ + *n*-alkane mixtures and were reused here (see Table 6). $J_{methane}$ and J_{ethane} were set to experimental values of the true ionization energies[1] (see Table 8, which is presented later in this paper).

In the case of methyl branched alkanes, the following analysis was made. From experimental values of the ionization energy, one may note that the ionization energy values of isomer alkanes generally are very close to one another (see Table 7), i.e., equal as a first approximation. Thus, the pseudo-ionization energies of methyl-substituted alkanes were set to the value of the corresponding linear *n*-alkane isomer. All these values are reported in Tables 6−8.

In regard to aromatic hydrocarbons, we followed the procedure outlined in the first paper in this series[1] to determine their pseudo-ionization energies, which consisted, first, in evaluating the k_{ij} values of selected mixtures, then deducing the $J_{aromatic}$ values, using relation 7. When possible, group contribution pseudo-ionization parameters are then determined via relation 8. As in the case of *n*-alkanes, CO$_2$ + aromatic systems were chosen for this work, because the value of J_{CO_2} is already known. The data are not as numerous as in the case of CO$_2$ + *n*-alkane; however, a sufficient amount of data is available for this task.

Benzene, toluene, ethyl benzene, and xylenes were again treated as specific compounds, each of them possessing a

Table 7. Pseudo-ionization Energies and Experimental Values of Ionization Energy of Alkane and Branched Alkanes

compound	experimental ionization energy (eV)[a]	pseudo-ionization energy, J (eV)
n-butane	10.57	9.77
iso-butane	10.57	9.77
n-pentane	10.37	9.23
2-methyl butane	10.32	9.23
n-hexane	10.29	8.88
2-methyl pentane	10.04	8.88
3-methyl pentane	10.04	8.88
n-octane	9.80	8.47
2-methyl heptane	9.84	8.47

[a] Experimental data are taken from NIST.[26]

Table 8. Pseudo-ionization Energies of Pure Compounds Treated Separately

component	experimental value of ionization energy (eV)[a]	pseudo-ionization energy, J (eV)
carbon dioxide	13.78	13.78
methane	12.61	12.61
ethane	11.52	11.52
H2S	10.45	10.45
N2	15.50	21.00
benzene	9.24	7.76
toluene	8.82	6.74
ethyl benzene	8.77	7.03
meta-xylene	8.56	7.00
para-xylene	8.52	7.00
ortho-xylene	8.56	7.00

[a] Experimental data are taken from NIST.[26]
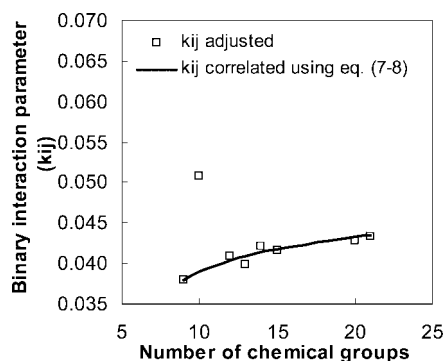
Figure 1. Relationship between the binary interaction parameter k_{ij} and the number of chemical groups in the alkyl benzene series, starting from propyl benzene.

specific pseudo-ionization energy. Note that, in the same spirit as that for branched n-alkane, a single pseudo-ionization energy value was set for the three xylenes. This assumption is supported by close experimental values of the ionization energy for these three compounds. No attempt was made at this level to use a group contribution method for the corresponding pseudo-ionization energy, because too few compounds were considered in this study.

