Functional-Segment Activity Coefficient Model. 1. Model Formulation

Rafael de P. Soares* and Renan P. Gerber

Departamento de Engenharia Química, Escola de Engenharia, Universidade Federal do Rio Grande do Sul, Rua Engenheiro Luis Englert, s/n, Bairro Farroupilha, CEP 90040-040, Porto Alegre, RS, Brazil

Ⓢ *Supporting Information*

ABSTRACT: At present, at least for engineering purposes, the most successful predictive models for activity coefficients are those based on functional groups such as UNIFAC and its variants. While these models require large amounts of experimental data, the ones based on COSMO-RS require the calibration of a small set of universal parameters. However, the resolution required by many engineering tasks is usually higher than that obtained by COSMO-RS models. Thus, in this work, a novel functional-segment activity coefficient (F-SAC) model is proposed. This new model is also based on the concept of functional groups, but the interaction energy between groups comes from the COSMO-RS theory. The model parameters were calibrated for 21 groups and 43 subgroups by using infinite dilution activity coefficient (IDAC) data only. Only non-hydrogen bonding mixtures were investigated while associating mixtures are studied in an accompanying paper. For the considered IDAC data set, the F-SAC fit was superior to the predictions obtained with both UNIFAC (Do) and COSMO-SAC. Finally, the predictive strength of the model was assessed by using vapor−liquid equilibrium data not considered in the model fitting process. Very good agreement with experimental data was possible over the entire composition range, as well as in the prediction of azeotropes.

INTRODUCTION

Reliable prediction of thermodynamic properties of substances in solution is the key for the design, efficient operation, and optimization of many industrial processes. In particular for separation processes, accurate prediction of activity coefficients is crucial.

Currently, for engineering purposes, the most successful predictive models for activity coefficients are group contribution methods such as UNIFAC and modified UNIFAC.[1,2] However, these models require a large amount of experimental data in order to fit their group interaction parameter matrices. As a consequence, even for a limited number of functional groups, it has not been possible yet to complete these matrices for all possible interactions. An attempt for the prediction of missing group interaction parameters was proposed by Gonzàlez et al.[3] Such a method would be very desirable and could save a lot of experimental effort. However, according to Mohs et al.,[4] while there are examples in which the method works quite well, often the procedure leads to poor results. More recently, Mustaffa et al.[5] revisited and improved the method.

Even for groups with existing interaction parameters, problems may be encountered. The number of functional groups is limited and unreliable predictions may be experienced for molecules with several functional groups or when functional groups appear in an unusual way.[6−10] In this sense, the GEQUAC model proposed by Egner et al.[11,12] has a stronger theoretical basis. In this model, the molecular surface is subdivided in segments that allows the description of associating and nonassociating liquid mixtures by an explicit account for different poles of molecular surface between which strong interactions take place in a mixture.[13] Unfortunately, this model has been parametrized only for a small number of

substances. Similarly to UNIFAC models, GEQUAC parameters are not a function of the groups (or surface segments) alone, but pairwise. Furthermore, it is difficult to remedy intramolecular effects by changing the model, one solution is to define new, larger, groups. But this does not only increase the number of parameters but also the new groups may become too complex to be described by simple models.[6] Another alternative is to introduce the so-called second-order groups.[8] In Abildskov et al.,[9] the addition of a few second-order group interaction parameters to the UNIFAC tables has improved the results for the cases of alcohols and aromatics. Lin and Sandler[14] also suggested a method to correct structure and proximity effects when predicting octanol−water partition coefficients.

On the other hand, it is always desirable to express the properties of a solution in terms that can be calculated completely from the properties of the pure components.[15] In this sense, an alternative for activity coefficient calculation is the use of models based on COSMO (conductor-like screening model). These models are based on electronic structure results from quantum chemistry calculations instead of experimental data and only a small set of universal parameters needs to be calibrated. The first model in this category was COSMO-RS (for real solvents).[16] Currently, these models are becoming more and more popular and slight modifications have been continuously proposed in the literature (e.g., Grensemann and Gmehling,[1] Gerber and Soares,[10] Klamt et al.,[17] Wang et al.,[18,19] Hsieh et al.,[20] Gerber and Soares,[21] and Soares[22]). Databases with pure component COSMO information are also

freely available.[23,24] One of the outstanding features of COSMO-RS models is the ability to predict activity coefficients based solely on pure compound information by using a contacting surface *segments* (or *patches*) theory. By contrast, all the other classic activity coefficient models rely either on molecular pairwise interaction parameters (e.g., Wilson, NRTL, and UNIQUAC) or on functional pairwise interaction parameters (e.g., UNIFAC and GEQUAC). Additionally, COSMO-RS models can, in principle, take into account different molecule conformations.

Although COSMO-RS models have exceptional theoretic characteristics and perform very well in qualitative, semi-quantitative, and solvent screening tests, the precision required for engineering tasks, such as the optimization of separation systems, is usually beyond the current model resolution.[1,25,26] Improved quantitative agreement with experimental data is usually obtained by means of empirical modifications. Just to mention a few examples, in the work of Grensemann and Gmehling[1] the authors have *corrected* the water apparent surface charge distribution and also empirically excluded hydrogen bond acceptor surface segments for the ether group. In the work of Gerber and Soares,[21] the authors introduced an empirical factor for scaling energetic contributions. In the work of Reinisch et al.,[27] surface areas were empirically scaled when working with polyether—water systems. In the work of Franke et al.,[28] a special parametrization for alkanes and olefins in alcohols is suggested.

Following the aforementioned empirical attempts to improve the quantitative performance of COSMO-RS models, in this paper an alternative activity coefficient model is suggested. A higher degree of empiricism is introduced leading to a reduced predictive strength of the model, but, hopefully, with increased resolution. This new model, here called F-SAC (functional-segment activity coefficient), is based on group contributions, such as UNIFAC, but the interaction energy between groups comes from the COSMO-SAC (segment activity coefficient)[29] formulation, which is a COSMO-RS variation. The proposed model considers that each pure substance consists of several functional groups, and the model parameters are the apparent surface charges of each group. As a consequence, the model depends only on *pure* functional group parameters and the interactions are computed from these pure properties.

The main difference between F-SAC and COSMO-RS or COSMO-SAC models is that the later ones rely on molecular properties determined by quantum chemical packages, while the new model (and other group contribution methods) relies on fitted molecular properties.

In the formulation proposed in this paper, three parameters are needed to describe the energetic (or residual) contribution of each functional group. In principle, once the parameters for each functional group are properly calibrated, they should work to describe the interactions with any other group. Therefore, the number of model parameters grows linearly with the number of functional groups. On the other hand, in classical models the number of interaction parameters exhibit quadratic growth with respect to the number of groups (or molecules). This is also true for the COSMOSPACE[30] method, in which the COSMO-RS theory is also partially adopted, but the formulation is developed in terms of pairwise interaction parameters.

Mu et al.[31,32] also developed a group contribution method to be used with the COSMO-SAC model. The authors tried to reproduce the apparent surface charges of pure substances computed by COSMO by using group contribution. With this approach, the result will be, at best, equivalent to the results when the full model is used. In the proposed method, parametrized *artificial* apparent surface charge distributions are calibrated directly with experimental data. The calibrated surface charge distribution obtained here may differ significantly from those calculated by COSMO methods, but the calibrated distribution usually resembles the one predicted by quantum chemical packages. On this regard, it is noteworthy that COSMO results are also subject to several kinds of approximations.

In the present study, we have considered 21 functional groups. Only nonassociating mixtures were selected. In this work, the F-SAC parameters were calibrated using only activity coefficients at infinite dilution (IDAC) from a database assembled previously.[10] This database as well as a demonstration FORTRAN code of the proposed method are freely available at http://www.enq.ufrgs.br/labs/lvpp. The calibrated model correlations were compared with a UNIFAC (Do) model using a parameter matrix available in the literature[33] and with a COSMO-SAC implementation[10] through the IDAC deviation for more than 1500 mixtures at different temperatures. Further, the predictive strength of the model was assessed by comparison with vapor—liquid equilibrium data not considered in the model fitting process.

