Functional-Segment Activity Coefficient Model. 2. Associating Mixtures

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ABSTRACT: In this work, the recently proposed Functional-Segment Activity Coefficient (F-SAC) model (*Ind. Eng. Chem. Res.*, DOI: 10.1021/ie400170a) is extended for mixtures where hydrogen bonds (HB) can form. The F-SAC model is based on the concept of functional groups with the group interaction energies calculated according to the COSMO-RS theory. In the extension proposed here, hydrogen bonds are described by one additional energy parameter for each HB donor−acceptor pair. The F-SAC parameters for substances not participating in hydrogen bonds were kept unchanged. Additional parameters were calibrated for 25 HB donor−acceptor pairs by using infinite dilution activity coefficient (IDAC) data complemented by VLE data for the ethanol/water system. For the considered IDAC data set, the F-SAC fit was superior to the predictions obtained with UNIFAC (Do). Finally, the predictive strength of the model was assessed using vapor−liquid equilibrium as well as water/alkane mutual solubility data not considered in the model fitting process. Similar to the performance for nonassociating systems, good agreement with experimental data was possible for several systems over the entire composition range, as well as in the prediction of azeotropes.

INTRODUCTION

The formation of hydrogen bonds (HB) deeply affects the behavior of pure fluids and solutions. For instance, vapor pressure curves and critical points of fluids with HB formation are usually shifted to higher temperatures. In mixtures, HB can cause a wide range of effects, from negative deviations of the Raoult's law to partial miscibility.

Modeling HB effects is not a trivial task, as the HB energies can vary from weak (slightly above van der Waals interactions) to very strong (covalent character). Further, these energies cannot be directly measured, being usually estimated.[1] These difficulties have led to the development of many different approaches to model HB effects. Early developments are reviewed in the excellent book of Prausnitz,[2] while recent attempts to model HB in the context of equations of state are summarized in the book of Kontogeorgis and Folas.[3]

When modeling hydrogen bonds, it is usually assumed that they are formed between a proton *donor* and a proton *acceptor*. An example of proton acceptor is the acetone oxygen and an example of proton donor is the chloroform hydrogen. The COSMO[4] apparent surface charge densities of acetone and chloroform are depicted in Figure 1.

Since the molecules in Figure 1 do not have both acceptor and donor *sites* in its structure, they cannot self-associate, but they can cross-associate in solution. These associations are usually modeled by means of one or more *energy* parameters. These pairwise parameters (acceptor−donor) are usually correlated by experimental data, although several attempts to predict these quantities are available in the literature, e.g., Wolbach and Sandler,[6] Ferrando et al.,[7] Klamt et al.[8]

In contrast to the use of HB pairwise parameters, in COSMO-RS models[9,10] the hydrogen bond contribution for each donor−acceptor contact is computed from pure-compound data alone. This is a potential advantage of the method, because it is always desirable to express the properties
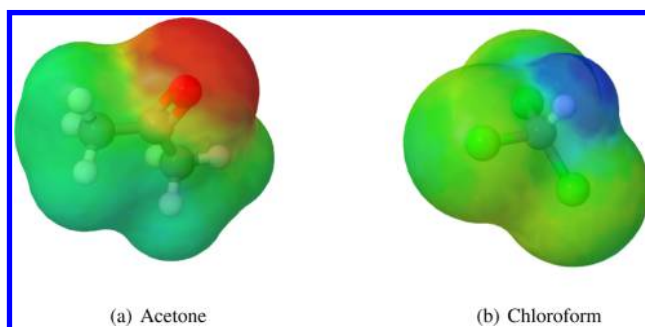

Figure 1. COSMO apparent surface charge densities showing the HB acceptor (red or positive) and donor (blue or negative) area portions, when computed as described by Gerber and Soares.[5]

of a solution as a function of the properties of the pure components.[2] For instance, in the revised COSMO-RS model[9] the HB contribution relies on only two universal parameters. In the modification of Hsieh et al.,[11] different energies for donor−acceptor pairs were considered in order to provide better experimental fit. Other kinds of modifications are reported in the literature for better agreement with experimental data. In Grensemann and Gmehling,[12] the authors have excluded HB acceptor surface segments for the ether group. In Gerber and Soares,[13] the authors introduced an empirical factor for scaling energetic contributions. In Reinisch et al.,[14] surface areas were empirically scaled when working with polyether−water systems. In Franke et al.,[15] a special parametrization for alkanes and olefins in alcohols is suggested.

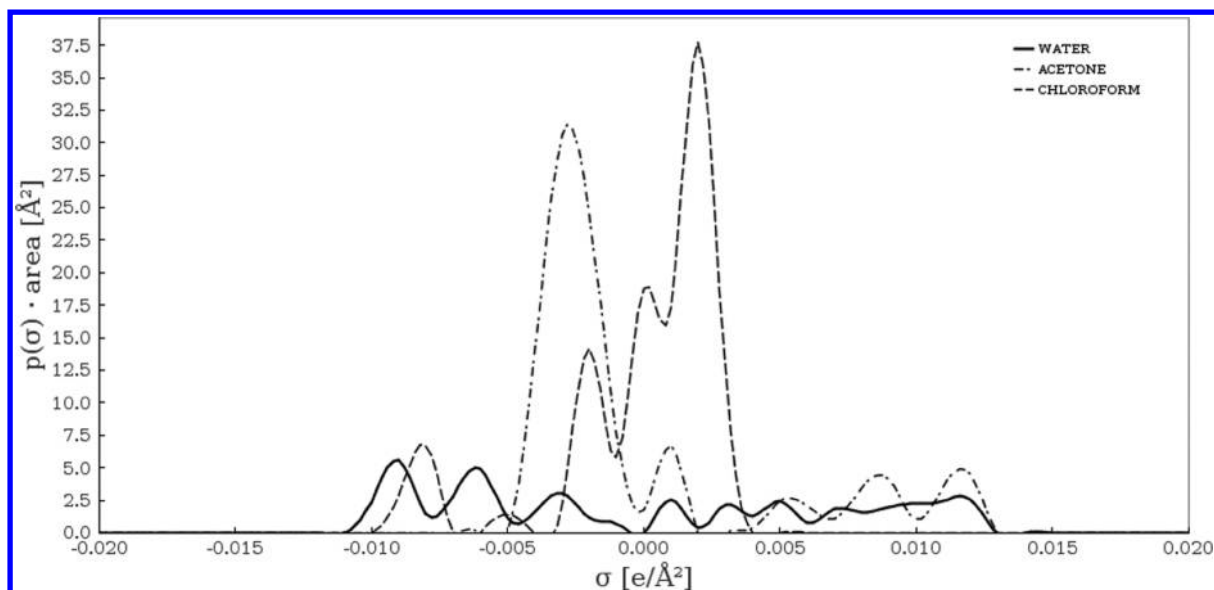Figure 2. σ-Profiles for molecules that can participate in HB, obtained as described by Gerber and Soares.[5]