However, the pseudo-ionization energies of the series of alkyl benzenes, starting from propyl benzene, were well-correlated by relation 8, except perhaps in the case of butyl benzene. (See the plot of k_{ij} versus carbon number, shown in Figure 1.) The group contribution pseudo-ionization energy values of the $(CH)_{BR}$ and $(C)_{AB}$ groups are given in Table 6.
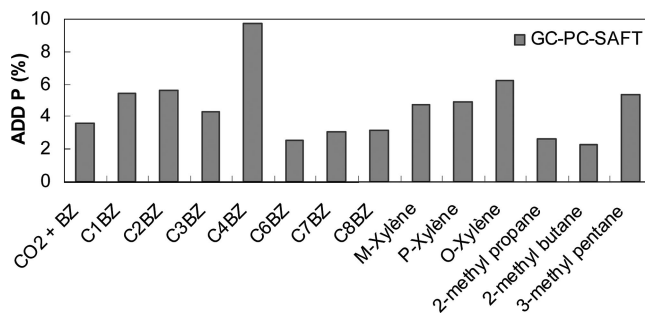
Figure 2. Overall average deviations in the VLE of CO_2 + hydrocarbon mixtures; the k_{ij} of the mixture is calculated using eqs 7 and 8.
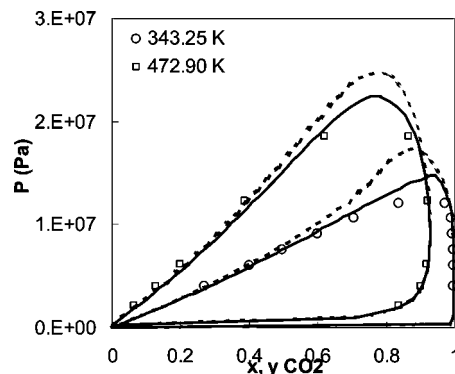
Figure 3. Vapor−liquid equilibrium (VLE) of the CO_2 + n-propyl benzene mixture, showing a comparison of the model calculations: (—) correlation result with polar GC−PC-SAFT ($k_{ij} = 0.038$, using eqs 7 and 8) and (- - -) correlation result with PC-SAFT, using the molecular parameters for pure CO_2 and n-propyl benzene, as provided by Gross and Sadowski[4] ($k_{ij} = 0.125$). Data taken from ref 61.

4.2.2. Nonhydrocarbon Light Compounds. As explained in a recent paper, the pseudo-ionization energies of methane, ethane, CO_2, and H_2S in this work were set to the experimental value of the true ionization energy.

Remember that, in the case of N_2, however, it was not possible to make the same hypothesis, as explained above. The value of J_{N_2} was obtained from $k_{N_2,propane}$, which already has been determined to represent the N_2 + propane mixture.

All the corresponding pseudo-ionization energy values are given in Table 8.

5. Results of the Correlation and Prediction of Phase Equilibria

5.1. Correlation Results. 5.1.1. CO_2 + Aromatic Systems (Quadrupolar + Quadrupolar). All the CO_2 + aromatic VLE mixtures data (11 systems) were, in fact, correlated to determine the pseudo-ionization energy values of the alkyl benzenes and xylenes.

The VLE representations obtained with GC−PC-SAFT are again satisfactory (within 4%−5%; see Figure 2), with the exception of the CO_2 + butyl benzene system, and they compare well to those computed using the original PC-SAFT (see Figure 3). All the detailed results are given in Table S1 in the Supporting Information.

In the case of the CO_2 + butyl benzene system, two data series (from two different groups of authors) are available. Our model is in slight disagreement, mainly with one of the data series, especially at high temperature; however, the qualitative shape of the computed phase envelopes remains realistic.
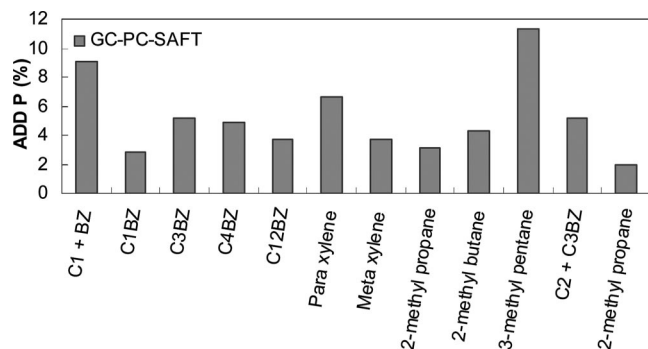
Figure 4. Overall average deviations in the VLE for the methane + hydrocarbon and ethane + hydrocarbon mixtures; the k_{ij} of the mixture is calculated using eqs 7 and 8.