■ NEW FUNCTIONAL-ACTIVITY COEFFICIENT MODEL: F-SAC

It is convenient to write Gibbs excess energy (G^E) models as the sum of two parts: (i) a *combinatorial contribution* that accounts for differences in size and shape and (ii) a *residual contribution*, which should include the differences in inter-molecular forces between components.[15] When dealing with Gibbs excess models, we are usually interested in the behavior of liquid phases, being pressure effects often disregarded. Thus, from standard thermodynamic relations, liquid-phase activity coefficients γ_i can also be calculated as a function of temperature and composition, as the sum of a combinatorial and a residual part:

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

All UNIFAC and COSMO-RS variants follow this formulation, as well as the model proposed here.

Combinatorial Term. The F-SAC combinatorial contribution remained similar to our previous COSMO-SAC implementations[10,22] which is like the one present in the modified UNIFAC (Do),[33] as follows:

$$\ln \gamma_i^{comb} = 1 - V_i' + \ln V_i' - \frac{5q_i}{q}\left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \tag{2}$$

$$V_i' = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \tag{3}$$

$$V_i = \frac{r_i}{\sum_j x_j r_j} \tag{4}$$

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{5}$$

$$F_i = \frac{q_i}{\sum_j x_j q_j} \qquad (6)$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \qquad (7)$$

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

In this formulation, the combinatorial contribution is a function of the molar fraction x_i, functional group volumes (R_k), and surface areas (Q_k). Each R_k volume was obtained from COSMO cavities previously[10] computed by using representative molecules containing the group k, assuming fixed atom radii 18% larger than the ones determined by Bondi.[34] The Q_k parameters were optimized for each group k for better experimental data fit. The starting value for this optimization was also taken from the COSMO cavity of representative molecules.

Regarding the normalization area q, a value of 2.5×10^9 cm^2/mol was derived by Abrams and Prausnitz[35] to be used with UNIQUAC. This is equivalent to 41.5 Å^2 per molecule. Considering the slightly larger area of the COSMO cavities, the normalization area q, in eq 2, was taken to be 50 Å^2.

Residual Term. In COSMO-RS models, the residual contribution is calculated based on a theory of contacting surface segments. First, each molecule is assumed to be inside of a cavity, immersed in a perfect conductor. In this hypothetical situation, apparent surface charges can be computed using the COSMO method. This is a numerical method in which the cavity surface needs to be discretized into *segments* or *patches* before the actual numerical solution. Typical results for the apparent surface charges, computed as described in the work of Gerber and Soares,[10] are depicted in Figure 1a.

(a) benzene and acetone immersed in a perfect conductor

(b) one contact between benzene and acetone with the conductor partially excluded
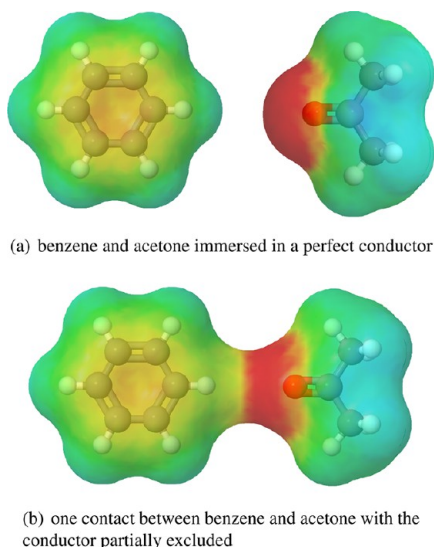
Figure 1. Representation of two molecules in a conductor (a) and in contact (b).

In essence, what the model takes into account is the energetic difference between two surface segments in contact, with respect to their initial contact with a perfect conductor. Figure 1b represents one possible contact. We should note that, for each contact between two molecules, the conductor is partially excluded. Eventually, we can imagine that each molecule initially immersed in a conductor is incrementally put in contact with other molecules until the real solution state

is achieved (where there is no conductor in between the molecules).

It is evident that, in the real solution, there are infinite possible arrangements for these contacts. Hence, a statistical thermodynamics treatment is necessary. This leads to a set of nonlinear equations that need to be solved by iteration, as described later. Actually, the solution of this system of equations cannot be accomplished in terms of the three-dimensional apparent surface charges. First, the charges are averaged and then projected onto a histogram, which is known as the σ-profile, $p_i(\sigma)$. The σ-profiles for the molecules in Figure 1a are shown in Figure 2.

The σ-profiles of the pure substances are then used to predict the activity coefficients of substances in mixtures. At this point the main difference between the COSMO-SAC and F-SAC models arises. For the new model, instead of using COSMO calculations to obtain the σ-profiles, it is proposed that each functional group has its own empirically calibrated σ-profile, $p_k(\sigma)$. In the present proposal, it is suggested that the 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° is given by the remaining area of the group surface area, $Q_k^\circ = Q_k - Q_k^+ - Q_k^-$. 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, we find the σ-profile of a group k as

$$p_k(\sigma)Q_k = \{(\sigma_k^-, Q_k^-); (0, Q_k^\circ); (\sigma_k^+, Q_k^+)\} \qquad (8)$$

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:

$$p_i(\sigma)q_i = \sum_k \nu_k^{(i)} p_k(\sigma) Q_k \qquad (9)$$

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

This representation is schematically exemplified for the benzene molecule in Figure 3. For this schematic representation, the benzene molecule was chosen since it contains only one functional group type, the aromatic CH.

With the σ-profiles defined, the same formulation present in COSMO-SAC[29] 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 to restore the charge in a pure liquid, i:

$$\ln \gamma_i^{\text{res}} = \frac{\beta(\Delta G_{i/s}^{*\text{res}} - \Delta G_{i/i}^{*\text{res}})}{RT} \qquad (10)$$

where β is an empirical factor introduced by Gerber and Soares,[21] set here as 1.0 because the apparent surface charges of the groups are adjusted in the model fitting process.

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

$$\frac{\Delta G_{i/s}^{*\text{res}}}{RT} = n_i \sum_{\sigma_m} p_i(\sigma_m) \ln \Gamma_s(\sigma_m) \qquad (11)$$

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
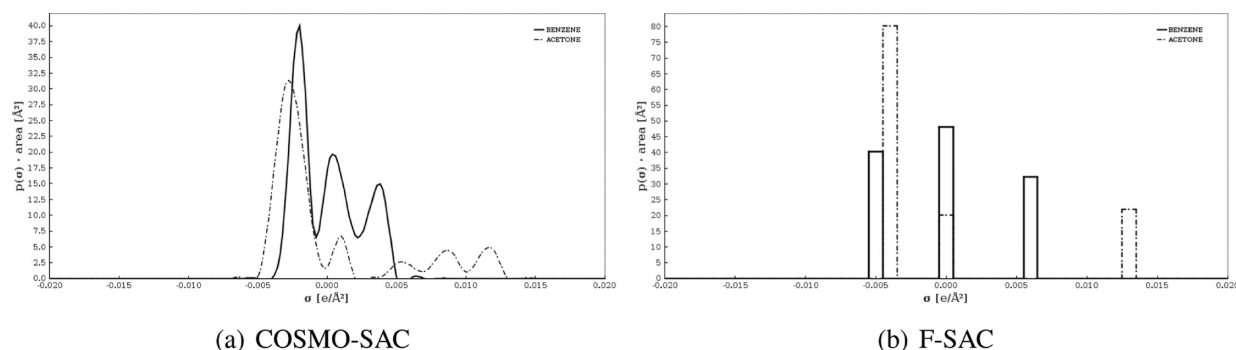
(a) COSMO-SAC

(b) F-SAC

Figure 2. σ-Profile of benzene and acetone for (a) COSMO-SAC[10] and (b) F-SAC.