In the present work, the recently proposed Functional-Segment Activity Coefficient (F-SAC) model[16] is extended to associating mixtures by taking into account HB formation. The F-SAC model is based on the concept of functional groups with the interaction energy between groups determined from the COSMO-RS theory. A new formulation for taking into account HB effects is suggested, given simply by the donor−acceptor pair formation energy. The F-SAC groups were extended to a total of 24 functional groups and 47 subgroups. The model parameters for substances not participating in hydrogen bonds (combinatorial and electrostatic parameters) were kept unchanged. The additional HB parameters were calibrated using infinite dilution activity coefficients (IDAC) from a database assembled previously,[5] complemented with vapor−liquid equilibrium (VLE) data for the ethanol/water system. This IDAC database as well as a demonstration FORTRAN code implementing the proposed method (original and extended for HB formation) are freely available at http://www.enq.ufrgs.br/labs/lvpp. The calibrated model correlations were compared with a UNIFAC (Do) model using parameters available in the literature[17] through the IDAC deviation for more than 1300 associating mixtures at different temperatures. Further, the predictive strength of the model was assessed by the comparison with vapor−liquid equilibrium data not considered in the model fitting process as well as with some water−alkane mutual solubility data.

■ F-SAC WITH HB FORMATION

In the F-SAC model,[16] as well as in UNIQUAC, UNIFAC, and COSMO-RS variants, the activity coefficient is given by the sum of a combinatorial and a residual part:

$$\ln \gamma_i = \ln \gamma_i^{res} + \ln \gamma_i^{comb} \tag{1}$$

The F-SAC combinatorial contribution is similar to the one studied by Soares[18] and to the one present in the modified UNIFAC (Do).[17] For substances that form hydrogen bonds, this contribution remains unchanged.

The F-SAC residual contribution is calculated based on the COSMO-RS theory[19] of contacting surface segments. However, instead of COSMO[4] computed apparent surface charge

densities the F-SAC model relies on *calibrated* apparent surface charge densities. Actually, it is suggested that the surface charge distribution (σ−profile) of each functional group can be represented by three empirical parameters: Q_k^+, Q_k^- and σ_k^+. Q_k^+ represents the functional group area of the positive segment; Q_k^- is functional group area of the negative segment; and σ_k^+ is the charge density of the positive segment. With these definitions, the neutral area Q_k^o is given by the remaining area of the group surface area, $Q_k^o = Q_k - Q_k^+ - Q_k^-$. Further, by a charge balance to keep each group neutral, the group negative charge density can be computed as $\sigma_k^- = -\sigma_k^+ Q_k^+/Q_k^-$.

Using these parameters, the σ-profile of each group k is given by the following:

$$p_k(\sigma)Q_k = \{(\sigma_k^-, Q_k^-); (0, Q_k^o); (\sigma_k^+, Q_k^+)\} \tag{2}$$

and finally, the σ-profile of a molecule i is given by the sum of the σ-profiles of the functional groups it consists of:

$$p_i(\sigma)q_i = \sum_k \nu_k^{(i)} p_k(\sigma)Q_k \tag{3}$$

where $\nu_k^{(i)}$ is the number of subgroups of type k in molecule i, and q_i is the total molecule area.

With the σ-profiles defined, the same formulation used in COSMO-SAC[10] was assumed for F-SAC. In this formulation, the residual contribution is calculated as the difference between the free energy to restore the charge around the solute molecule in solution, s, and the free energy to restore the charge in a pure liquid, i:

$$\ln \gamma_i^{res} = \frac{(\Delta G_{i/s}^{*res} - \Delta G_{i/i}^{*res})}{RT} \tag{4}$$

The free energy to restore the charge around the molecule of solute can be obtained by the following:

$$\frac{\Delta G_{i/s}^{*res}}{RT} = n_i \sum_{\sigma_m} p_i(\sigma_m)\ln \Gamma_s(\sigma_m) \tag{5}$$

where n_i is the total number of segments in a molecule and $\ln \Gamma_s(\sigma_m)$ is the logarithm of the activity coefficient of a segment of charge σ_m, given by the following:
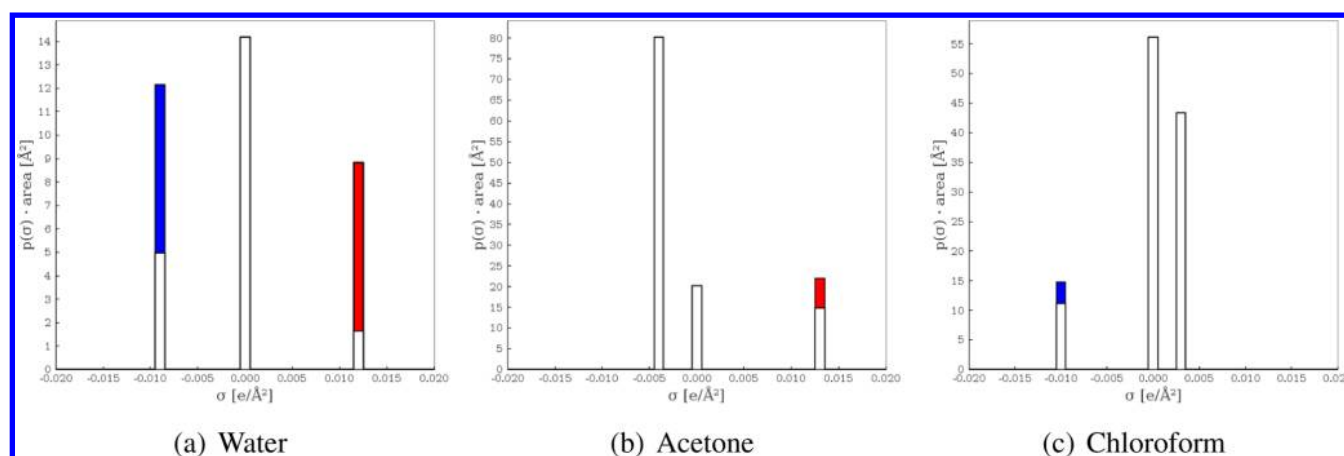
Figure 3. F-SAC σ-profiles for hydrogen bonding molecules, showing the HB donor (blue or negative) and acceptor (red or positive) area portions.

$$\ln \Gamma_s(\sigma_m) = -\ln\left\{\sum_{\sigma_n} p_s(\sigma_n)\Gamma_s(\sigma_n)\exp\left[\frac{-\Delta W(\sigma_m, \sigma_n)}{RT}\right]\right\} \tag{6}$$

$$\Delta W(\sigma_m, \sigma_n) = \frac{\alpha'}{2}(\sigma_m + \sigma_n)^2 - \frac{E^{HB}(\sigma_m, \sigma_n)}{2} \tag{7}$$

where α' is the constant for the misfit energy which evaluates[10] to 35 750 kJ Å^4/mol e^2 with the *standard* contact radius of 1.07 Å assumed in the F-SAC model; and E^{HB} is the HB formation energy.

