

Considering the dispersive interactions in the COSMO-SAC model for more accurate predictions of fluid phase behavior

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Abstract

A term to consider the contribution of the dispersive interactions to the non-ideality of mixtures is introduced into the COSMO-SAC model on the basis of molecular simulation data from classical model force fields. This dispersion term is a one-constant Margules equation, where the constant is determined from the molecular dispersion parameter of the components. Furthermore, an atomic contribution method is proposed to calculate the dispersion parameter for a given molecule. For binary systems containing molecules consisting of C, H, N, O, F and Cl atoms, a total of 13 global parameters is introduced with the COSMO-SAC-dsp model. These parameters are obtained from regression to a large training set of binary vapor-liquid equilibrium (VLE) data from experiment. The overall deviations for VLE calculations on this training set are reduced by 25% in terms of the vapor pressure and 12% in terms of the vapor phase mole fraction. This dispersion term can provide a significant improvement for infinite dilution activity coefficient predictions, where the accuracy was increased by around 33%.

Keywords: Phase equilibria, infinite dilution activity coefficient, prediction, dispersive interaction, COSMO-SAC

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Highlights

- A dispersion contribution to the activity coefficient calculation is introduced into the COSMO-SAC model
- This contribution is based on molecular simulation data for classical model force fields
- All parameters in the proposed term are adjustment to VLE data and the overall deviations are reduced by 25% in terms of the vapor pressure and 12% in terms of the vapor phase mole fraction
- The accuracy of infinite dilution activity coefficient predictions is improved significantly, the overall deviation is reduced by about 33%

1. Introduction

Information on the distribution of chemical species between coexisting phases is of fundamental importance in the chemical industry, environmental engineering and the pharmaceutical industry [1-5]. While such information can be obtained from experimental work, it is crucial to have reliable predictive thermodynamic models because of the significant time and cost associated with measuring experimental data. Many researchers have thus expended significant efforts in establishing methods to predict the thermodynamic properties and the phase behavior of pure fluids and mixtures [3-6].

Due to the advances in computing power, methodological efficiency and the development of accurate force fields (which describe the inter- and intramolecular interactions), numerical simulation methods (Monte Carlo or molecular dynamics) can be used to study many different problems, including the estimation of thermophysical properties and phase equilibria [6-10]. Molecular simulation methods are applicable with very few constraints, as both equilibrium or non-equilibrium conditions can be studied and both static and dynamic thermodynamic data can be sampled [11]. Furthermore, with a good description of the molecular interactions through force fields, molecular simulation can provide very accurate predictions of the thermophysical properties including phase equilibria for pure fluids and mixtures. In addition to accurate results, molecular simulation also provides an insight into the mechanisms on the microscopic level and detailed information about the effect of different interactions. However, such simulations require a large computational effort (which translates to hours for a typical vapor-liquid equilibrium state point on today's computer equipment) to obtain results [12].

The scope of predictive thermodynamic models can range from simple cubic

equations of state (EOS), excess Gibbs energy (G^{ex}) models, and their combinations through G^{ex} -based mixing rules [3-5]. Through research over the past two decades, a new class of predictive methods has emerged that utilizes the results from computational chemistry. These COSMO-based methods (such as COSMO-RS [13-15] and its variants COSMO-SAC [16-19], COSMO-RS(OI) [20] or COSMO-vac [21]), determine the liquid-phase non-ideality on the basis of the molecular surface charge distribution derived from first-principles solvation calculations [22,23]. This type of models does not contain any species-dependent parameters and fluid phase equilibria can be predicted with the molecular structure as the only input. Thus, COSMO-based methods do not suffer from the problem of missing parameters. With the advantage of relying only on a few global and atomic parameters, these methods have become more important and are broadly applied to the prediction of the thermophysical properties and the phase behavior of pure fluids and mixtures [1,24]. With a combination of cubic EOS and G^{ex} -based mixing rules, the application of COSMO-based models can be extended to high pressure systems including supercritical fluids [25-30]. In preceding works, the electrostatic interactions of the COSMO-SAC model were revised to provide good predictions for phase equilibria of organic mixtures [19,31]. However, the neglect of the dispersive interactions in activity coefficient calculation for mixtures remains unsolved in the COSMO-based models.

The dispersive interaction is the most general attractive intermolecular interaction in the condensed phase. It is caused by spontaneous temporary polarities in individual molecules that polarize their neighbors. The net effect of dispersive interactions is a short-range and weak attraction (compared with other molecular interactions) which, however, dominates in non-polar liquids. This interaction is expressed as a function of molecular properties (e.g., exposed surface area or surface tension) in some

thermodynamic models [13,32-34], whereas the composition of the solutes and solvents is taken into account in other thermodynamic models [35]. In the COSMO-based methods, the dispersive interaction is considered as the function of exposed surface area and atomic type of surface segments. Furthermore, this interaction is taken into account only for the determination of vaporization data (such as vapor pressure or enthalpy of vaporization of pure fluids) [16,17,36]. For mixtures, dispersive interaction was neglected until now in the development of the COSMO-SAC model [16]. In this study, a new dispersion term to consider the contribution of the dispersive interaction to the non-ideality of mixtures is introduced into the COSMO-SAC model on the basis of molecular simulation data from classical model force fields. It is termed COSMO-SAC-dsp model.