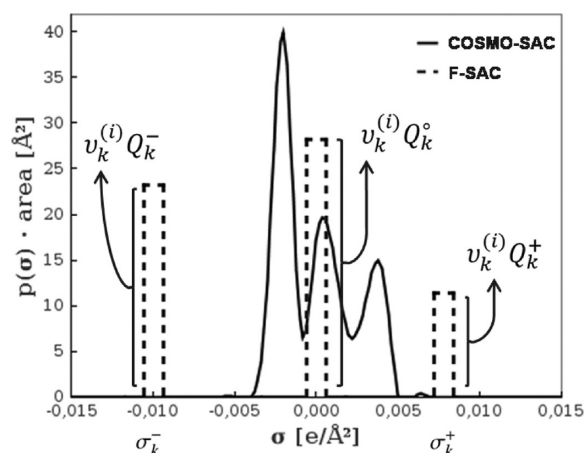**Figure 3.** σ-Profile of benzene for COSMO-SAC and schematic representation for F-SAC.

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

$$(12)$$

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

$$(13)$$

where α' is the constant for the misfit energy which evaluates[29] to 8544.6 kcal $\text{Å}^4/(\text{mol e}^2)$ with the *standard* contact radius of 1.07 Å assumed here.

The E^{HB} term in eq 13 should account for hydrogen bonding effects, ignored in the present work. The system of equations given by eq 12 needs to be iterated for convergence, as described elsewhere.[16,29] In this sense, the F-SAC model is similar to GEQUAC, since both need a numerical procedure for convergence. This is also a characteristic of all COSMO-based models, in contrast to explicit models like Wilson, NRTL, UNIQUAC, or UNIFAC variants.

Group Selection. Different group contribution methods use different groups to represent the same molecule. Further, ambiguities can arise making the group identification not unique. Trying to determine the uniqueness of group definitions, Wu and Sandler[7] developed a simple theoretical basis for defining functional groups:

1. The geometry of a functional group (i.e., bond angles, etc.) shall be the same independent of the molecules in which the group occurs.
2. Each atom in a functional group should have approximately the same charge in all molecules in

which the group occurs, and the group should be approximately electroneutral.
3. Each functional group should be the smallest entity such that a molecule can be divided into a collection of electroneutral groups.

In the present work, we followed these recommendations, but the second condition was more strictly applied: the groups' electroneutrality should be enforced. This rigorous imposition comes from the F-SAC assumption that each group σ-profile needs to be electroneutral. This is an important aspect because depending on how the functional groups are defined, it is possible to end up with partially charged groups. This is the case for many groups in UNIFAC and modified UNIFAC models (e.g., CH_3CO, CH_3COO, CH_3O) as well as in the proposal of Wu and Sandler.[7]

Thus, in order to define the functional groups for the new model, the 3D apparent surface charges generated by COSMO calculations (as described in Gerber and Soares[10]) were inspected. First, the functional group center should be located, usually related to an heteroatom. Then, the group is expanded from its center to encompass an electro-neutral area of the molecule. This was made by visual inspection.

As a first example, let us consider the ketone group, where the center of the functional group is the C=O. As can be seen in Figure 4, the effect of the heteroatom extends until the hydrogens of the first sibling carbon. Then, in order to maintain the electroneutrality of the group, it is necessary to include these sibling atoms. As explained below, there will be *groups*
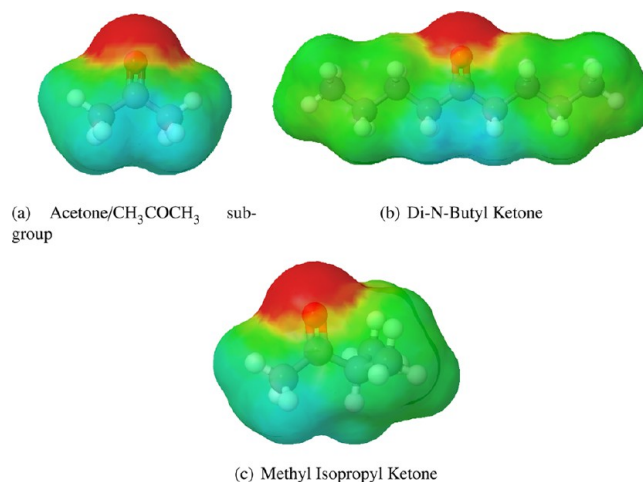

(a) Acetone/CH_3COCH_3 sub-group

(b) Di-N-Butyl Ketone

(c) Methyl Isopropyl Ketone

Figure 4. COSMO surfaces for the inspection of the C=O effect in ketones.

and *subgroups* in the proposed model. As an example, for acetone, the subgroup should be the entire molecule CH_3COCH_3. For di-*n*-butyl ketone, it should be CH_2COCH_2 and for methyl isopropyl ketone, CH_3COCH, as illustrated in Figure 5 by means of opened surfaces. These group definitions differ from the one proposed by Wu and Sandler[7] (CH_3CO and CH_2CO for ketones).

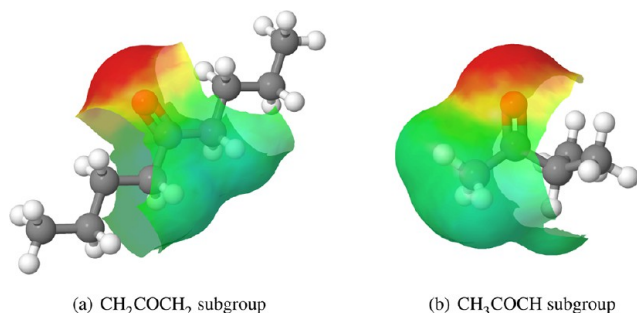(a) CH_2COCH_2 subgroup   (b) CH_3COCH subgroup

Figure 5. Examples of subgroup assignments for the ketone group, illustrated by opened surfaces.

The need to create groups more strictly neutral can lead to a large number of groups. For the ketone case, there are ten different combinations CH_3COCH_3, CH_3COCH_2, CH_3COCH, etc. Thus, in order to reduce the number of parameters, we have assumed that these different combinations are *subgroups* of a common group. By making all subgroups have identical electrostatic parameters (Q_k^+, Q_k^-, and σ_k^+), the number of parameters can be strongly reduced. Then, in the present proposal, each subgroup will differ only in terms of total area Q_k and volume R_k, hence they will also differ in the neutral area $Q_k^\circ = Q_k - Q_k^+ - Q_k^-$.

The molecule fragmentation can get more complex when two or more nonhydrocarbon groups are too close. In these cases an interaction between the functional groups apparent surface charges will raise and a less comprehensive group, comprising the interacting chemical functions, needs to be created. This is the case of triacetin and diethyl phthalate shown in Figure 6, where the ester group COO is too close to another COO. This interaction affects the σ-profile, as can be seen in Figure 7, and cannot be properly taken into account by simply adding single COO groups. For this and other similar cases, a new group was created.

Further, as suggested by Wu and Sandler,[7] the geometry of a functional group should be the same regardless the molecules in which the group occurs. It is clear that a cyclic ester, Figure 6c, has different bond angles when compared to a linear one, Figure 6d. Thus, different groups are needed to distinguish between linear and cyclic molecules. For instance, for γ-butyrolactone, a new specific group was added.

A similar procedure was carried out to identify all the other groups and subgroups, introduced in the next section. By following this procedure, a larger number of subgroups is needed when compared with UNIFAC models. However, as the group parameters are computed for pure groups instead of pairwise, the total number of parameters of the F-SAC model is still smaller.

