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Modeling VLE of H₂ + Hydrocarbon Mixtures Using a Group Contribution SAFT with a k_{ij} Correlation Method Based on London's Theory

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Received December 16, 2008. Revised Manuscript Received March 5, 2009

A group contribution perturbed-chain statistical associating fluid theory (GC-PC-SAFT) equation of state (Tamouza et al. *Fluid Phase Equilib.* **2004**, 222–223, 67–76) combined with a recent method for correlating k_{ij} using only pure compound parameters (NguyenHuynh et al. *Ind. Eng. Chem. Res.*, **2008**, 47(22), 8847–8858) is extended here to model vapor–liquid phase equilibria of H₂ + alkanes and H₂ + aromatics mixtures. The correlation of k_{ij} is inspired by London's theory of dispersive interactions, and uses “pseudo-ionization energies” J_i and J_j of compounds i and j as adjustable parameters. The GC-PC-SAFT parameters for alkanes and aromatics were reused from previous works when available. Otherwise, the missing parameters were estimated by regression of corresponding pure vapor–liquid equilibrium (VLE) data. Those of H₂ were determined in this work by correlating some VLE data of H₂ + n-alkane systems. Using the parameters thus obtained, the phase envelopes of other H₂ + alkane and H₂ + aromatic systems were fully predicted. The prediction tests were as comprehensive as possible. Correlations and predictions are qualitatively and quantitatively satisfactory. The deviations are within 5–6%, that is, comparable to those obtained on previously investigated systems. Mixtures containing H₂ are modeled here with deviations that compare well with those of the Grayson–Streed model (Grayson, H.G.; Streed, C.W.; *Proc., 6th World Pet. Congress*, 1963, 169–181), which is often used by process engineers for hydrogen and hydrocarbon mixtures.

1. Introduction

In previous articles,^{1–4} it was shown that the group contribution equation of state (EOS) statistical associating fluid theory (GC-SAFT) developed by Tamouza et al.⁵ could be successfully applied to several systems of interest in the petroleum industry. Vapor–liquid equilibria (VLE) of pure aliphatic and aromatic hydrocarbons, alkanols, esters, and some of their mixtures were modeled without binary interaction parameters ($k_{ij} = l_{ij} = 0$). More recently,^{6–8} GC-PC-SAFT was extended to asymmetric systems containing a light specific compound such as CO₂, CH₄, C₂H₆, N₂, and H₂S and a hydrocarbon. In that case, however, nonzero k_{ij} values are necessary to obtain an accurate repre-

sentation of the VLE and liquid–liquid equilibria (LLE) phase envelopes, apparently diminishing the prediction capability of our approach. However, in one of our previous works⁶ it was shown that the k_{ij} values could be accurately correlated by a group contribution using (small molecule)–(group) binary parameters. This method allowed a good representation of the VLE of CO₂ + n-alkane and H₂ + n-alkane series but cannot be used to make prediction on other mixture series such as H₂ + aromatics without adjusting additional parameters.^{7,8} This fact motivated the search for a more efficient way of correlating and predicting the k_{ij} values. An alternative method was recently proposed^{7,8} to correlate and/or predict the k_{ij} values on the basis of London's dispersion interaction theory. Indeed, it is possible to obtain semitheoretical expressions for correlating k_{ij} using only pure compound parameters (diameter, ionization energy) to be taken from literature, or otherwise adjusted. Such methods have some advantages over the ones computing k_{ij} from group–group parameters.^{7,8} First, in the former method, a n dimensional vector of pure parameters is needed, whereas the latter method requires a n^2 dimensional matrix of parameters, that is, requires the availability of a rather large amount of mixture data. Second, the latter method applies well for predictions in a given series of mixtures but is not easily transferable to other systems: for instance, k_{ik} cannot be obtained from the knowledge of k_{ij} and k_{jk} and thus should be adjusted. A correlation method of k_{ij} with pure parameters allows us to overcome this difficulty and, as a result, is more appealing for prediction purposes. Such a method has been proposed in previous articles^{7,8} and is tested further here on systems

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containing H₂ that are of great industrial importance today (in hydro-treatment, hydro-cracking, etc.). These systems are difficult to model for the following reasons. First, H₂ cannot be treated in the frame of the group contribution (i.e., decomposed in several groups) since it does not belong to a well-identified chemical family. Second, as explained by Ghosh et al.,⁹ the vapor–liquid coexistence for pure hydrogen occurs at very low temperatures (14–33 K) where quantum effects predominate. The EOS parameters fitted conventionally to vapor pressure and pure compound liquid density data are thus not expected to be applicable at temperatures of industrial interest (~298.15 K and higher). SAFT parameters for H₂ were therefore determined following a specific procedure described in details below.

The approach was tested in a correlative manner on some H₂ + n-alkane systems and in a fully predictive manner on other H₂ + n-alkane systems and H₂ + aromatics systems. The prediction tests were as comprehensive as possible.

2. GC-SAFT Equation of State

GC-SAFT is the combination of a SAFT equation of state (EOS) with built-in group contribution relations for computing energy ϵ , segment diameter σ , and chain length m parameters. In previous works, three different versions of SAFT EOS were considered: the original SAFT slightly modified,^{10,11} PC-SAFT from Gross and Sadowski,¹² and VR-SAFT.¹³ As shown in recent works^{6,14,15} the asymmetric systems containing a species such as CO₂ and H₂ in supercritical conditions are generally best described by PC-SAFT. For this reason, it was decided to use only this version in the present work.