5.2. Predictions Results. The results are presented in an order of expected increasing complexity, in terms of intermolecular interactions.

5.2.1. Methane + Hydrocarbon and Ethane + Hydrocarbon Systems (Nonpolar + Nonpolar and Nonpolar + Quadrupolar). The hydrocarbons considered here are either methyl branched alkanes (four systems) or aromatics (nine systems), because the case of *n*-alkanes has already been investigated in the first paper in this series.[1] The total number of systems for which data are available is relatively small, and most of the mixtures encountered are methane + aromatics. All the results presented were fully predicted using the pseudo-ionization energy values and relations 7 and 8. The general agreement between experimental phase envelopes and the model is comparable to that obtained earlier for other systems. The average deviation is within 5%−6% (see Figure 4), and all the detailed results are given in Table S2 in the Supporting Information.

In some cases, however, and especially for the methane + benzene and methane + 3-methyl-pentane binary mixtures, larger deviations are observed (see Table S2 in the Supporting Information). For the latter system, the largest deviations are, in fact, observed under conditions that are close to the mixture critical point, as expected. It is indeed difficult to represent the critical zone using a classical EOS; such deviations already have been observed with GC-SAFT for other systems in previous works.[2,3,15] Nevertheless, the qualitative shape is reproduced rather well. With regard to the methane + 3-methyl pentane system, GC−-PC-SAFT systematically underestimates the boiling pressure, but no further conclusion can be drawn, because, in fact, only one author made measurements on this system.

The phase envelopes of other systems seem to be predicted more accurately (see Figure 5), and no significantly higher deviations are observed in the case of the most asymmetrical systems.

5.2.2. CO₂ + Methyl Branched Alkanes (Quadrupolar + Nonpolar). The VLE data available for this type of mixture are not numerous (only three mixtures have been reported). All of the results presented in Table S3 in the Supporting Information were purely predicted, and the k_{ij} values of the mixtures were calculated using relations 7 and 8. The computations obtained with the GC−PC-SAFT EOS are satisfactory (within 2%−4%; see Figure 2). An example of the phase envelopes for these mixtures is shown in Figure 6.

5.2.3. N₂ + Hydrocarbon Mixtures (Quadrupolar + Quadrupolar and Quadrupolar + Nonpolar). The detailed database, and the computed and predicted results for a total of 19 N₂ + hydrocarbon mixtures are reported in Table S4 in the Supporting Information. Most of these systems are of the type
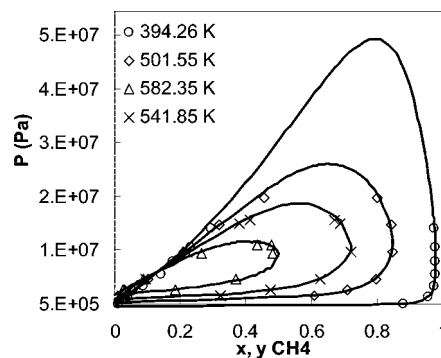

Figure 5. VLE phase envelopes of the methane + *meta*-xylene mixture (the solid lines represent the predicted results using polar GC−PC-SAFT EOS and data points denote experimental results); the k_{ij} of the mixture is calculated using eq 7. Data taken from ref 62.
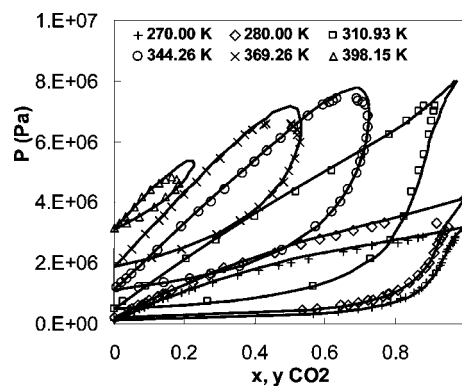