■ RESULTS AND DISCUSSION

In the present work, the group selection procedure introduced in the previous section was used to identify and calibrate the
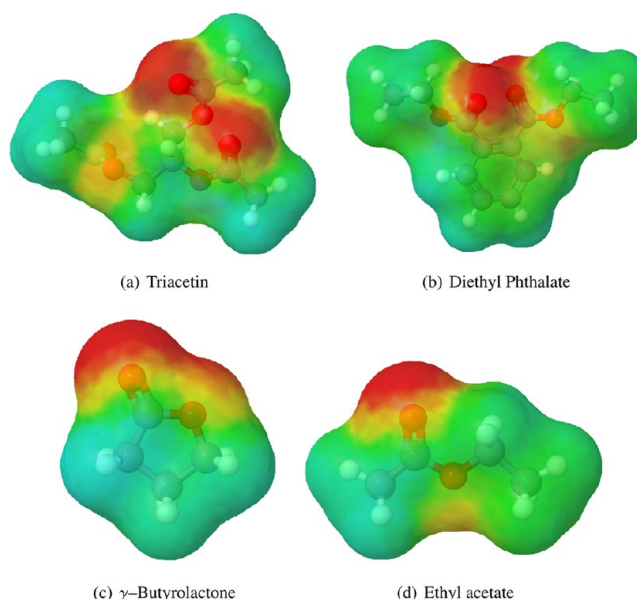

(a) Triacetin   (b) Diethyl Phthalate

(c) γ–Butyrolactone   (d) Ethyl acetate

Figure 6. Differences of several configurations of the ester group showing the need for different groups.

parameter for 21 functional groups and 43 subgroups. Group assignment examples can be found for nearly 200 molecules in the Supporting Information as well as in the demonstration FORTRAN code. The calibrated model correlations for IDAC were then compared with the UNIFAC (Do) (parameter matrix available in the literature[33]) and COSMO-SAC (σ-profiles and parameters determined in a previous work[10]) models for nearly 1400 mixtures at different temperatures (250 to 450 K). The predictive strength of the model was assessed by comparison with vapor−liquid equilibrium data, that was not considered in the model fitting process.

Parameter Calibration. In order to estimate the F-SAC group parameters (Q_k^+, Q_k^-, σ_k^+, and Q_k), a previously assembled infinite-dilution activity coefficient (IDAC) experimental database[10] was used. Unlike the work of Mu et al.,[31,32] that used a group contribution method to reproduce the results of COSMO calculations, in the present work the F-SAC energetic model parameters were calibrated directly with IDAC experimental data.

It should noted that the residual contribution assumed for the model proposed here is identical to the one used by COSMO-SAC models and is given by the difference between the free energy in solution and in pure liquid, eq 10. The difference between solution and pure liquid is more important than absolute values, and this can lead to multiple solutions of the parameter estimation problem. In order to circumvent this problem, the electrostatic parameters of the CH_2 group were fixed as being completely apolar ($Q_k^+ = Q_k^- = 0$). This is also in agreement with the general assumption that interaction parameters between alkane groups (CH_3, CH_2, CH, and C) are zero.[36]

With the electrostatic parameters of the CH_2 group set, the area (Q_k) parameters obtained from COSMO cavities of sample molecules were further optimized for the CH_2 subgroups (CH_3,CH_2, etc.) by using the data set of athermal mixtures studied by Soares.[22] The resulting values can be seen in Table 1. Note the negative area values for the subgroups CH and C. Similar behavior was also observed in the group contribution method of Tihic et al.,[37] explained here by taking the example
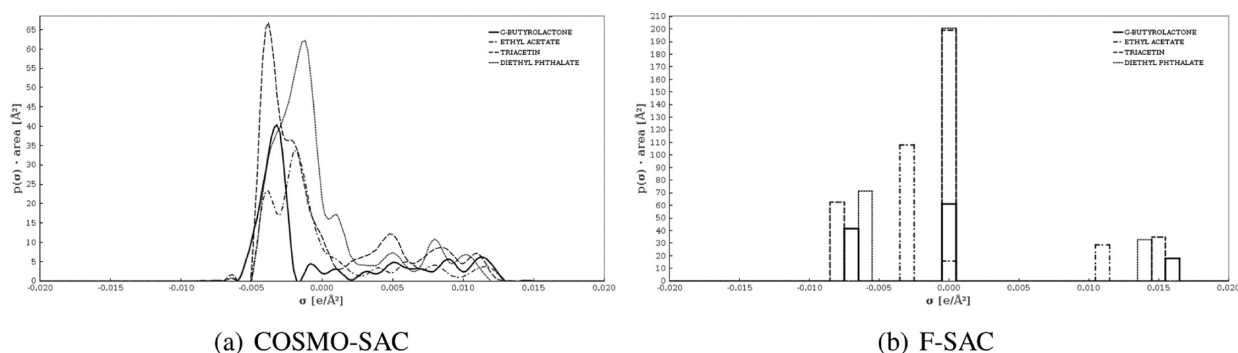
(a) COSMO-SAC (b) F-SAC

Figure 7. σ-Profile of different esters for (a) COSMO-SAC[10] and (b) F-SAC.

Table 1. F-SAC Subgroup Volume (R_k) and Area (Q_k) Parameters Determined in This Work[a]

group	subgroup	$R_k/\text{Å}^3$	$Q_k/\text{Å}^2$	group	subgroup	$R_k/\text{Å}^3$	$Q_k/\text{Å}^2$
CH_2	CH_3	31.91	46.689	triacetin	triacetin	278.61	296.41
	CH_2	24.54	24.639	GBLactone	GBLactone	112.74	120.60
	CH	14.03	−0.53	CH_3COOCH_3	CH_3COOCH_3	103.98	143.72
	C	6.53	−20.88		CH_3COOCH_2	96.61	107.86
	c-CH_2	24.12	27.00		CH_3COOCH	88.27	95.89
	c-CH	16.21	5.47		CH_2COOCH_2	89.24	96.93
C=C	CH_2=CH	48.16	59.52	phthalate	phthalate	228.61	207.91
	CH=CH	36.86	33.33	CH_2COOAC_3	CH_2COOAC_3	120.93	95.94
	CH_2=C	38.52	33.38	CH_3OCH_2	CH_3OCH_3	77.1	103.58
	CH=C	28.54	11.59		CH_3OCH_2	63.03	62.75
	c-CH=CH	36.86	51.45		CH_3OC	52.26	31.42
ACH	ACH	19.26	20.11		CH_2OCH_2	55.66	56.09
	AC	10.89	1.76		CHOCH	44.83	10.12
CH_3COCH_3	CH_3COCH_3	92.62	122.37	c-CH_2OCH_2	c-CH_2OCH_2	55.66	52.13
	CH_3COCH_2	85.04	90.18	$N(CH_2)_3$	$N(CH_2)_3$	55.65	35.64
	CH_3COCH	78.44	68.92	DMSO	DMSO	102.83	99.04
	CH_2COCH_2	77.35	66.27	CH_2Cl	CH_2Cl	55.24	58.08
	CH_2COCH	69.37	27.33	CCl_4	CCl_4	129.47	138.83
CH_2CHO	CH_3CHO	69.23	90.533	$CH3CCl_3$	CH_3CCl_3	131.4	146.92
	CH_2CHO	61.86	67.25	$ClAC_3$	$ClAC_3$	79.94	76.57
CH_3COAC_3	CH_3COAC_3	105.83	105.66	$CHCl_3$	$CHCl_3$	108.67	114.25
c-CH_2COCH_2	c-CH_2COCH_2	77.35	77.88				

[a]The area parameters were optimized.

Table 2. F-SAC Group Electrostatic Parameters Determined in This Work[a]

group	$Q_k^+/\text{Å}^2$	$Q_k^-/\text{Å}^2$	$\sigma_k^+/e/\text{Å}^2$	group	$Q_k^+/\text{Å}^2$	$Q_k^-/\text{Å}^2$	$\sigma_k^+/e/\text{Å}^2$
CH_2	0.00	0.00	0.0000	CH_2COOAC_3	12.59	64.23	0.0158
C=C	6.16	3.70	0.0050	CH_3OCH_2	13.01	22.71	0.0091
ACH	5.38	6.71	0.0056	c-CH_2OCH_2	8.12	27.20	0.0143
CH_3COCH_3	21.97	80.23	0.0133	$N(CH_2)_3$	3.60	28.58	0.0175
CH_2CHO	14.85	81.88	0.0172	DMSO	11.36	22.84	0.0188
CH_3COAC_3	9.56	16.68	0.0162	CH_2Cl	9.30	9.07	0.0089
c-CH_2COCH_2	13.93	42.78	0.0166	CCl_4	18.40	26.23	0.0062
CH_3COOCH_3	28.94	107.69	0.0109	CH_3CCl_3	40.07	20.28	0.0039
triacetin	34.68	62.83	0.0146	$CHCl_3$	43.32	14.76	0.0035
GBLactone	18.05	41.30	0.0161	$ClAC_3$	37.41	12.13	0.0026
phthalate	33.60	69.26	0.0132				

[a]CH_2 parameters were chosen as a reference.

of isobutane. This molecule has 3 CH_3 and 1 C subgroup but has a small surface area, when compared to another molecules with several CH_3 or CH_2 subgroups. Then, in order to counterbalance the smaller area present in molecules with the CH and C subgroups, negative areas are needed. Similarly for the subgroup volumes, but positive values were still obtained.