In the original F-SAC formulation, the E^{HB} term in eq 7 was ignored. In the first COSMO-RS revision of Klamt et al.[9] the HB contribution was given by the following:

$$E^{HB}(\sigma_m, \sigma_n) = c_{hb}\max[0, \sigma_{acc} - \sigma_{hb}]\min[0, \sigma_{don} - \sigma_{hb}] \tag{8}$$

where σ_{acc} and σ_{don} denote the larger and smaller values of σ_m and σ_n, respectively; σ_{hb} is the HB surface charge density cutoff; and c_{hb} is a universal constant.

The potential advantage of eq 8 is the computation of HB effects based on pure component properties alone and good correlation between COSMO polarization charge densities and HB formation energies was recently reported by Klamt et al.[20] However, the observed accuracy of ∼2 kJ/mol is probably too high for some engineering applications. Currently, most COSMO-based models make use of some modification of eq 8. For instance, in the modification of Hsieh et al.[11] different c_{hb} energies for some donor–acceptor pairs were considered for better experimental fit.

The purpose of the σ_{hb} parameter in eq 8 is to determine the portion of the molecule surface that can participate in a hydrogen bond. The σ-profiles for some HB molecules, obtained as described by Gerber and Soares,[5] can be seen in Figure 2. From this figure, it is clear that any value around the typical value for the HB cutoff of 0.008 e/Å^2 will produce the expected behavior. The water molecule should have both donor and acceptor HB regions, while acetone should act as an acceptor only and chloroform as donor only.

However, the HB acceptor regions of water and acetone end up very similar and, consequently, the HB formation effects for water–ketone mixtures, as well as alcohol–ketone mixtures, will be exaggerated if a universal HB formation energy is considered. This illustrates the potential problems when trying

to represent associating effects using only information form the σ-profiles.

In the present work, instead of using a parameter for determining the HB area portion directly from the σ−profiles, it is assumed that all donor and acceptor *sites* have an area identical to the F-SAC standard contact area of 3.6 Å^2 (contact radius of 1.07 Å). Thus, for each functional group, the number of HB donor and acceptor sites just needs to be enumerated. The number of acceptor and donor sites assumed in this work for each functional group are listed in Table 2.

As can be seen in Figure 3, the HB donor and acceptor areas for water are identical (two sites, 7.2 Å^2 each). For chloroform, one donor site was assumed (3.6 Å^2) while two acceptor sites were considered for acetone (7.2 Å^2).

With the number of sites defined for each functional group, the HB formation energies were directly estimated for each acceptor−donor pair based on experimental data.

■ RESULTS AND DISCUSSION

In the present work, the number of F-SAC functional groups is extended to 24 and the number of subgroups is extended to 47 by adding the following self-associating groups: H_2O, CH_2OH, and CH_3OH. For all other groups, the electrostatic parameters determined in the original work[16] were kept unchanged. This was possible even for groups with either donor or acceptor sites because in the previous work all mixtures containing both donor and acceptor sites were filtered out. Group assignment examples can be found in the demonstration FORTRAN code or in the Supporting Information of the previous paper.[16] The area and volume parameters for the subgroups are listed in Table 1, while the number of donor and acceptor sites assumed for each group are listed in Table 2. The parameter estimation procedure is similar to the one described in Soares and Gerber,[16] but vapor−liquid equilibrium (VLE) data for the ethanol/water system were also considered for better experimental correlation. The calibrated model correlations for IDAC were then compared with the predictions given by UNIFAC (Do)[17] model for nearly 1300 mixtures at different temperatures. The predictive strength of the model was assessed by comparison with VLE as well as LLE data that was not considered in the model fitting process. For the LLE comparisons, the UNIFAC-LLE[21] parametrization was also used.

In addition to the 103 parameters previously calibrated for non associating mixtures, 38 new parameters were optimized in

Table 1. F-SAC Subgroup Volume (R_k) and Area (Q_k) Parameters Optimized in the Original F-SAC Model[16] and in This Work[a]

group	subgroup	R_k (Å³)	Q_k (Å²)
CH₂	CH₃	31.91	46.689
	CH₂	24.54	24.639
	CH	14.03	−0.53
	C	6.53	−20.88
	c-CH₂	24.12	27.0
	c-CH	16.21	5.47
C=C	CH₂=CH	48.16	59.52
	CH=CH	36.86	33.33
	CH₂=C	38.52	33.38
	CH=C	28.54	11.59
	c-CH=CH	36.86	51.45
ACH	ACH	19.26	20.11
	AC	10.89	1.76
CH₃COCH₃	CH₃COCH₃	92.62	122.37
	CH₃COCH₂	85.04	90.18
	CH₃COCH	78.44	68.92
	CH₂COCH₂	77.35	66.27
	CH₂COCH	69.37	27.33
CH₂CHO	CH₃CHO	69.23	90.53
	CH₂CHO	61.86	67.25
CH₃COAC₃	CH₃COAC₃	105.83	105.66
c-CH₂COCH₂	c-CH₂COCH₂	77.35	77.88
triacetin	triacetin	278.61	296.41
GBLactone	GBLactone	112.74	120.60
CH₃COOCH₃	CH₃COOCH₃	103.98	143.7
	CH₃COOCH₂	96.61	107.86
	CH₃COOCH	88.27	95.89
	CH₂COOCH₂	89.24	96.93
phthalate	phthalate	228.61	207.91
CH₂COOAC₃	CH₂COOAC₃	120.93	95.94
CH₃OCH₂	CH₃OCH₃	77.1	103.58
	CH₃OCH₂	63.03	62.75
	CH₃OC	52.26	31.42
	CH₂OCH₂	55.66	56.09
	CHOCH	44.83	10.12
c-CH₂OCH₂	c-CH₂OCH₂	55.66	52.13
N(CH₂)₃	N(CH₂)₃	55.65	35.64
DMSO	DMSO	102.83	99.04
CH₂Cl	CH₂Cl	55.24	58.08
CCl₄	CCl₄	129.47	138.83
CH₃CCl₃	CH₃CCl₃	131.4	146.92
ClAC₃	ClAC₃	79.94	76.57
CHCl₃	CHCl₃	108.67	114.25
CH₃OH[b]	CH₃OH	53.13	68.25
CH₂OH[b]	CH₂OH	45.36	43.84
	CHOH	37.67	23.02
H₂O[b]	H₂O	29.45	35.19

[a]The area parameters were optimized. [b]Added in this work.