Figure 6. VLE phase envelopes of the CO₂ + 2 methyl propane mixture (solid lines represent the predicted results using the polar GC−PC-SAFT EOS, and the data points represent experimental results); the k_{ij} values of the mixture are calculated using eqs 7 and 8. Data taken from refs 63−66.
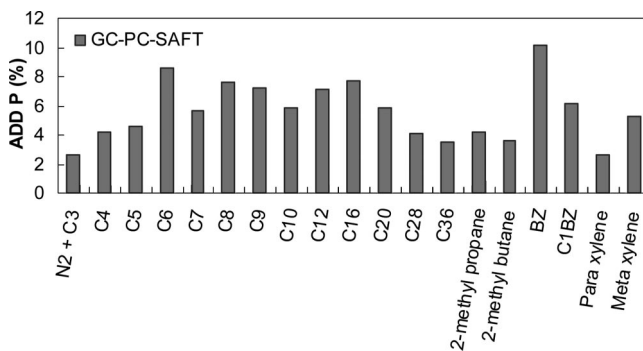

Figure 7. Overall average deviations in the VLE of the N₂ + hydrocarbon mixtures; the k_{ij} values were calculated using eqs 7 and 8.

N₂ + *n*-alkane (up to C₃₆). Only 4 N₂ + aromatics systems are included in the database.

All the phase equilibria, with exception of those of the N₂ + propane system, were purely predicted. Predictions are within deviations of 6% (see Figure 7), i.e., within errors that are comparable to those obtained on the methane + hydrocarbon and ethane + hydrocarbon systems. These deviations are slightly worse than those on the CO₂ + hydrocarbon systems, but remember that the corresponding VLE were, in fact, correlated.

Typical phase envelopes of one of these mixtures are plotted in Figure 8.

Although the overall deviation is satisfactory and no degradation of the predictions is observed in the case of heavy hydrocarbons, if compared to lighter ones, the description of
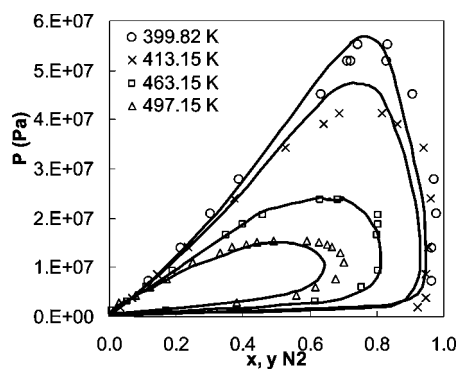
Figure 8. VLE phase diagram of the N_2 + n-heptane system; symbols represent experimental data, and solid lines represent results predicted by GC−PC-SAFT EOS with k_{ij} calculated using eqs 7 and 8). Data taken from refs 67−69.
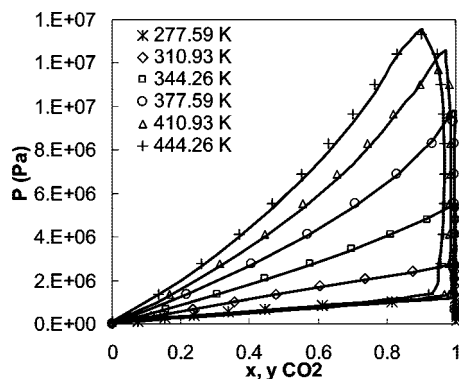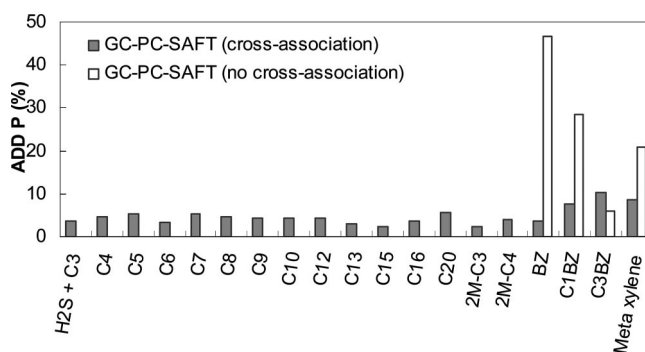