The other electrostatic parameters in Table 2 were obtained by the sequential addition of new groups, starting from the reference values for CH_2. The Q_k of all the other subgroups were also considered in the estimation procedure, and the resulting values can be found in Table 1.

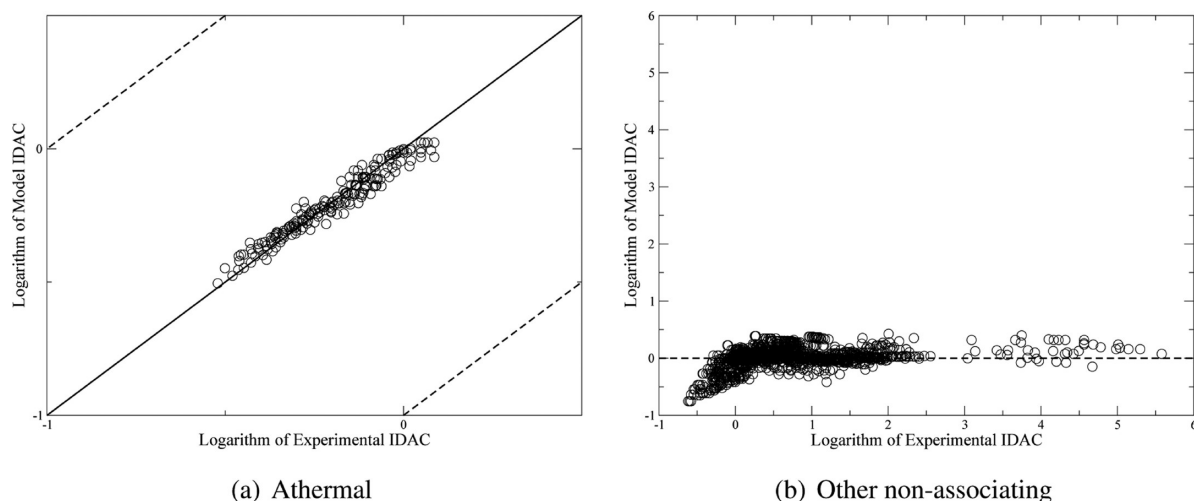(a) Athermal

(b) Other non-associating

Figure 8. Logarithm of experimental IDAC versus logarithm of the F-SAC combinatorial contribution eq 2 for (a) athermal mixtures, (b) other nonassociating mixtures.
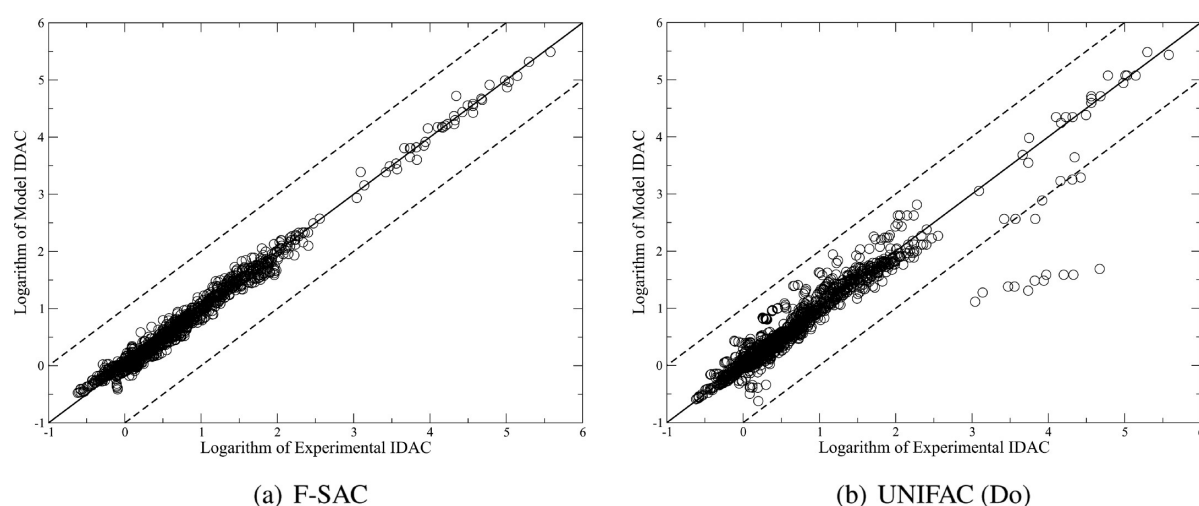

(a) F-SAC

(b) UNIFAC (Do)

Figure 9. Logarithm of experimental IDAC versus logarithm of model IDAC of 1390 data points for (a) F-SAC and (b) UNIFAC (Do).

Since the model considered is highly nonlinear, the parameter estimation problem is expected to show multiple minima. Thus, for each new group added, a *dividing rectangles* global optimization algorithm was first executed.[38] The best solution found by the global search was refined by a direct search method.[39] When necessary, after the addition of a new group, the parameters of the previously added groups, except the hydrocarbons, were recalibrated by the local search method.

For the 21 groups and 43 subgroups considered, a total of 103 parameters were calibrated. The electrostatic parameters for the hydrocarbon group were fixed as a reference and the area and volume parameters of subgroups were directly obtained by differences in area and volume of COSMO cavities of some sample molecules, with the areas being further refined in the parameter estimation procedure. In order to represent the same amount of molecules (used in the F-SAC parameter estimation) with the modified UNIFAC (Do) model, 18 groups and 31 subgroups were necessary. However, for these 18 groups, the binary interaction parameter matrices have 510 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 sound physical meaning and the interaction energies, given by eq 13, are symmetrical.

Combinatorial Contribution. According to Fredenslund and Rasmussen,[40] the Staverman−Guggenhein term (which is included in the proposed method) gives only a small contribution to the activity coefficients when *realistic* area and volume values are used. While *artificial* values can greatly improve the correlation of some VLE data, they can lead to a combinatorial contribution at infinite dilution much larger than unity ($\ln \gamma_i^{comb}$ larger than zero). In the work of Abildskov et al.,[41] the authors list several mixtures for which adjusted geometry parameters have led to very large combinatorial contributions.

In Figure 8, the F-SAC combinatorial contribution, eq 2, was evaluated for all mixtures studied in this work using the area and volume parameters shown in Table 1.