Table 2. F-SAC Group Electrostatic Parameters Optimized in the Original F-SAC Model[16] and in This Work, and Number of HB Acceptor/Donor Sites

group	Q_k^+ (Å²)	$Q_{\bar{k}}^-$ (Å²)	σ_k^+ (e·Å⁻²)	N_{acc}[a]	N_{don}[a]
CH₂	0.00	0.00	0.0000	0	0
C=C	6.16	3.70	0.0050	0	0
ACH	5.38	6.71	0.0056	1	0
CH₃COCH₃	21.97	80.23	0.0133	2	0
CH₂CHO	14.85	81.88	0.0172	0	0
CH₃COAC₃	9.56	16.68	0.0162	2	0
c-CH₂COCH₂	13.93	42.78	0.0166	2	0
CH₃COOCH₃	28.94	107.69	0.0109	2	0
triacetin	34.68	62.83	0.0146	6	0
GBLactone	18.05	41.30	0.0161	2	0
phthalate	33.60	69.26	0.0132	4	0
CH₂COOAC₃	12.59	64.23	0.0158	2	0
CH₃OCH₂	13.01	22.71	0.0091	0	0
c-CH₂OCH₂	8.12	27.20	0.0143	2	0
N(CH₂)₃	3.60	28.58	0.0175	1	0
DMSO	11.36	22.84	0.0188	2	0
CH₂Cl	9.30	9.07	0.0089	0	0
CCl₄	18.40	26.23	0.0062	0	0
CH₃CCl₃	40.07	20.28	0.0039	0	0
CHCl₃	43.32	14.76	0.0035	0	1
ClAC₃	37.41	12.13	0.0026	0	0
CH₃OH[a]	8.31	4.72	0.0132	2	1
CH₂OH[a]	7.34	4.69	0.0145	2	1
H₂O[a]	8.84	12.16	0.0123	2	2

[a]Added in this work.

Table 3. F-SAC Hydrogen Bond Formation Energies for Acceptor-Donor Pairs, Optimized in This Work

donor	acceptor	E^{HB} (kJ·mol⁻¹)
CH₃OH	ACH	2.59
	CH₃COCH₃	2.36
	CH₃OH	9.25
	CH₂OH	11.12
	H₂O	2.49
CH₂OH	ACH	1.12
	CH₃COCH₃	1.31
	CH₃COOCH₃	4.60
	CH₃OCH₂	7.89
	CH₃OH	6.25
	CH₂OH	8.01
	H₂O	4.18
CHCl₃	ACH	1.76
	CH₃COCH₃	3.64
	CH₃COOCH₃	7.68
	CH₃OCH₂	12.53
	CH₃OH	8.63
	CH₂OH	8.22
H₂O	ACH	0.90
	CH₃COCH₃	19.44
	CH₃COOCH₃	21.90
	CH₃OCH₂	23.90
	CH₃OH	24.04
	CH₂OH	22.58
	H₂O	21.84

this work. Namely, the area (Table 1) and electrostatic parameters (Table 2) for self-associating groups; and HB energies for 25 acceptor−donor pairs (Table 3).

In order to represent the same amount of molecules used in the F-SAC parameter estimation with the modified UNIFAC (Do) model, 21 groups and 35 subgroups were necessary. However, for these 21 groups, the binary interaction parameter matrices have 778 nonzero elements. Clearly, when using the proposed model, new specific and less comprehensive groups

can be added with less cost and with a reduced need of experimental data. Further, all F-SAC model parameters have a
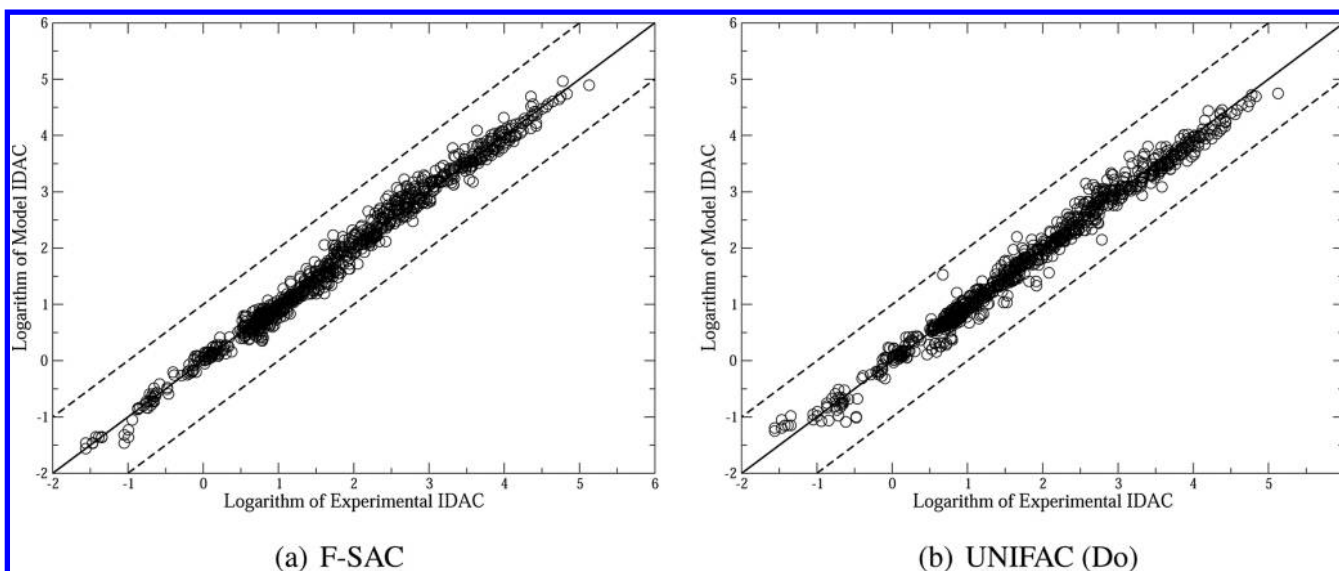
Figure 4. Logarithm of experimental IDAC versus logarithm of calculated IDAC of 1009 data points of associating mixtures (water excluded).
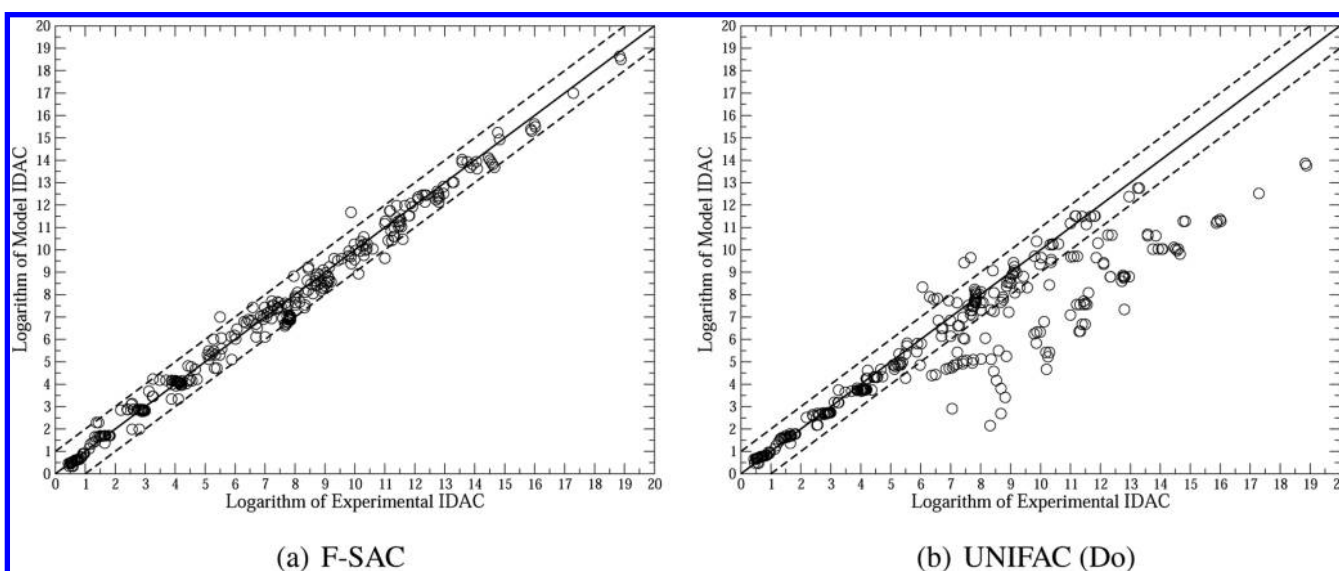