Figure 10. Overall average deviations in the VLE of the H_2S + hydrocarbon mixtures; the k_{ij} value is calculated from eqs 7 and 8. Note that, for the H_2S + aromatic mixtures, four cross-association sites were assumed.
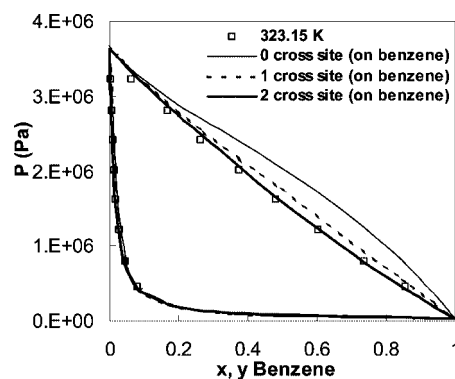

Figure 9. VLE phase diagram of the H_2S + n-decane system; symbols represent experimental data, and the solid lines represents results from GC−PC-SAFT EOS, with k_{ij} values calculated from eqs 7 and 8. Data taken from ref 70.

Figure 11. Influence of the number of donor−acceptor sites on the VLE phase diagram of the H_2S + benzene mixture at 323.15 K; the k_{ij} value was calculated using eq 7. Data taken from ref 71.

two systems is slightly worse (namely, N_2 + benzene at low N_2 concentration and N_2 + n-hexane). In the case of the former system, numerous VLE data are in the critical zone, which is known to be difficult to represent, as already noted above. This may at least partially explain the larger deviations observed for this system, and perhaps also the deviations of ∼7% for the N_2 + C_8, N_2 + C_9, N_2 + C_{12}, and N_2 + C_{16} systems.

However, these deviations may be considered to be acceptable, because they were obtained using a predictive model.

5.2.4. H_2S + Hydrocarbon Systems (Associative + (Nonpolar or Quadrupolar)). The state of the database is comparable to that of the N_2 + hydrocarbon system: 13 mixtures containing an n-alkane (up to C_{20}) and 2 mixtures with a branched alkane. VLE data for 4 H_2S + aromatics mixtures are available. Details are reported in Table S5 in the Supporting Information.

The VLE of the H_2S + alkane series of mixtures are described accurately using GC−PC-SAFT EOS, combined with the k_{ij} correlation method (as observed, for instance, in Figure 9). The overall deviation in bubble pressure is <5% (see Figure 10).

To predict the VLE of H_2S + aromatics systems accurately, the cross association between these two compounds (donor−acceptor interaction, with the aromatic compound being the H-acceptor)[27] must be taken into account explicitly. If not, large average deviations in bubble pressure are observed (see Figure 11). Because the systems in the database are few, we made simple hypotheses that are supposed to apply to the entire series. Therefore, these interactions were treated here in a simple way, similar to that used for modeling ester + 1-alkanol systems.[28] A single set of cross-association parameters (κ_{cross} and ε_{cross})

was used. The two values were set, as a first approximation, to those of the auto-association κ_{H_2S} and ε_{H_2S} parameters of H_2S. The number of cross-association sites was determined, to obtain the best fit of the H_2S + benzene phase diagram. A total number of four sites for cross association were determined to be suitable (see Figure 11): two sites on H_2S (one site on each hydrogen) and two sites on benzene.