The experimental data set of Figure 8a is the same studied previously by Soares,[22] for athermal mixtures. This database contains IDAC experimental data for linear and branched alkanes ranging from C_4 to C_{36}, which assures a variety of dissimilarities in size and shape. For these mixtures, the F-SAC residual contribution is zero and the combinatorial contribution alone agrees very well with experimental data. For all other
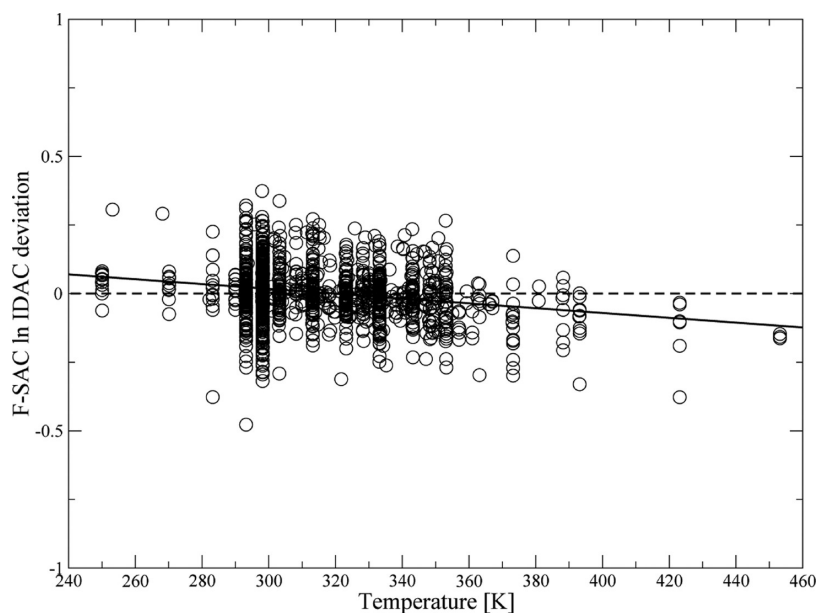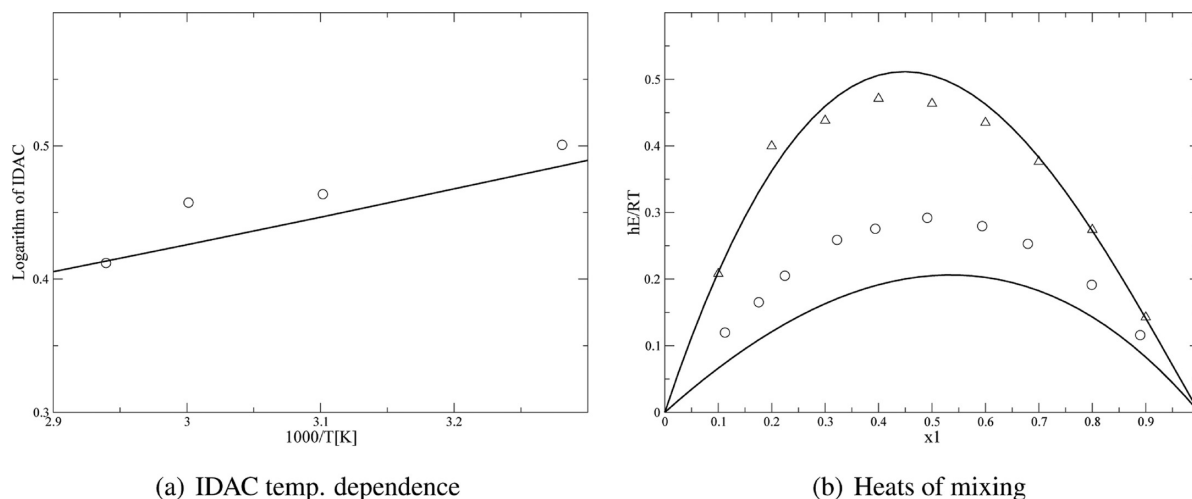
Figure 10. F-SAC IDAC deviation as a function of temperature along with a linear fit (solid line).

(a) IDAC temp. dependence

(b) Heats of mixing

Figure 11. (a) IDAC for the mixture tetrahydrofuran/*n*-hexane as a function of temperature. (b) Heats of mixing for acetone/cyclohexane (exp. data from Campbel and Anand[42]—triangles) and for tetrahydrofuran/*n*-hexane (exp. data from Gmehling et al.[43]—circles). Solid lines are the F-SAC predictions.

mixtures present in the data set studied in this work, the combinatorial contribution alone is shown in Figure 8b. As can be seen, the combinatorial contribution never exceeds 0.5 ln units and very large values were not observed. This is probably because we are not adjusting the volume parameters and only small corrections were made to the area parameters.

However, even small positive values of $\ln \gamma_i^{comb}$ can be taken as unrealistic, and the model can be improved in this sense. Further, we should note that free-volume differences are being neglected. Then, poor results are expected if the present formulation is applied without modification for polymer/solvent systems.

IDAC Comparison. The calibrated model correlations were compared with a UNIFAC (Do) model implementation using a parameter matrix from the literature[33] and with a COSMO-SAC model previously calibrated[10] with the same IDAC database used to fit the F-SAC parameters. The comparison was made through the absolute average deviation (AAD) for

1390 experimental data of IDAC from mixtures at different temperatures, defined as:

$$AAD = \frac{1}{NP} \sum_i |\ln \gamma_{i,exp}^\infty - \ln \gamma_{i,model}^\infty| \tag{14}$$

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

The F-SAC fit quality is shown in Figure 9a. As can be seen in this figure, for the experimental data considered, the F-SAC model showed a very good fit, with AAD equals to 0.073. Predictions with UNIFAC (Do) resulted in a deviation of 0.14, results in Figure 9b.

In a previous work,[10] using the same IDAC database for model calibration, we have obtained a deviation of 0.22 for COSMO-SAC. 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 mixtures involving cyclic
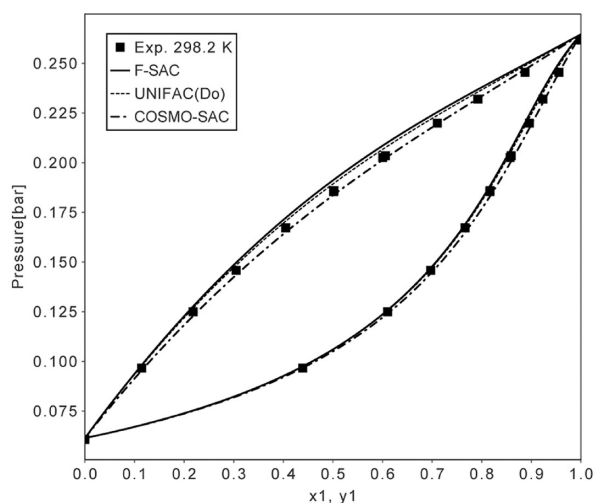
(a) Chloroform/n-heptane at 298 K, experimental data from Bissell and Williamson [47].
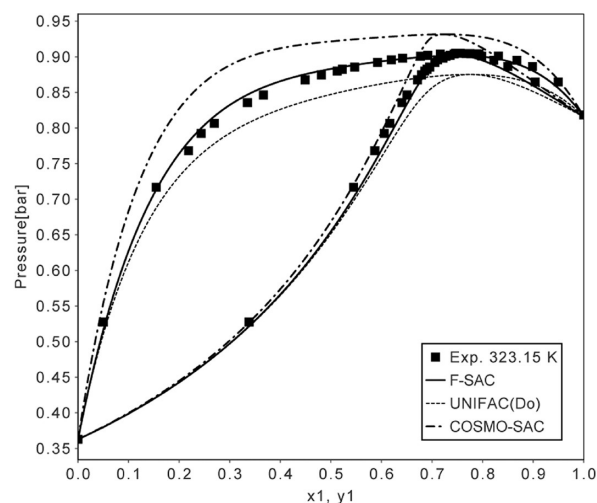
(b) Acetone/cyclohexane at 323 K, experimental data from Colin et al. [48].

Figure 12. F-SAC and UNIFAC (Do) VLE predictions for mixtures with IDAC values considered in the F-SAC fit.

esters stands out negatively,[10] for which the standard ester group was used.

IDAC Temperature Dependence and Heats of Mixing.
A perfect statistical model should be able to express the free energy and the functions derived therefrom in terms of temperature-independent parameters.[6] Although the parameters of the F-SAC model are temperature independent, the formulation inherited from the COSMO-RS theory, eq 12, naturally introduces temperature effects in the residual part. The IDAC database used for the F-SAC parameter estimation covers a wide range of temperatures (250−453 K). The model deviations (ln $\gamma^{\infty}_{i,\exp}$ − ln$\gamma^{\infty}_{i,\text{calc}}$) are shown in Figure 10 as a function of the temperature.

The linear fit (solid line in Figure 10) suggests a small systematic error, with activity coefficients at higher temperatures being larger than the experimental ones. The introduction of some universal parameter in eq 13 might remedy this effect. However, the correlation coefficient of the linear fit in Figure 10 was only 0.044 indicating that only a small percentage of the deviations can be explained by the temperature. Thus, refinements on the temperature dependence are left for future work.

In order to supplement the general results shown in Figure 10, some illustrative applications are also presented in this section. First, IDAC data for mixtures of tetrahydrofuran diluted in n-hexane were selected in temperatures ranging from 304 to 340 K. As can be seen in Figure 11a, the general temperature trend was followed by the model.