Figure 5. Logarithm of experimental IDAC versus logarithm of calculated IDAC for 328 data points of mixtures with water.

sound physical meaning[16] as well as the extension proposed in this work. For instance, the estimated F-SAC HB formation energy for water is 21.8 kJ/mol (see Table 3). This value is very close to the value of 23.3 kJ/mol estimated by Suresh and Naik,[22] which is also similar to other values reported by Wendler et al.,[1] ranging from 20.4 to 23.3 kJ/mol.

IDAC Comparison. The calibrated model correlations were compared with a UNIFAC (Do) model[17] using the same IDAC database employed to fit the F-SAC parameters. The comparisons were accomplished in terms of both the absolute average deviation in ln-units as well as the absolute percent deviation from IDAC experimental data of mixtures with HB formation (both self-association and cross-association) at different temperatures, defined as follows:

$$\ln \text{AAD} = \frac{1}{\text{NP}} \sum_i \left| \ln \gamma_{i,\text{exp}}^{\infty} - \ln \gamma_{i,\text{model}}^{\infty} \right| \tag{9}$$

$$\text{AAD\%} = \frac{1}{\text{NP}} \sum_i \left| \frac{\gamma_{i,\text{exp}}^{\infty} - \gamma_{i,\text{model}}^{\infty}}{\gamma_{i,\text{exp}}^{\infty}} \right| \tag{10}$$

where NP is the number of experimental points; and $\gamma_{i,\text{exp}}^{\infty}$ and $\gamma_{i,\text{model}}^{\infty}$ are the experimental and calculated activity coefficients at infinite dilution, respectively.

The F-SAC fit quality for the associating mixtures available in the IDAC database (water excluded) is shown in Figure 4-a. As can be seen in this figure, for the experimental data considered, the F-SAC model showed a very good fit. As can be seen in Figure 4-b, UNIFAC (Do) also performed very well for these HB mixtures. The lnAAD for the proposed model was 0.109, while the predictions with UNIFAC (Do) resulted in a deviation of 0.113. The resulting percent deviations were both 11.1%.