The detailed expression of PC-SAFT EOS is not recalled here (see the original papers for more details¹²). When polar compounds such as aromatics (quadrupolar) are present in the considered systems, the use of additional polar terms in the EOS improves its prediction capability.^{15–21} In terms of molar free energy:

$$a = a^{\text{non-polar}} + a^{\text{QQ}} \quad (1)$$

where $a^{\text{non-polar}}$ refers to a PC-SAFT EOS and a^{QQ} is a term accounting for quadrupole–quadrupole interactions. The a^{QQ} term used here is an extension to chain molecules of the theory

of Gubbins and Twu,²² originally developed for spherical molecules. The extension is based on the “segment-approach” proposed by Jog and Chapman^{23,24} that assumes well-localized polar moments on certain segments of the chain. The expression of a^{QQ} is provided in NguyenHuynh et al.^{2,15}

In the segment approach, an additional parameter to the quadrupole moment Q is introduced: the quadrupolar fraction ($x_{p\alpha}^Q$) defined by the product $x_{p\alpha}^Q m_\alpha$ that is the total number of quadrupole moments Q (all taken identical here) in the chain α .

In GC-SAFT, the EOS segment parameters (ϵ , σ , m) of the molecule are calculated through group contribution relations inspired from the Lorentz–Berthelot combining rules found in refs 5 and 14. Three different kinds of EOS group parameters are then involved: ϵ_i , σ_i , and R_i , respectively, energy, diameter, and chain contribution of group i . The values of different group parameters are found in refs 2, 5, 14, and 15.

The relations generally apply to compounds belonging to well-defined chemical families (n-alkane, 1-alkanol, ...) with the exception of the first or even first two members (methane, ethane, methanol, ...) that should be treated specifically.

3. Description of the k_{ij} Correlation Method

PC-SAFT applies to mixtures using the van der Waals one-fluid model¹² and modified Lorentz–Berthelot mixing rules that relate the potential parameters ϵ_{ij} and σ_{ij} between segments of molecules i and j .

$$\epsilon_{ij} = (1 - k_{ij})\sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (2)$$

$$\sigma_{ij} = (1 - l_{ij})\left(\frac{\sigma_{ii} + \sigma_{jj}}{2}\right) \quad (3)$$

In the case of the mixtures investigated here, nonzero binary interaction parameters k_{ij} and/or l_{ij} are necessary to provide realistic phase equilibria calculations. In earlier works,^{1–3} however, l_{ij} could be set to zero with satisfactory results. This hypothesis was also retained here.

As already discussed before,^{7,8} a useful correlation for k_{ij} may be obtained on the basis of London’s dispersive interaction theory by modifying the Hudson and McCoubrey²⁵ expression on semiempirical grounds. The proposed modification introduces an adjustable parameter J (called pseudo-ionization energy). The correlation reads:

$$1 - k_{ij} = \frac{2\sqrt{(J_i J_j)}}{(J_i + J_j)} \quad (4)$$

where subscripts i and j refer to segments in molecule i and j . Notice that in the original expression of Hudson and McCoubrey,²⁵ k_{ij} depends explicitly on diameters. The corresponding term was dropped here because it is expected to be close to unity as a first approximation (the segment diameter values in GC-PC-SAFT are generally close). Elsewhere, preliminary calculations showed that the proposed eq 4 is superior^{7,8} to the original Hudson and McCoubrey²⁵ expression.

In view of making useful predictions for engineering, a group contribution method for computing pseudo-ionization energies

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was also proposed. For a given molecule composed of n_k groups of type k one has:

$$J_{\text{molec}} = \left(\sum_{k=1}^{n_{\text{group}}} n_k \right) \sqrt{\left(\prod_{k=1}^{n_{\text{group}}} J_k^{n_k} \right)} \quad (5)$$

where J_k is the contribution of group k to the pseudo-ionization of the segments in the considered molecule. Again, this relation may be applied to compounds belonging to well-defined chemical series with the exception of the first or even first two members.

Equations 4 and 5 give the basic relations for correlating and predicting k_{ij} values to be used in GC-PC-SAFT. These relations are further tested in the next two sections.

4. Pure Compound Parameters Determination

The mixtures considered in this article contain some species such as n-alkanes (C1, C2, C3, ...), cyclohexane, alkyl-benzenes (C1BZ, C2BZ, ...) and xylenes (OX = orthoxylene, MX = metaxylene, PX = paraxylene) that were already treated in earlier works in the frame of GC-SAFT.² The pseudo-ionization potentials of these compounds were determined by regressing some CO_2 + hydrocarbon or CH_4 + hydrocarbon VLE data. For more details on the determination of the corresponding parameters see the original articles.^{2,5} In a spirit of developing a predictive method, these parameters are reused for other mixtures without reevaluation.

Regarding species not yet modeled using GC-SAFT or reconsidered here, detailed explanations are given below. We have tried, as much as possible, to reuse the maximum number of parameters already determined.


















The results of the adjustment are given in Table 1, and the parameters may be found in Tables 2 (group contribution parameters) and 3 (parameters for specific species including pseudoionization energy values).