In Figure 11b, heats of mixing are compared for the acetone/cyclohexane and tetrahydrofuran/n-hexane systems. As can be seen, for the first case the heats of mixing were slightly overestimated while for the second case they were underestimated by the model. Actually, an extensive study is needed in order to elucidate if the current F-SAC temperature dependence is already suitable for nonassociating mixtures or if additional parameters will be needed for precise prediction of heats of mixing. In general, activity coefficients decay with temperature for simple mixtures but much more complex behavior is observed for associating mixtures. According to Constantinescu et al.,[44] neither UNIFAC nor some COSMO-

RS variants were able to describe the change of excess enthalpy with temperature, which was observed especially in mixtures containing hydrogen bonding components.

Nevertheless, even for simple mixtures there is room for improvement in the proposed model. For instance, in the present work we have considered cyclic alkanes as a subgroup of the alkanes group (CH_2). In this case, the F-SAC heat of mixing will be zero for alkane/cyclic alkane mixtures while there is an appreciable heat of mixing for the n-hexane/cyclohexane mixture.[45]

VLE Prediction. It is worth mentioning that all experimental data presented in Figure 9 were considered in the F-SAC fit. A much larger experimental database would be necessary for assessing the predictive strength of all groups by means of separate fit and test sets. Thus, in order to verify the prediction strength of the F-SAC method we have selected some vapor−liquid equilibrium (VLE) data which were not considered in the fit. Similar tests were accomplished by Bastos et al.[46] 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 nonassociating mixtures.

In order to evaluate the performance of the F-SAC model alone, only low to moderate pressure experiments were considered, enabling the use of the modified Raoult's law. For the pure compound vapor pressures, correlations freely available in the literature were used. Bubble point deviations in pressure and vapor phase composition were computed as

$$\Delta P\% = \frac{100}{\text{NP}} \sum_{i}^{\text{NP}} \frac{|P_{i,\exp} - P_{i,\text{model}}|}{P_{i,\exp}} \tag{15}$$

$$\Delta y\% = \frac{100}{\text{NP}} \sum_{i}^{\text{NP}} |y_{i,\exp} - y_{i,\text{model}}| \tag{16}$$

First, we have selected VLE data of mixtures included in our IDAC database and some results are depicted in Figure 12. Results for this class of data were referred as type 1 in Table 3. Taking the results in Figure 12 as example, the experimental database contains data points for chloroform/n-heptane at 293

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dx.doi.org/10.1021/ie400170a | *Ind. Eng. Chem. Res.* 2013, 52, 11159−11171

Table 3. Deviations in the F-SAC Predictions of VLE, Categorized by IDAC Data Used in the Model Fitting Process

type	description	N_{VLE}	NP	$\Delta P\%$	$\Delta y\%$
1	IDAC of mixture	41	674	1.35	0.53
2	no IDAC data for the specific mixture	30	483	1.37	0.78
3	no IDAC data for group interaction	6	85	2.08	0.83
4	no IDAC data for compound	9	138	1.47	0.48
total		86	1318	1.57	0.88

and 323 K while the VLE data was measured at 298 K. Similarly, one IDAC experimental for cyclohexane/acetone at 298 K was considered in the F-SAC fitting procedure.

As can be seen in Figure 12, finite dilutions were well-predicted by the F-SAC model calibrated solely with infinite dilution data. Similar results were observed with UNIFAC (Do) and COSMO-SAC, but with larger deviations for the acetone/cyclohexane system.

As a second test set (type 2 in Table 3), VLE data for mixtures not included in the IDAC database were selected. For instance, for the mixture benzene/n-decane, the IDAC database contains IDAC data for benzene in several linear hydrocarbons and *vice versa*, but no data for the particular mixture of benzene/n-decane. As can be seen in Figure 13a, very good agreement with experimental data was obtained for this system. The experimental database also contains several IDAC experimental points for hydrocarbons in n-butyl acetate, but no data is available for the n-heptane/n-butyl acetate mixture. Predictions for this mixture is in good agreement with experimental data, as shown in Figure 13b. The results with UNIFAC (Do) were also in good agreement with experimental data for these tests. Again, the COSMO-SAC model provided larger deviations.

Predictions for alkene/ether and alkene/ester mixtures are shown in Figure 14. An interesting aspect in these results is that the IDAC database, considered in the model fit, contains no data for these families in mixture (type 3 in Table 3). Nevertheless, the F-SAC model predicted with good accuracy nearly ideal systems (Figure 14a) as well as azeotropic mixtures

(Figure 14b). For the azeotropic mixture, UNIFAC (Do) showed a small deviation from the experimental data while the COSMO-SAC implementation provided large deviations.

Finally, some VLE data for mixtures with substances not considered in the fit were selected (type 4 in Table 3). For instance, the IDAC database contains no data for isobutyraldehyde (there is data for other aldehydes), and predictions of the VLE for the isobutyraldehyde/n-heptane are shown in Figure 15a. The same is valid for methyl n-butyl ether (there is data for other ethers), with results depicted in Figure 15b. Again, good results were obtained with F-SAC. The small deviation for the isobutyraldehyde system is caused by a poor pure component vapor pressure calculation.

The results were also summarized in Table 3. As can be seen, the predictions were similar regardless the IDAC data availability, indicating a good prediction capability for the proposed model. Detailed results for the VLE prediction are also available as Supporting Information.

Table 4 shows an overall comparison of F-SAC results with UNIFAC (Do) and COSMO-SAC. For the VLE studied, F-SAC performed as well as or better than UNIFAC (Do). It is important to recall that the F-SAC model was calibrated solely based on infinite dilution data. A better performance would be obtained if other kinds of experimental data (e.g., VLE, h^E, azeotropic composition) were used in the parameter fitting procedure. As expected, COSMO-SAC presented the worst results when compared with the other models.

■ CONCLUSIONS

In this paper, a new activity coefficient model was suggested, here called F-SAC (functional-segment activity coefficient). This method is based on group contributions, such as UNIFAC, but the energetic interactions come from a theory of contacting surface segments, similar to the COSMO-RS variation known as COSMO-SAC.

In the F-SAC method, each functional group is described by only three *electrostatic* parameters—in contrast to molecular (or functional) pairwise parameters. Therefore, the proposed model can be genuinely predictive since it is able, in principle, to compute the behavior of mixtures with functional groups never experienced together. For the 21 groups and 43
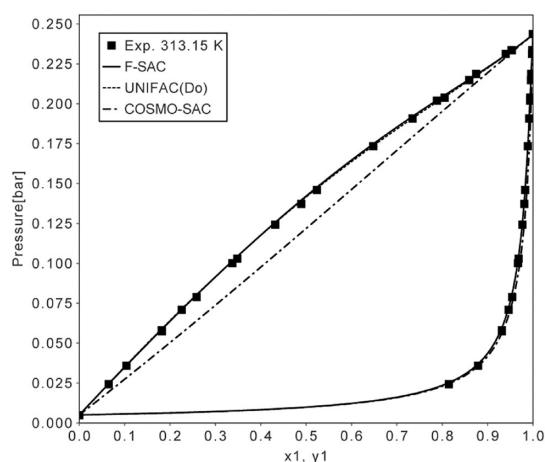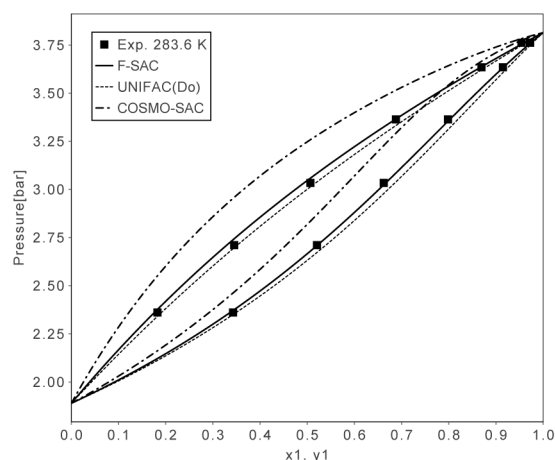