For aqueous mixtures, the results are shown in Figure 5. The F-SAC correlation deviated from experiment by 0.338 ln-units while UNIFAC (Do) predictions deviated by 1.23. The
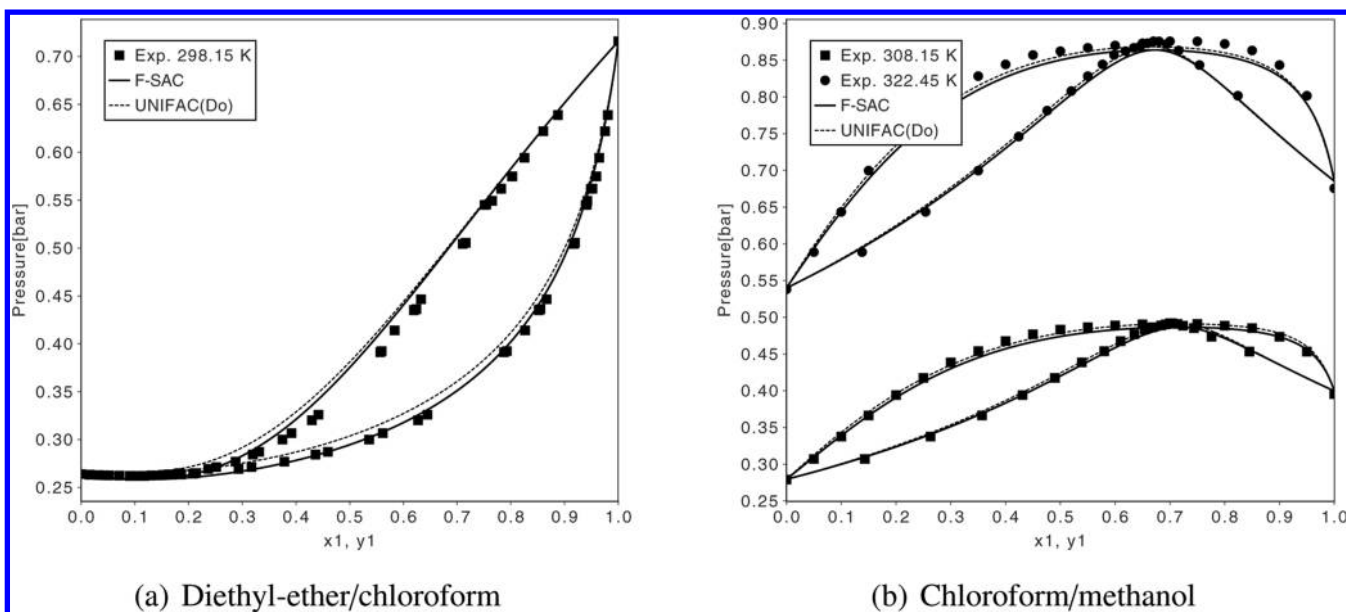
Figure 6. F-SAC and UNIFAC (Do) VLE predictions for HB mixtures of chloroform, experimental data from Becker et al.[26] and Sitnikov.[27].
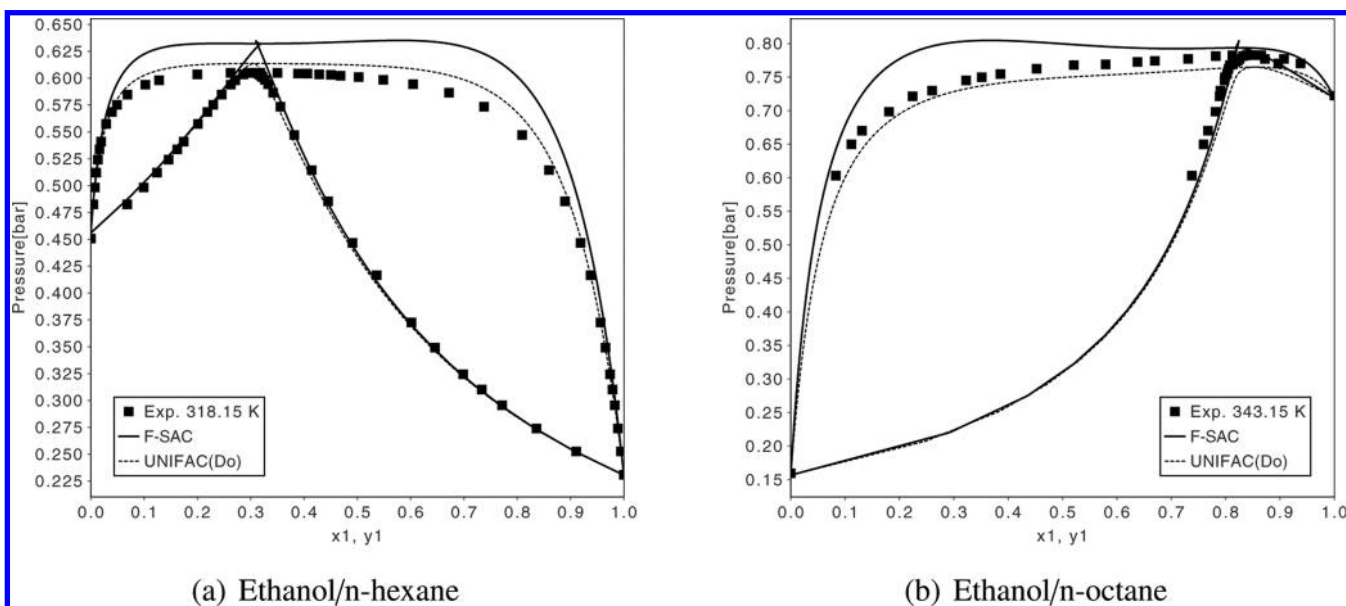

Figure 7. F-SAC and UNIFAC (Do) VLE predictions for ethanol/alkane mixtures, experimental data from O'Shea and Stokes[30] and Hiaki et al.[31]

observed percent deviations were 32.1% and 52.4% for the proposed method and UNIFAC (Do), respectively.

It should be noted that the F-SAC model was able to correlate all mixtures within a narrow range of error. Regarding UNIFAC, the prediction of aqueous mixtures with large IDAC values stands out negatively. Actually, this is expected since very large IDAC values are usually not considered when fitting UNIFAC parameters, under the assumption that IDAC data with large values are less reliable.[23] The poor performance in predicting IDAC of aqueous mixtures was also observed in several works in the literature.[13,24] However, as can be seen in Figure 5, both small and very large IDAC values of mixtures with water were well correlated by the F-SAC model with a single parameter set.

VLE Prediction. In this section, the F-SAC method extended for HB formation is experienced in the prediction of vapor−liquid equilibrium (VLE) data, not considered in the

parameter fitting process. In order to evaluate the performance of the activity coefficient model alone, only low to moderate pressure experiments were included in the analysis, enabling the use of the modified Raoult's law. For the pure compound vapor pressures, correlations freely available in the literature were used. Similar tests were accomplished in the original F-SAC paper as well as by Bastos et al.[25] when UNIFAC parameters were calibrated with IDAC data only. The authors found good results for systems with small activity coefficient values, which is usually the case for mixtures without HB formation.