All the other VLE of the H_2S + aromatics systems were predicted using the cross association parameters determined above. A reasonable accuracy is obtained (see Figure 10). The deviations in bubble pressure are somewhat higher than in the case of the H_2S + n-alkane systems but remain however acceptable, given the simplicity of the treatment. To improve the model, a more-realistic treatment would involve other assumptions regarding κ_{cross} and ε_{cross}, but it would also require more experimental data to be tested. For most systems, indeed, the available data are taken from a single source.

The qualitative shapes of the computed phase diagram are well-reproduced, and no systematic degradation tendency is observed for the most asymmetric systems.

5.2.5. Binary Systems Containing Small Molecules. As a further test of our approach, the VLE of small-species binary mixtures were fully predicted within a very good accuracy. (Details are reported in Table S6 in the Supporting Information; also see Figures 12−14).

In the case of the H_2S + CO_2 system, cross-association interactions (donor−acceptor) were explicitly taken into account, following the work of Altmann and Ford[29] (ab initio calculations). Unrealistic results are obtained (see Figure 15) if one neglects the cross-association interaction between CO_2 and H_2S. The cross-association interactions were treated in the same simple fashion as in the H_2S + aromatic systems. The best
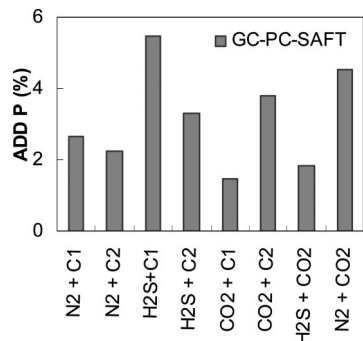
Figure 12. Overall average deviations in the VLE of small gases that contain binary mixtures; the k_{ij} values are calculated using eq 7.
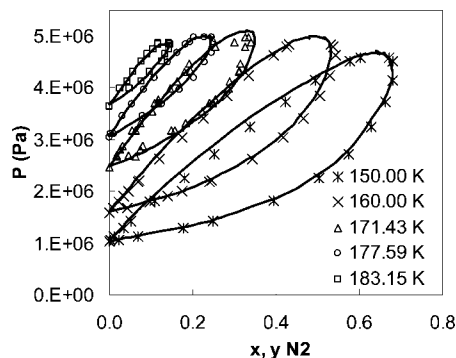

Figure 13. VLE phase diagram of the N_2 + methane system; the symbols represent experimental data, and the solid lines represent results predicted by GC−PC-SAFT EOS, with the k_{ij} values calculated using eq 7. Data taken from refs 72−74.
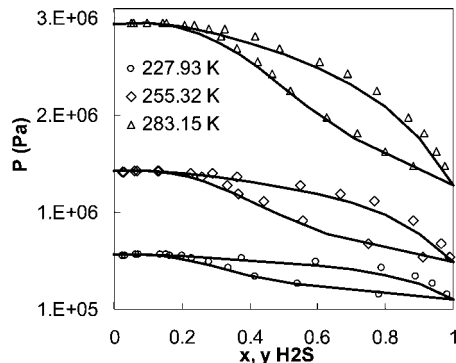

Figure 14. VLE phase diagram of the H_2S + ethane system; the symbols represent experimental data, and the solid lines represent results predicted by GC−PC-SAFT EOS, with the k_{ij} values calculated using eq 7. Data taken from ref 75.

prediction results were obtained if four sites for cross association between H_2S and CO_2 were assumed (see Figure 15): two sites on H_2S (one site on each hydrogen, as mentioned above) and two sites on CO_2 (one site on each oxygen).