4.1. Methyl-cyclohexane (C1-Cyclohexane). Like the n-alkanes, this compound is a nonpolar and nonassociative species that had to be considered separately from other series as shown by preliminary calculations. Specific parameters were then assumed for this compound that were determined in this work by regression of pure vapor pressure and saturated liquid phase densities raw data taken from DIPPR.²⁶

The pseudo-ionization energies $J_{\text{methyl-cyclohexane}}$ were obtained as follows. First, the binary interaction parameter $k_{\text{CH}_4, \text{methyl-cyclohexane}}$ was adjusted by VLE regression on CH_4 + methyl-cyclohexane mixtures. Then, using eq 4 combined with the value of J_{CH_4} already known,⁷ $J_{\text{methyl-cyclohexane}}$ was deduced.

4.2. 1,2,4-Trimethyl-benzene (1,2,4-TMB) and 1,3,5-Trimethyl-benzene (1,3,5-TMB). These two quadrupolar compounds are treated in the frame of the group contribution. In these species, three different chemical groups are involved: (CH_3) in the substituting methyl chain and $(\text{CH})_{\text{BR}}$ and $(\text{C})_{\text{AB}}$ in the benzene ring. The values of $(\text{CH})_{\text{BR}}$ and $(\text{C})_{\text{AB}}$ group parameters were reused from previous studies² as well as the values of σ_{CH_3} and $\varepsilon_{\text{CH}_3}$.⁵ As in the case of xylenes, a distinction between the two isomers 1,2,4-trimethyl-benzene and 1,3,5-trimethyl-benzene is made through the chain contribution R_{CH_3} . The parameter R_{CH_3} value of one substituted (CH_3) group was set to that of n-alkanes, the other ones were considered dependent on the relative position ortho, meta, and para from this first group. All these values were determined previously and were reused here. Notice that concerning the para position it was assumed that $R_{\text{CH}_3}(\text{para}) = R_{\text{CH}_3}(\text{alkane})$.

Table 1. Deviation on Vapor Pressure and Liquid Density (GC-PC-SAFT)^a

Compound	Chemical formula	temperature, T (K)	Npt	AAD%P	temperature, T (K)	Npt	AAD% ρ_{liq}
Cyclohexane		280-553	29	1.25	280-553	29	2.13
Methyl-cyclohexane		260-572	35	1.48	260-572	33	1.98
ethyl-cyclohexane		294-433	15	0.61	250-383	14	0.61
n-propyl-cyclohexane		313-459	30	1.73	249-383	13	0.14
n-butyl-cyclohexane		333-484	21	0.74	255-383	24	0.44
n-decyl-cyclohexane		325-645	33	1.95	273-383	12	1.83
124 TriMethyl-Benzene		253-645	41	2.00	278-366	12	7.46
135 Trimethyl-Benzene		253-635	40	2.20	280-438	39	3.08
Naphthalene		353-748	145	1.11	333-748	49	1.80
Phenanthrene		372-699	102	4.69	372-593	13	3.03
Anthracene		490-673	36	3.14	488-593	25	2.79
Benzanthracene		433-979	11	1.95	293-293	2	4.85
Chrysene		531-979	20	3.09	288-293	2	8.98
Naphacene		630-987	11	1.00	298-298	2	14.76
Triphenylene		593-773	12	7.90			
1-methyl naphthalene		363-772	147	1.53	273-753	54	3.38
2-methyl naphthalene		423-761	83	3.45	273-753	69	1.46
1,3-dimethyl naphthalene		283-580	32	3.12			
1,4-dimethyl naphthalene		283-763	49	5.11			
1,5-dimethylnaphthalene		423-773	39	2.22			
1,6-dimethyl-naphthalene		421-771	36	4.41			
2,6-dimethyl naphthalene		384-778	50	2.23			
2,7-dimethyl naphthalene		369-773	45	1.46	293-303	3	4.19
1,2-dimethyl naphthalene		402-542	15	5.34			
1,8-dimethyl naphthalene		328-413	10	1.33			

^a All data are taken from the raw data base provided by DIPPR.²⁶ $\text{AAD}\%P = (1)/(N_{\text{pt}}) \sum_{N_{\text{pt}}} (|P_{\text{exp}} - P_{\text{calc}}|)/(P_{\text{exp}}) \times 100$, where P stands for vapor pressure; $\text{AAD}\%\rho_{\text{liq}} = (1)/(N_{\text{pt}}) \sum_{N_{\text{pt}}} (|\rho_{\text{liq,exp}} - \rho_{\text{liq,calc}}|)/(\rho_{\text{liq,exp}}) \times 100$, where ρ_{liq} stands for saturated liquid density.

These two aromatic compounds were also considered as quadrupolar, each species possessing a specific quadrupole moment that was adjusted since it is unknown. The product of quadrupolar fraction and chain parameter was taken from the study of xylenes and alkyl-benzenes, that is, $x_p^Q m = 0.250$.

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Table 2. Group Contribution Parameters for Alkane, Alkyl-benzenes, PAHs, and Methyl-naphthalene, Polar GC-PC-SAFT EOS

groups <i>i</i>	group position or compound	ε_i/k , K	σ_i , Å	R_i	J_i , eV
(CH ₂)		261.0866	3.9308	0.3821	7.35 ^a
(CH ₃)		189.9628	3.4873	0.7866	12.99 ^a
(C) _{AB}		391.5410	4.2783	0.0016	3.88 ^b
(C) _{BR}		294.2235	3.7572	0.3805	8.45 ^b
(C) _{PA}	naphthalene	698.7420	4.4441	0.0002	
	phenanthrene			0.0218	
	anthracene			0.0343	
	benzanthracene			0.0420	
	chrysene			0.0499	
	naphthalene			0.0504	
	triphenylene			0.0537	
(CH ₃) in xylenes ^c	para	189.9628	3.4873	0.7866	
	ortho			0.8593	
	meta			0.7796	
(CH ₃) in methyl-naphthalene ^c	[1]	189.9628	3.4872	0.8172	
	[2]			0.7937	
	[3]			0.7675	
	[4]			0.7767	
	[5]			0.7923	
	[6]			0.7358	
	[7]			0.7557	
	[8]			0.9037	

^a Valid for n-alkane series starting from n-propane. ^b Valid for alkyl-benzene series starting from propyl-benzene. ^c Group positions are defined on Figure 2.