In Figure 6, some predictions for mixtures with chloroform are depicted. The proposed model as well as UNIFAC (Do) performed very well for these cases. For the diethyl-ether/chloroform mixture, a negative deviation from the Raoult's law is observed as a consequence of the cross-association hydrogen bonds formed only in mixture. For the chloroform/methanol
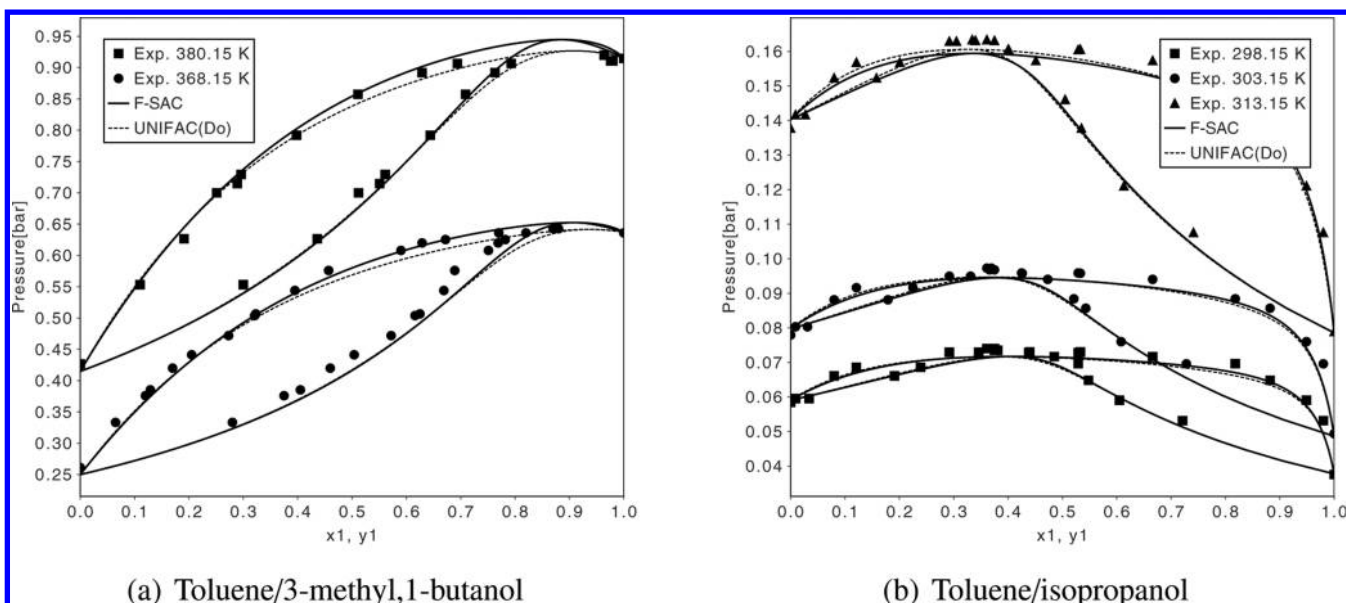
Figure 8. F-SAC and UNIFAC (Do) VLE predictions for HB mixtures of toluene/alcohol, experimental data from Reddy and Rao[32] and Ashcroft et al.[33]
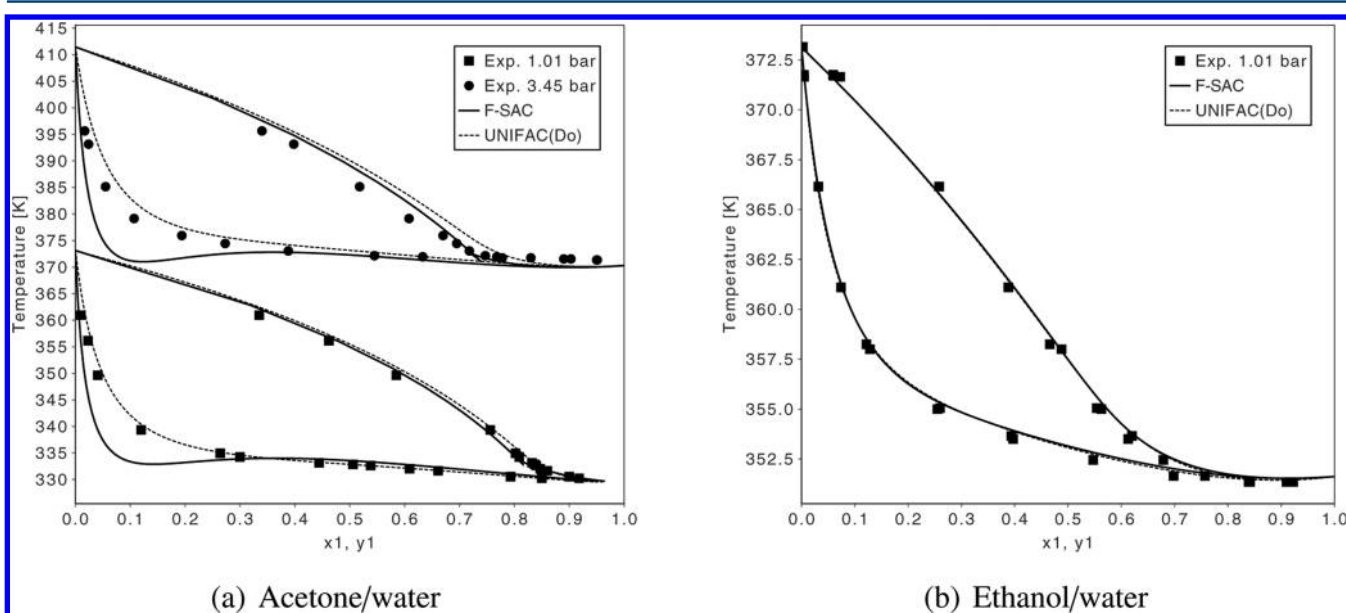

Figure 9. F-SAC and UNIFAC (Do) VLE for aqueous mixtures, experimental data from Othmer et al.[34] and Dalager.[35]

case, positive deviations are observed because the chloroform HB donor competes with the alcohol donor in the mixture.

In Figure 7, some predictions for ethanol/alkane systems are presented. As can be seen, the proposed model overestimates the positive deviations, while UNIFAC (Do) performed better for these cases. In these particular cases, the experimental IDAC data considered in the parameter fitting might be the source of the deviations. For instance, for the system ethanol/n-hexane at 313.2 K, our database[5] contains different IDAC values, ranging from 32.50 to 38.30. According to Kikic et al.,[28] under the assumption of absence of systematic deviations, the main methods for experimental determination of IDAC values have a similar variance in ln γ_i^∞ which is smaller than 0.05 ln-units. However, differences as large as 100% can be found by comparing different literature sources, even when using the same experimental technique, probably because of systematic

deviations.[29] Thus, better results would probably be obtained by also considering VLE data in the parameter correlation or by a critical evaluation of the IDAC data.

Figure 8 presents some predictions for mixtures with toluene/alcohol. For these cases, both models predicted the experimental trends very well.

In Figure 9, predictions for the acetone/water system are shown as well as for the ethanol/water system. As can be seen, the F-SAC model deviated considerably from the experimental data for the acetone/water mixture. It should be noted that the experimental IDAC database considered in the parameter estimation step contains data only for ketones in water and no data of water diluted in ketones. This poses additional difficulties in predicting the behavior of this mixture. Similar deviations were also observed for the ethanol/water system when fitting the parameters solely based on IDAC data. Then,
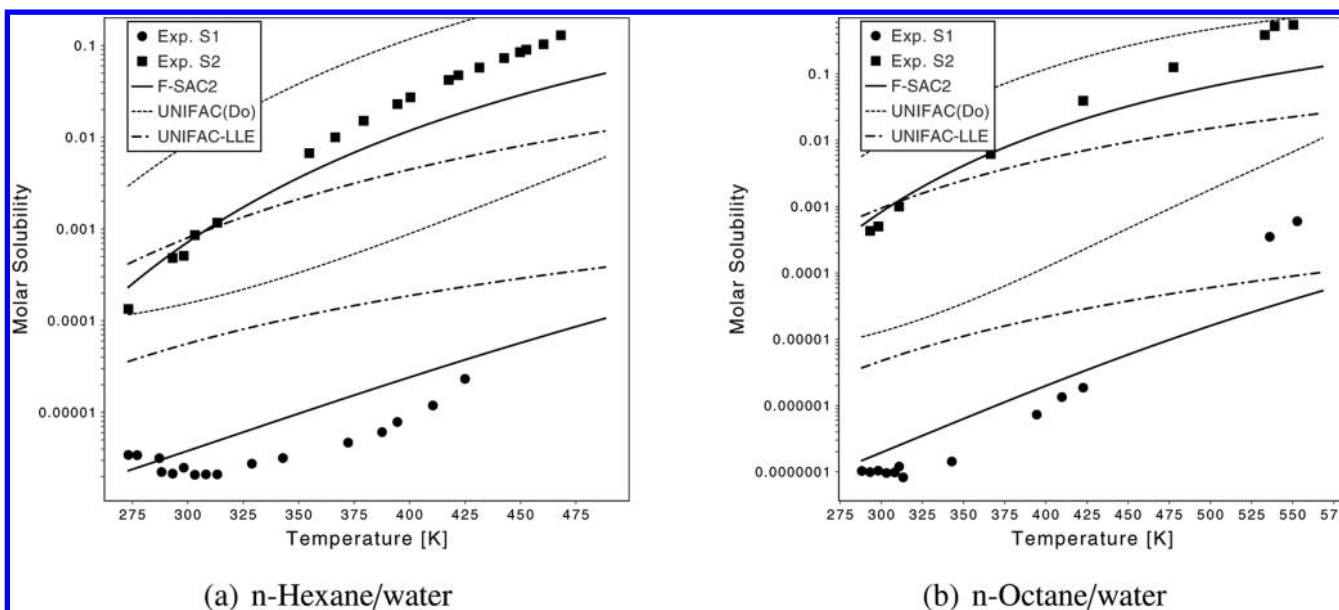
Figure 10. F-SAC, UNIFAC (Do), and UNIFAC-LLE predictions for alkane/water (S1) and water/alkane (S2) solubilities, experimental data from Maczynski.[37]