6. Discussion and Conclusion

Because of the importance of the chemical species considered here in the petroleum industry, a large number of papers that involve the modeling of the vapor−liquid equilibria (VLE) of their mixtures have been published over the last three decades. Over 50 significant publications about the subject were indeed found in the literature (and this search is not claimed to be comprehensive). Most of the works are based on a cubic equation of state (EOS) (Peng−Robinson (PR), Soave−Redlich− Kwong (SRK), or a modified version).
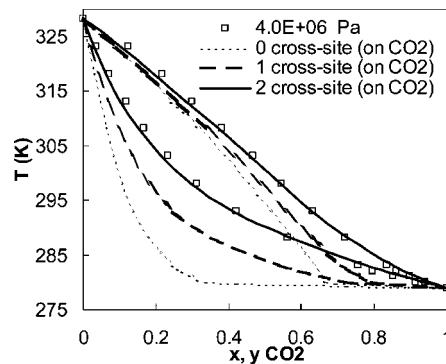

Figure 15. Predicted phase envelopes of the H_2S + CO_2 mixture; the symbols represent experimental data, and the solid line represent results by GC−PC-SAFT EOS, with the k_{ij} values calculated using eq 7. Cross-association parameters were set equal to the association parameter of H_2S. Data taken from ref 76.

However, recently, the interest has slightly shifted to EOS expressions that involve statistical mechanics (perturbed-chain statistical associating fluid theory (PC-SAFT), by Garcia-Sánchez et al.[30] and Tihic et al.;[31] VR-SAFT, by Zhao et al.[6]), although such types of equation were already used almost 30 years ago (perturbed-hard-chain theory (PHCT), by Donohue and Prausnitz[32]) and during the last three decades (chain-of-rotators group contribution (CORGC), by Pults et al.[33] Shariat et al.,[34] Shariati et al.,[35] and Zia-Razzaz and Moshfeghian[36]). Only some authors incorporated a group contribution method in their EOS to compute pure and binary parameters (CORGC, by Shariat et al.;[34] predictive Soave−Redlich−Kwong (PSRK) and modified versions, by Holderbaum and Gmehling,[37] Chen et al.,[38] and Li et al.;[39] group-contribution equation of state (GC-EOS), by Skjold-Jorgensen;[40] and cubic equations, reported by Tochigi et al.,[41] Abdoul et al.,[42] and Jaubert et al.[43]). Generally, the binary interaction parameters are computed using group−group contribution parameters, which sometimes are asymmetrical. The other authors proposed various correlations of the k_{ij} parameters for specific system series (see Moysan et al.,[44] Puhala and Elliott,[45] Vetere,[46] Gao et al.,[47] and Tihic et al.[31]), in terms of the acentric factor or other characteristics.

Besides the specific modeling of some of the mixtures series considered here, such as N_2 + hydrocarbon (Avlonitis et al.,[48] Garcia-Sanchez et al.,[30] Keshtkar et al.[49]), H_2S + hydrocarbon (Stamataki and Magoulas,[50] Valderrama et al.[51]), and CO_2 + hydrocarbon (Berro et al.,[52] Keshtkar et al.,[53] Yoo and Lee[54]), several authors attempted a more-general treatment of the light gas + hydrocarbon systems.

The most complete treatment was probably made by Cotterman et al.,[55] using PSCT and Nishiumi et al.[56] with the PR EOS. Mixtures of the light gases (CH_4, C_2H_6, N_2, H_2S, CO_2) with n-alkanes, alkyl benzenes, and alkyl cyclohexanes were considered. Binary interaction parameters are needed for accurate modeling of the VLE of these systems.