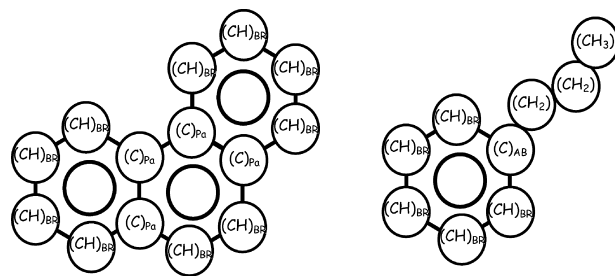
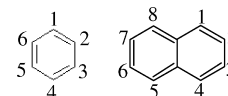
Table 3. Specific Parameters for Species Considered in This Study, PC-SAFT Model^a

	ε/k , K	σ , Å	m	Q , B ^b	$x_p m$	J , eV
H ₂ (Set 1)	30.32	2.86	1.25			15.00
H ₂ (Set 2)	26.62	2.91	1.11			15.00
CH ₄	147.42	3.66	1.03			12.61
C ₂ H ₆	189.00	3.51	1.64			11.52
benzene	GC	GC	GC	8.52	0.250	7.76
toluene	GC	GC	GC	9.17	0.250	6.74
ethyl-benzene	GC	GC	GC	8.78	0.250	7.03
ortho-xylene	GC	GC	GC	9.72	0.250	7.00
meta-xylene	GC	GC	GC	10.11	0.250	7.00
para-xylene	GC	GC	GC	9.52	0.250	7.00
cyclohexane	274.59	3.82	2.59			7.20
methyl-cyclohexane	277.84	3.97	2.73			7.50
ethyl-cyclohexane	GC	GC	GC			8.90
propyl-cyclohexane	GC	GC	GC			7.00
1,2,4-trimethyl-benzene	GC	GC	GC	9.64	0.250	7.82
1,3,5-trimethyl-benzene	GC	GC	GC	10.88	0.250	7.90
naphthalene	GC	GC	GC	8.52	0.200	6.30
1 methyl-naphthalene	GC	GC	GC	8.52	0.200	5.35
2 methyl-naphthalene	GC	GC	GC	8.52	0.200	5.35
phenanthrene	GC	GC	GC	8.52	0.30	5.80
anthracene	GC	GC	GC	8.52	0.30	
benzanthracene	GC	GC	GC	8.52	0.40	
chrysene	GC	GC	GC	8.52	0.40	
naphthalene	GC	GC	GC	8.52	0.40	
triphenylene	GC	GC	GC	8.52	0.40	

^a GC parameters obtained using the group contribution relations of Tamouza et al.^{5,14} ^b 1 Buckingham = 3.335641 × 10⁻⁴⁰ C m².

All the missing parameters were obtained by pure VLE data (vapor pressure and saturated liquid density) regression. Data were taken from ref 27.

The pseudoionization energies (*J*) of these two compounds were determined from VLE data of two mixtures ethyl-benzene + 1,2,4-trimethyl-benzene and n-propane + 1,3,5-trimethyl-benzene. Close values were found for these two species, respectively, 7.82 and 7.80 eV. Such a result has already been observed for other isomers.^{8,15} Thus, consistent with our previous work, a single value has been set for pseudo-ionization energies: $J_{1,2,4\text{-trimethyl-benzene}} = J_{1,3,5\text{-trimethyl-benzene}} = 7.80$ (eV).

**Figure 1.** Group decomposition of phenanthrene and propyl-benzene.**Figure 2.** Identification of alkyl position.

4.3. Polyaromatic Hydrocarbons (PAHs). The compounds considered here have either no branching or one single alkyl chain branching. These compounds have already been treated in a previous work⁴ but using a molecule approach to account for multipolar interactions. These interactions were reconsidered here using the segment approach of Jog and Chapman^{23,24} that is now implemented in polar GC-PC-SAFT. The GC and EOS parameters are determined in a similar manner as before.²

For more clarity, the group decomposition is depicted below on Figure 1. Five different groups appear: (CH₂) and (CH₃) in the substituting chain, (C)_{AB} where the alkyl chain is connected to a ring, (CH)_{BR} in a ring, and (C)_{PA} referring to carbon shared by two different rings. Carbons (C)_{PA} and (C)_{AB} were a priori distinguished here. As confirmed by further preliminary tests, (C)_{PA} could not be assimilated to the group (C)_{AB} in alkyl-benzenes.

All the group parameters values of the chemical groups (CH)_{BR} and (C)_{AB} were reused from alkyl-benzenes.²

To allow distinction between two chains of rings differently connected such as in the case of phenanthrene and anthracene or triphenylene and chrysene, it was decided to set different values to $R_{(C)PA}$ for each isomer. The other parameters, $\sigma_{(C)PA}$ and $\varepsilon_{(C)PA}$, were assumed to have the same values for all the polyaromatic molecules.