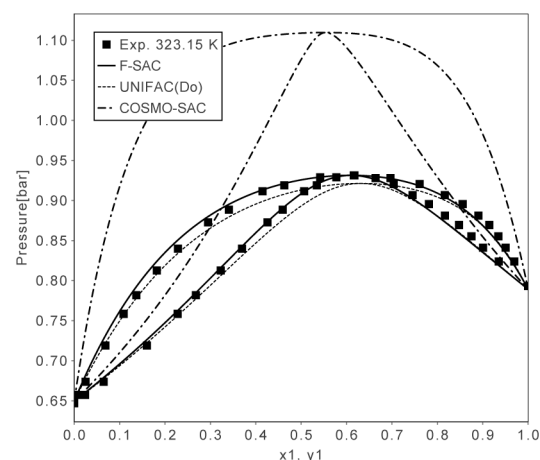(a) Benzene/n-decane at 313 K, experimental data from Góral[49].
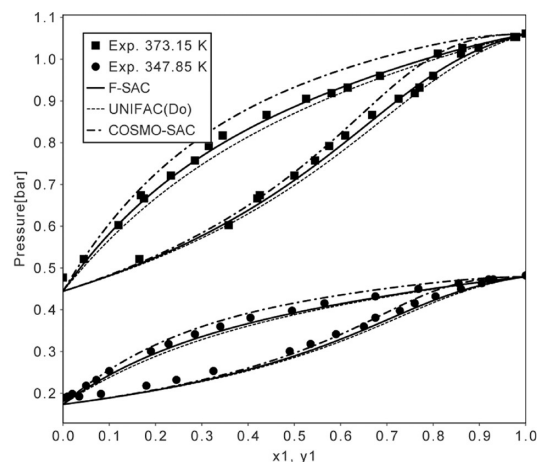
(b) n-heptane/butyl acetate at 347 K and 373 K, experimental data from Scheller et al.[50].

Figure 13. F-SAC and UNIFAC (Do) VLE predictions for mixtures not considered in the F-SAC parameter fit.
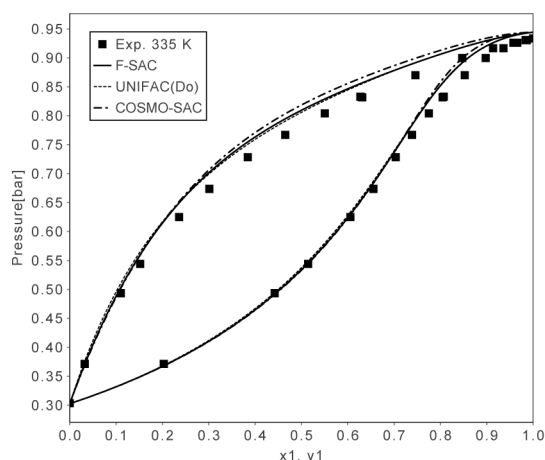
(a) Dimethyl ether/1-butene at 283 K, experimental data from de Fernandez et al.[51].

(b) Methyl acetate/1-hexene at 323 K, experimental data from Gmehling[52].

Figure 14. F-SAC and UNIFAC (Do) VLE predictions for mixtures of functional groups with no IDAC considered in the F-SAC parameter fit.

(a) Isobutyraldehyde/n-heptane acetate at 335 K, experimental data from Shealy and Sandler[53].
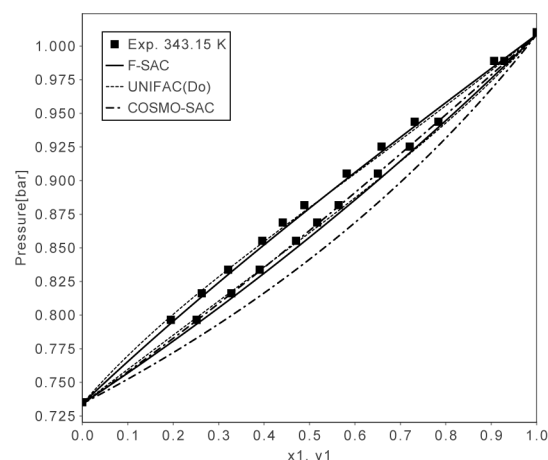
(b) Methyl n-butyl ether/benzene at 343 K, experimental data from Treszczanowicz and Lu[54].

Figure 15. F-SAC and UNIFAC (Do) VLE predictions for substances not considered the F-SAC fit.

Table 4. Deviations of 67 Different VLE with 997 Data Points for F-SAC, UNIFAC (Do), and COSMO-SAC Models

	$\Delta P\%$		$\Delta y\%$	
	mean	max	mean	max
F-SAC	1.42	4.51	0.63	4.22
UNIFAC (Do)[33]	1.46	4.15	0.64	4.28
COSMO-SAC[10]	7.85	137.7	1.27	7.35

subgroups considered, only 103 parameters were calibrated (electrostatic parameters for the CH_2 group were fixed as a reference and volume parameters were directly determined by COSMO cavities). In order to represent the same amount of substances studied in this work with the UNIFAC (Do) model, 18 groups and 31 subgroups were used. However, for these 18 groups, the UNIFAC (Do) interaction parameter matrices have 510 nonzero elements. Clearly, when using the proposed model, new specific and less comprehensive groups can be added much less costly and with a reduced need for experimental data.

In the present study, the F-SAC parameters were fit solely based on infinite dilution activity coefficient (IDAC) data available in the literature. The calibrated model was compared with UNIFAC (Do) and COSMO-SAC implementations by the IDAC deviation average in ln units for nearly 1400 mixtures at different temperatures (250−450 K). Only non-hydrogen bonding mixtures were investigated, associating mixtures are studied in an accompanying paper. For the data considered, the F-SAC model showed a very good fit, with an average deviation of 0.073 ln units. For this data set, the UNIFAC (Do) and COSMO-SAC deviated from experimental values by 0.14 and 0.22, respectively.

While IDAC data was used for calibrating the proposed model, the prediction strength was assessed by using vapor−liquid equilibria (VLE) data. Very good agreement with experimental data was possible in the entire composition range, as well as in the prediction of azeotropes. The deviation in the pressure and vapor phase compositions were 1.42% and 0.63%, respectively, against 1.46% and 0.64% for UNIFAC (Do). This outcome is particularly interesting because no VLE data was considered in the model fitting procedure. Good

results were obtained even for molecules not included in the fitting data set illustrating the potential of the proposed model.

At present, the number of F-SAC functional groups is being expanded. 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 equations of state and Gibbs excess mixing rules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Sample group assignments as well as detailed VLE results. This information is available free of charge via the Internet at http://pubs.acs.org/. Demonstration FORTRAN code for the F-SAC method is freely available via Internet at http://www.enq.ufrgs.br/labs/lvpp/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rafael@enq.ufrgs.br. Phone: +55 51 33083528. Fax: +55 51 33083277.

Notes

The authors declare no competing financial interest.

■ LIST OF SYMBOLS

α' = constant for the misfit energy, kcal Å^4/(mol e^2)
$\Delta W(\sigma_m, \sigma_n)$ = total energy for the pair $\sigma_m-\sigma_n$, kcal/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 the 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 $\sigma_m-\sigma_n$, kcal/mol
F_i = surface area fraction
$p(\sigma)$ = sigma profile of a mixture
$p_i(\sigma)$ = σ-profile of molecule i
$p_k(\sigma)$ = σ-profile of functional group k
q = universal normalization area parameter, Å^2
Q_i = surface area of molecule i, Å^2
q_i = total surface area of molecule of type i, Å^2
Q_k = surface area of subgroup k, 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° = absolute neutral area of the functional group k, Å^2
R = ideal gas constant kcal/(mol K)
r_i = total volume of molecule of type i, Å^3
R_k = volume of subgroup k, Å^3
V_i = volume fraction
x_i = mole fraction of component i in solution

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on April 17, 2013, with errors in Figure 9. The corrected version was reposted on May 2, 2013.

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dx.doi.org/10.1021/ie400170a | *Ind. Eng. Chem. Res.* 2013, 52, 11159−11171