Cotterman et al.[55] gave a table of recommended k_{ij} values for each system. As in a previous similar work (Donohue et al.[32]) that was based on PHCT and limited to light gases + n-alkane systems, one may notice that the k_{ij} values become constant for large hydrocarbons. A typical agreement of 3%−7% is obtained, with regard to the k-factors. Perhaps of more interest for our work (in the same spirit as this paper) is the paper by Nishiumi et al.,[56] which correlated the k_{ij} values for the Peng−Robinson original EOS to pure compound characteristics (v_C, ω), using a modification of the Hudson−McCoubrey[57] correlation. The modified correlation has been detailed in the first paper in this series[1] and, as noted before, does not always
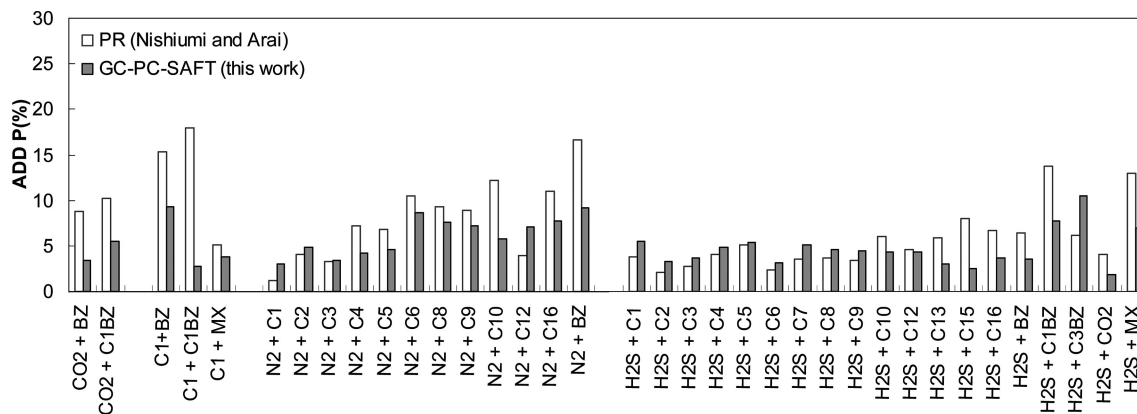
Figure 16. Comparison between our approach and that of Nishiumi et al.[56]

seem very accurate (as in the case of mixtures with H_2S, for instance; see Figures 22 and 23 in the work by Nishiumi et al.[56]). This may probably explain large deviations that are observed sometimes. A direct comparison (using calculations that we performed) for some typical systems is provided in Figure 16, which shows that our approach compares well to that of Nishiumi et al.[56] and has also the advantage (for prediction purposes) of incorporating a group contribution method. Far-more-accurate group contribution cubic EOS expressions exist,[43,58,59] but for computing k_{ij}, one generally needs group−group parameters.

Extensive investigations of the light gas + hydrocarbon systems were also performed by Moysan et al.[44] (using SRK and k_{ij} values that were correlated to the acentric factor and critical temperature), Puhala and Elliott[45] (with ESD and correlations of k_{ij} values, in terms of the difference in cohesive energy density), Vetere[46] (applying an empirical method based on NRTL, combined with RK EOS for fugacity calculation and Hildebrand solubility parameters), and, finally, Abdoul et al.[42] (using tPR EOS with g^E mixing rules). Generally, the deviations in bubble pressure that are observed are within 3%−6% (and sometimes higher; see Puhala and Elliott[45]), i.e., comparable to our results.

Also of interest are the works of several authors who tested their models on large but slightly smaller databases than ours i.e., those which contained essentially VLE data of light gas + n-alkane systems. Among the equations used, one finds the following: GC-EOS of Skjold-Jorgensen,[40] which incorporates a group contribution method for computation of k_{ij}; SRK, combined with an ASOG-type group-contribution method, by Tochigi et al.;[41] PSRK modified by Li et al.[39] and Chen et al.;[38] CORGC used by Shariat et al.;[34] SRK and PR EOS with an alternate combining rule from Juris and Wenzel,[60] which was tested by Gao et al.;[47] and simplified PC-SAFT with pure compound parameters correlated with the molecular weight and specific k_{ij} values (Tihic et al.[31]). Again, the deviations in bubble pressures that are observed are comparable to those obtained by our approach.

As a conclusion, our approach has proved to give satisfactory computations and predictions of numerous VLE and LLE of light gas + hydrocarbon systems. It is a promising tool to be tested on more systems.

Supporting Information Available: Detailed database used in calculation and detailed results. (PDF) This material is available free of charge via the Internet at http://pubs.acs.org.

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