Energy ε and diameter σ parameters of (CH₃) groups determined earlier⁵ were also reused. In the same spirit as before, the methyl-naphthalene isomers were distinguished through the chain parameters R_{CH_3} of the chemical group (CH₃) directly connected to the ring. These parameters R_{CH_3} thus become position dependent as in the case of branched alkanes⁵ or xylenes. The different positions are defined in Figure 2. All the other parameters R_i are reused.

Each aromatic ring is supposed to possess its own quadrupole moment Q_0 that was set, for the sake of simplicity to the constant value of 8.52 B (that of benzene). The quadrupolar fraction is written in terms of the number of aromatic cycles N_{cycle} in the molecule:

$$x_p^O = N_{\text{cycle}} \frac{b}{m} \quad (6)$$

where *b* is an adjustable parameter.

A single couple of values for polar parameters (quadrupolar moment Q , and quadrupolar fraction $x_p^O m$) was used for all isomers of methyl-naphthalene and taken to be equal to those of naphthalene.

The unknown parameters' values were determined by VLE data (vapor pressure and liquid saturation volume) regression

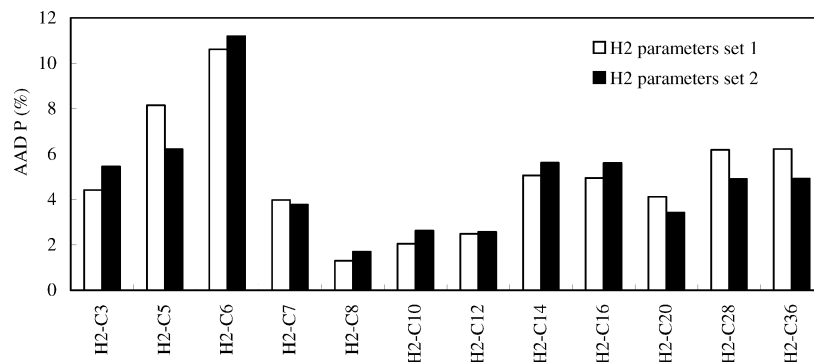


Figure 3. Results of correlation and prediction for hydrogen and n-alkane mixtures, using GC-PC-SAFT. k_{ij} for the mixture is calculated by eqs 4 and 5.

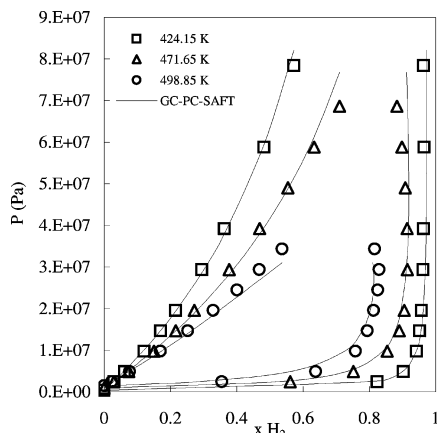


Figure 4. VLE phase envelopes of the hydrogen + n-heptane mixture. Solid lines are predicted results with GC-PC-SAFT EOS using parameters set 2 for hydrogen. k_{ij} for the mixture is calculated using eqs 4 and 5.

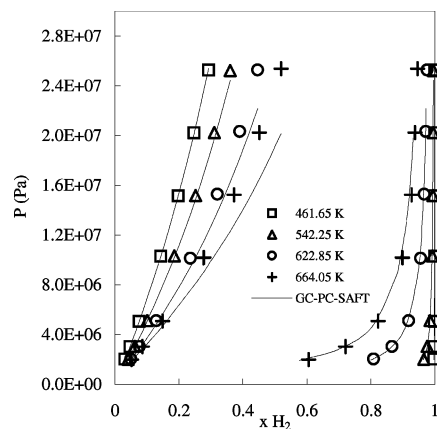


Figure 5. VLE phase envelopes of the hydrogen + n-hexadecane mixture. Solid lines are predicted results with GC-PC-SAFT EOS using parameters set 2 for hydrogen. k_{ij} for the mixture is calculated by eqs 4 and 5.

of the series of 7 PAH compounds from naphthalene to chrysene together with VLE mixture data of naphthalene + n-tetradecane. Let us recall that the use of some mixture data in the regression process were found to be necessary to obtain reliable parameter values.²

The pseudo-ionization energies of three PAHs (naphthalene, 1-methyl-naphthalene, and phenanthrene) for which mixture VLE data with H_2 are available were determined here. The corresponding values were adjusted so as to fit VLE of CH_4 + naphthalene, CH_4 + 1-methyl-naphthalene, and CH_4 + phenanthrene using eq 4 for estimating k_{ij} . Inspired by the result of the preceding section, we supposed that the pseudo-ionization energy of 2-methyl-naphthalene can be reused from its isomer, 1-methyl-naphthalene.

4.4. Hydrogen. This compound is treated similarly as before,⁶ following a procedure inspired by that used by Ghosh et al.⁹ for modeling H_2 + alkene systems.

The pure H_2 parameters, σ_{H_2} , m_{H_2} , and ε_{H_2} values were determined by regression of some H_2 + alkane mixture VLE data. Pure VLE data for H_2 were excluded from the regressed database because they correspond to very low temperature (the critical temperature of H_2 is 33 K) where quantum effects predominate. As pointed out by Ghosh et al.,⁹ parameters determined by fitting the corresponding VLE data are not expected to be applicable at temperatures of industrial interest. Including those pure VLE data in the regression procedure would require a very efficient EOS capable of representing thermodynamic properties in a wide range of temperature. Unfortunately, SAFT does not allow this, as shown by preliminary tests that provided disappointing results.