especially for the ethanol/water case, VLE data were also considered in the fit, leading to very good results, shown in Figure 9-b. This indicates again that even better results could be obtained by also considering VLE data in the F-SAC parameter estimation procedure.

LLE Prediction. When working with UNIFAC models, separate parameter tables are usually considered for VLE and LLE correlation. This is mainly because of the difficulties in predicting LLE from parameters obtained by regression of experimental VLE data.[21,36] In this section, we have selected mutual solubilities of alkane/water systems for assessing the F-SAC predicting strength for LLE systems. In Figure 10, the predictions for F-SAC, UNIFAC (Do), and UNIFAC-LLE[21] are shown.

As can be seen, F-SAC performed better even than UNIFAC-LLE. No model was able to predict the minimum solubility of alkanes in water, usually near to room temperature.[37] Although the parameters of the F-SAC model are temperature independent, the formulation inherited from the COSMO-RS theory naturally introduces temperature effects in the residual part. In the original work,[16] a small systematic error with respect to the temperature was already suggested. From the results in Figure 10, it is clear that either new effects or parameters need to be incorporated into the model in order to better represent mutual miscibility in wide temperature ranges.

■ CONCLUSIONS

In this work, the recently proposed activity coefficient model known as F-SAC (Functional-Segment Activity Coefficient) was extended to consider hydrogen bond (HB) formation.

In the F-SAC method, each functional group is described by only three *electrostatic* parameters in addition to the area and volume parameters of each subgroup. This is in contrast to the usual molecular (or functional) pairwise parameters. In the extension proposed here, there is only one additional parameter for each acceptor–donor HB pair. The number of functional groups of the F-SAC method was extended to 24, and the number of subgroups was extended to 47. In addition to the 103 parameters calibrated in the original version for non

associating mixtures, 38 new parameters were calibrated in this work, namely, the area and electrostatic parameters for self-associating groups plus HB formation energies for 25 acceptor–donor pairs. In order to represent the same amount of substances studied in this work with the UNIFAC (Do) model, 21 groups and 35 subgroups were necessary. However, for these 21 groups, the binary interaction parameter matrices have 778 nonzero elements. Clearly, when using the proposed model, more specific and less comprehensive groups can be added with less cost and with a reduced need of experimental data. Further, all F-SAC model parameters have a sound physical meaning as well as the extension proposed in this work.

As in the original F-SAC work, the model parameters were fit based on the infinite dilution activity coefficient (IDAC) data available in the literature. Additionally, vapor–liquid equilibrium data for the ethanol/water mixture were also included in order to improve the response of the model for this specific system. The calibrated model was compared with a UNIFAC (Do) implementation by the IDAC absolute average deviation in ln-units as well as percentage deviations. For nearly 1000 associating mixtures (water excluded), the proposed model deviated from the experimental data by 0.109 ln-units, while the UNIFAC (Do) predictions deviated by 0.113. In terms of percent deviations both models performed with 11.1% of error. When considering nearly 300 aqueous mixtures the deviations where 0.338 and 1.23 ln-units for F-SAC and UNIFAC (Do), respectively, or in terms of percent deviations, 32.1% and 52.4% for F-SAC and UNIFAC (Do), respectively. The proposed model was able to correlate all mixtures within a narrow range of error. With regard to UNIFAC, the prediction of aqueous mixtures with large IDAC values stands out negatively.

While IDAC data were used for calibrating the proposed model, the prediction strength was assessed by using VLE as well as LLE data. Good agreement with several VLE experiments was possible in the entire composition range, as well as in the prediction of azeotropes. According to the studied systems, even better agreement with VLE data could be achieved by also considering VLE data in the parameter fitting

procedure. Regarding LLE, predicted mutual solubilities of alkane/water were compared with experimental data. For the cases tested, F-SAC performed better than UNIFAC (Do) and UNIFAC-LLE. No model was able to represent the solubility minimum of alkanes in water near to room temperature. Thus, either new effects or new parameters need to be introduced in the model in order to improve the agreement with experimental solubility data in wide ranges of temperature.

At present, the number of F-SAC functional groups is being expanded as well as the acceptor–donor HB formation energies table. Multicomponent and multiphase equilibria are also being evaluated. The new model is also being experienced at high-pressure and high-temperature conditions in association with cubic equations of state and by means of the SCMR.[38] Tests with island type systems,[39,40] which are very difficult to correlate and predict, are also in progress.

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Notes
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■ LIST OF SYMBOLS

α' = Constant for the misfit energy J Å^4/mol e^2
$\Delta W(\sigma_m,\sigma_n)$ = Total energy for the pair σ_m–σ_n J/mol
$\Gamma(\sigma_m)$ = Segment activity coefficient
γ_i^∞ = Infinite dilution activity coefficient
γ_i^{comb} = Combinatorial contribution to the activity coefficient
γ_i^{res} = Residual contribution to the activity coefficient
γ_i = Activity coefficient of substance i in solution
σ_k^+ = Charge density of the positive segment of the functional group k e/Å^2
σ_k^- = Charge density of the negative segment of the functional group k e/Å^2
$E^{HB}(\sigma_m,\sigma_n)$ = Energy due to hydrogen bonding for the pair σ_m–σ_n J/mol
$p(\sigma)$ = Sigma profile of a mixture
$p_i(\sigma)$ = σ−profile of molecule i
$p_k(\sigma)$ = σ−profile of functional group k
q_i = Total molecule area Å^2
Q_k^+ = Absolute area with positive charge of the functional group k Å^2
Q_k^- = Absolute area with negative charge of the functional group k Å^2
Q_k^o = Absolute neutral area of the functional group k Å^2
R = Ideal gas constant J/mol K

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