To reduce the total number of adjusted parameters, it was decided to set pseudo-ionization energy of hydrogen (J_{H_2}) to the experimental value, that is, 15 eV. Indeed, for several light compounds (CH_4 , C_2H_6 , H_2S , CO_2) this approximation proved to provide accurate computations.^{7,8}

To test the sensitivity of the model to the chosen adjusted mixture data (in order to obtain reliable EOS parameters for H_2), the VLE of two series of systems were adjusted. The first series is as before:⁶ H_2 + C_3 , H_2 + C_7 , H_2 + C_{10} , and H_2 + C_{20} systems; the second series is made of the following systems: H_2 + C_3 , H_2 + C_5 , H_2 + C_{14} , and H_2 + C_{36} .

5. Molecular Simulation Data

Experimental data concerning hydrogen + alkylbenzene are very scarce in the literature. However, such data are of first importance to validate GC-PC-SAFT predictions on these systems. It was therefore decided to generate “pseudo-experimental” data from molecular simulation. Indeed, molecular simulation is becoming an efficient method to accurately describe thermodynamic properties of a wide variety of pure compounds and mixtures.²⁸ More precisely, it has been shown that Monte Carlo molecular simulations of hydrogen + hydrocarbon mixtures are able to predict hydrogen solubility in aromatic solvents with an average deviation of about 4%.²⁹ Therefore, similar calculations are

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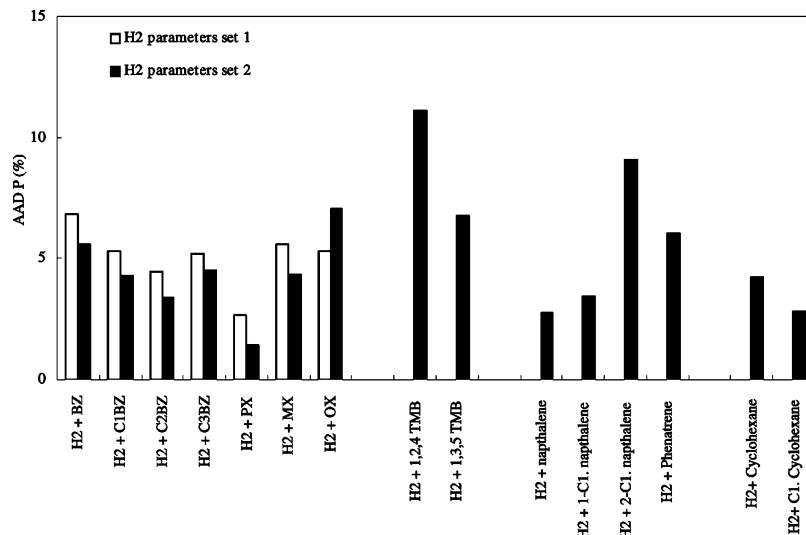


Figure 6. Results of prediction for hydrogen + aromatics mixtures with the 2 sets of hydrogen parameters, using GC-PC-SAFT. k_{ij} for the mixture is calculated by eqs 4 and 5.

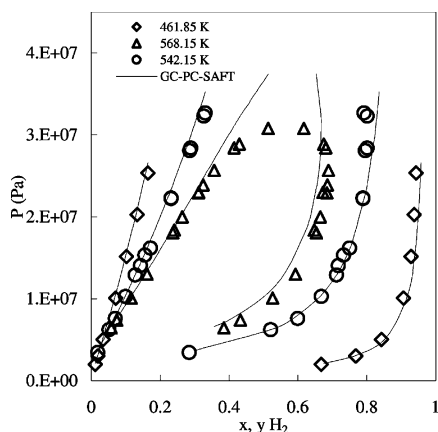


Figure 7. VLE phase envelopes of the hydrogen + toluene mixture. Solid lines are predicted results with polar GC-PC-SAFT EOS. k_{ij} for the mixture is calculated by eqs 4 and 5.

performed in this work to predict hydrogen solubility in *para*-xylene, *ortho*-xylene, 1,3,5-trimethylbenzene, ethylbenzene, and propylbenzene at 423 and 523 K.

The force field used for the dihydrogen molecule is taken from Darkrim et al.,³⁰ which consists in an unique Lennard–Jones sphere and includes three partial electrostatic charges aimed to mimic the quadrupole moment of the molecule. For alkylbenzene molecules, the nonelectrostatic AUA4 force field is used.²⁸ The Lorentz–Berthelot combining rules are employed for cross interactions. The Monte Carlo molecular simulations are performed in the isothermal–isobaric Gibbs ensemble, with a total number of 500–700 molecules depending on the thermodynamic conditions simulated. A production run of 50 million steps is carried out, each step corresponding to a Monte Carlo move. For Lennard–Jones interactions, a spherical cutoff equal to half of the simulation box was used, and classical tail correction was employed.³¹ The electrostatic energy is computed with the reaction field method after having first checked that identical results are obtained with the Ewald sum method.²⁹ The molecules of xylene and 1,3,5-trimethylbenzene are assumed fully rigid. For ethylbenzene and propylbenzene, the alkyl chain

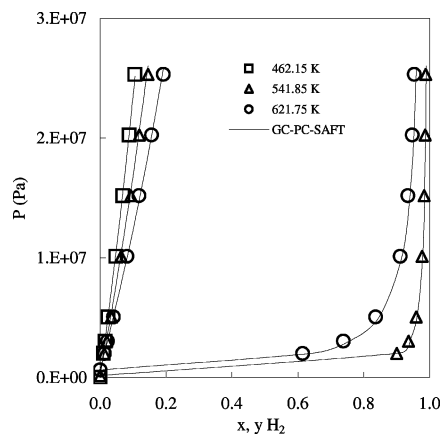


Figure 8. VLE phase envelopes of the hydrogen + 1 methyl-naphthalene mixture. Solid lines are predicted results with polar GC-PC-SAFT EOS. k_{ij} for the mixture is calculated by eqs 4 and 5.

is assumed flexible. The different Monte Carlo moves and their probabilities are (for more details see ref 29): translation (39.5% for rigid molecules, 15% elsewhere), rigid rotation (20% for rigid molecules, 15% elsewhere), volume change (0.5%), transfer from one box to another (40% for rigid molecules, 39.5% elsewhere) with insertion bias,³² internal rotation (15% for flexible molecules) and configurational-bias regrowth³³ (20% for flexible molecule).

All the molecular simulation results in terms of hydrogen content in the liquid and vapor phases are summarized in Table S1 in the Supporting Information.

6. Results of Correlation and Prediction of Phase Equilibria

6.1. Pure Hydrocarbons. The VLE computations were made following a standard iterative bubble point algorithm already described.⁵ Data to be regressed are taken from DIPPR.²⁶ Deviations on pressure are given in Table 1. The values of parameters are found in Tables 2 (GC parameters) and 3 (specific parameters). The model gives reasonable results (within

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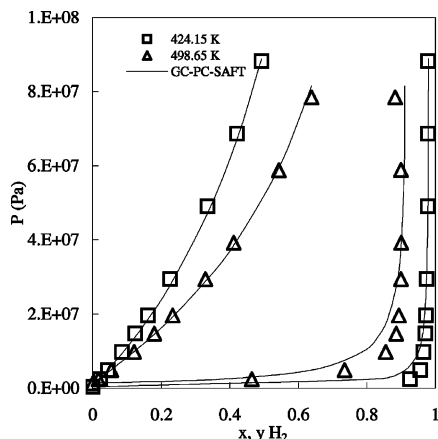


Figure 9. VLE phase envelopes of the hydrogen + methyl-cyclohexane mixture. Solid lines are predicted results with GC-PC-SAFT EOS. k_{ij} for the mixture is calculated by eqs 4 and 5.

1–3% error on vapor pressure), that is, comparable to what was observed in earlier works.^{2,3,5}

6.2. H_2 + n-Alkane Binary Systems. A rather large database (see Table S2 in the Supporting Information) is available for these systems, ranging from methane up to C_{36} . The database consists in bubble pressure and vapor phase composition mainly at moderate hydrogen mole fraction (for many data, $x_{H_2} < 0.3$). Only high-temperature data (above room temperature and higher, i.e., corresponding to industrial applications) were considered in the regression process. Very low temperature data are indeed of less interest in the petroleum industry.

As described in Section 4, only some mixtures were used in the regression process. Remember that two sets of mixtures were in fact considered, allowing us to determine two different sets of parameters for H_2 . VLE of the other systems were then fully predicted using the adjusted parameters of H_2 and the k_{ij} values estimated using eqs 4 and 5.

The two sets of parameters for H_2 are given in Table 3. The parameters values of set 1 are roughly of the same order as

those of set 2, which means that H_2 parameters appear rather little sensitive to the chosen binary systems H_2 + alkane considered in the regression process. This result gives us some confidence in the order of magnitude of the H_2 parameters.

Using both sets of parameters, the whole H_2 + n -alkane VLE series is rather well-modeled, with errors on the bubble pressure within 5% (see Figure 3). Globally, we find that both sets of hydrogen pure parameters may be used to correlate or predict mixtures VLE within comparable accuracies. At this level, it is not possible to choose one set rather than another.

The phase diagrams are qualitatively well represented as observed for some examples on Figures 4 and 5.

6.3. Predictions. All the results presented here and detailed in Table S2 in the Supporting Information were purely predicted using pure compound parameter values previously obtained and k_{ij} values calculated using eqs 4 and 5.

Binary Systems: H_2 + Aromatics and H_2 + Alkyl-cyclohexane. Some of these mixtures were used to select the parameters of pure hydrogen. In Figure 6, one may see that parameters set 2 provides slightly better predictions than parameter set 1. The influence of the regressed H_2 + n -alkane mixtures data set on the quality of GC-SAFT appears not very dramatic. However, it was decided, from this point on, to use the second set of parameters for all the computations in the rest of the work.

The average results on series H_2 + aromatics and H_2 + alkyl-cyclohexane are given in Figure 6. All the details are given in Table S2 in the Supporting Information. The average relative deviation obtained on the bubble pressure of the mixtures is close to 5%. These results are good and are especially appreciable for the systems containing polyaromatics. These mixtures are indeed very asymmetric, as witnessed by the relatively large values of the binary interaction parameter k_{ij} (around 0.10–0.12).

Examples of predicted diagrams are given in Figures 7–9.

Ternary and Quaternary Mixtures Containing H_2 . Multicomponent mixtures VLE were also predicted. Comparison with

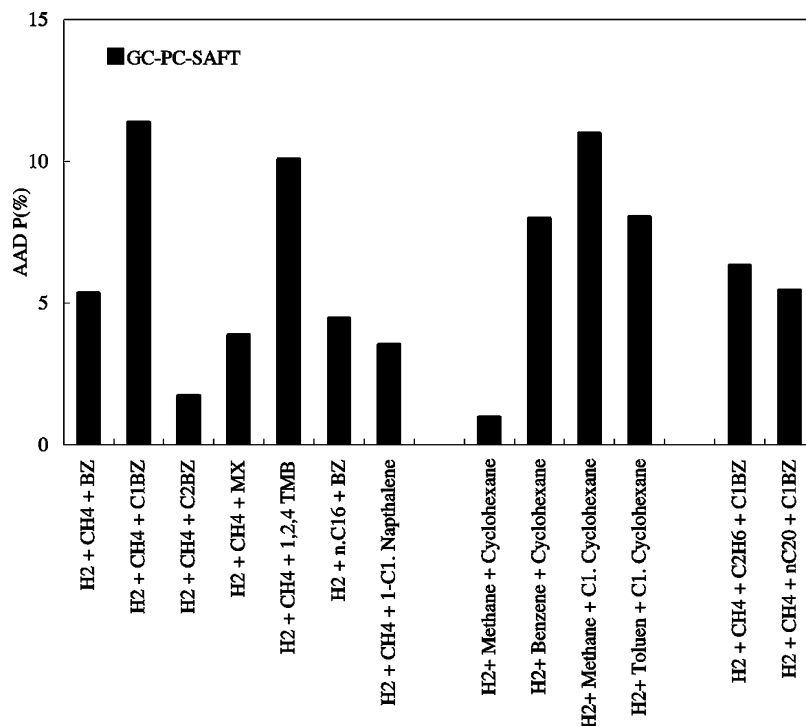


Figure 10. Results of prediction for multicomponent mixtures containing hydrogen, using polar GC-PC-SAFT. k_{ij} for the mixture is calculated by eqs 4 and 5.

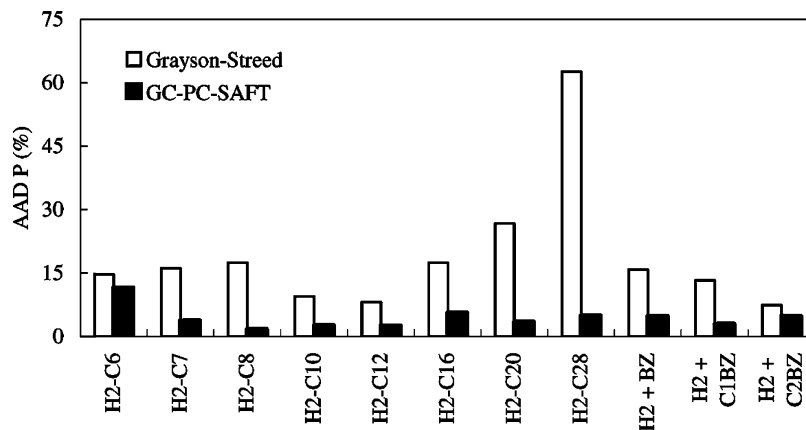


Figure 11. Results of prediction for mixtures containing hydrogen, comparison between polar GC-PC-SAFT and the Grayson–Streed³⁴ model.

the available data in the literature appears satisfactory as seen on Figure 10 (deviation on bubble pressure within 6–7%).

7. Discussion and Conclusion

In this paper, the method for correlating and predicting k_{ij} based on London's theory and developed recently^{7,8} has been applied successfully to correlate and predict phase behavior of systems containing hydrogen using Polar GC-PC-SAFT (here only quadrupole–quadrupole polar interactions are involved). The representations and predictions results obtained here, using a simple approach for computing k_{ij} , may be regarded as satisfactory when compared to experimental data. The accuracy of the present model is very comparable to that of Chi et al.⁶ (a previous version of GC-PC-SAFT), and it is not possible to determine which is the best one on this sole basis. But, let us remind (see the Introduction) that the latter model cannot be easily used to make true predictions (e.g., to predict VLE of H_2 + aromatic compounds), whereas the present model appears more versatile from this point of view.

In comparison to the Grayson–Streed³⁴ method, which is considered as a “reference” model in the petroleum industry, the improvement is significant, especially when the hydrocarbon molecule is a long chain (Figure 11). Let us recall that the Grayson–Streed model is a combination of the Redlich–Kwong equation of state (vapor phase fugacities computation) with the Hildebrand activity model.

More recently, Florusse et al.³⁵ measured and modeled VLE of some H_2 + n-alkane (C₁₀, C₁₆, C₂₈, C₃₆, C₄₆) systems using SOFT-SAFT equation of state within 1.5% error on pressure (overall absolute average deviation with respect to their measurements). They proposed a simple method for estimating k_{ij} in this case (they observed that the product $(1 - k_{ij})m$, where m is the n-alkane chain length, varies linearly with the carbon number). Although a very good representation of their VLE is obtained, their study is, however, limited to binary n-alkane-containing systems.

It may be concluded that our approach to estimate the binary interaction parameter (k_{ij}) combined with the group contribution polar PC-SAFT can be used as a predictive tool to model the phase equilibrium of mixtures containing hydrogen and an hydrocarbon if an accuracy of a few percent is acceptable.

Acknowledgment. The authors are grateful to Petro Viet Nam Oil and Gas Group for financial support through a Ph.D. and a Master grants.

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

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