2. COSMO-SAC model

In the original publication of the COSMO-SAC model [18], the activity coefficient of molecule i in mixture S can be determined from

$$\ln \gamma_{i/S} = \frac{\Delta G_{i/S}^{*chg} - \Delta G_{i/i}^{*chg}}{RT} + \ln \gamma_{i/S}^{SG}, \quad (1)$$

where $\Delta G_{i/j}^{*chg}$ is the solvation charging Gibbs energy of molecule i in solvent j ($j=i$ for pure solvent i and $j=S$ for mixture S). The Staverman-Guggenheim (SG) combinatorial term [37,38] was used to consider molecular size and shape effects

$$\ln \gamma_{i/S}^{SG} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j, \quad (2)$$

with $\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$, $\phi_i = \frac{x_i r_i}{\sum_j x_j r_j}$, $l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1)$, where $z = 10$ is the

coordination number, while q_i and r_i are the normalized surface area and volume of component i (the standard surface area and volume for normalization were 79.53 \AA^2 and 66.69 \AA^3).

According to Ben-Naim's definition [39], the solvation Gibbs energy ΔG^{*sol} is the Gibbs energy difference of a molecule (solute) in its ideal gas phase state and in a real solution (solvent) at the same temperature and pressure. The solvation Gibbs energy is usually determined from two contributions: cavity formation Gibbs energy ΔG^{*cav} and charging Gibbs energy ΔG^{*chg} . These are based on a hypothetical solvation process: first, a hard solute molecule is inserted into the solvent and then the interactions between solute and solvent are turned on. According to the previously developed solvation model [17,33,40-42], the charging Gibbs energy of solute i in the mixture solvent S is calculated from four Gibbs energy contributions: ideal solvation (is), charging-averaging correction (cc), restoring (rst) and dispersion (dsp)

$$\Delta G_{i/S}^{*chg} = \Delta G_i^{*is} + \Delta G_i^{*cc} + \Delta G_{i/S}^{*rst} + \Delta G_{i/S}^{*dsp} \quad (3)$$

ΔG_i^{*is} accounts for the energy difference of molecule i in the ideal conductor and in the ideal gas state. ΔG_i^{*cc} considers the energy shift due to the charge-averaging process for the molecule. The charge-averaging correction is required because pairwise interactions between independent segments are assumed in the COSMO-SAC model [17,18]. Since these two terms are obtained from quantum mechanical calculations considering only molecule i , they are pure component properties and cancel out in the activity coefficient calculation. Then, Eq. (1) becomes

$$\begin{aligned} \ln \gamma_{i/S} &= \frac{\Delta G_{i/S}^{*rst} - \Delta G_{i/i}^{*rst}}{RT} + \frac{\Delta G_{i/S}^{*dsp} - \Delta G_{i/i}^{*dsp}}{RT} + \ln \gamma_{i/S}^{SG} \quad , \\ &= \ln \gamma_{i/S}^{res} + \ln \gamma_{i/S}^{dsp} + \ln \gamma_{i/S}^{SG} \quad . \end{aligned} \quad (4)$$

The residual term $\ln \gamma_{i/S}^{res}$ mainly considers the permanent electrostatic interactions between molecules in the mixture and is obtained by

$$\ln \gamma_{i/S}^{res} = \frac{\Delta G_{i/S}^{*rst} - \Delta G_{i/i}^{*rst}}{RT} = \frac{A_i}{a_{eff}} \sum_t \sum_{\sigma_m} p_i^t(\sigma_m^t) \ln [\Gamma_{i/S}^t(\sigma_m^t) - \Gamma_{i/i}^t(\sigma_m^t)], \quad (5)$$

where A_i is the molecular surface area and a_{eff} is the surface area of a standard surface segment. The σ -profile $p_i(\sigma_m)$ is a histogram of surface area normalized by molecular surface area with a screening charge density of σ_m for molecule i . In the COSMO-SAC model, for a better description of the hydrogen-bonding (hb) interactions, the molecular surface segments are categorized into three types: non-hydrogen-bonding (nhb), hydroxyl groups (OH) and other hydrogen bonding groups (OT), i.e. O, N, F and H bound to N and F. Therefore, the σ -profile of molecule i is the summation of these three contributions, $p_i(\sigma) = p_i^{nhb}(\sigma) + p_i^{OH}(\sigma) + p_i^{OT}(\sigma)$ [19]. The segment activity coefficient $\Gamma_{i/j}(\sigma_m)$ of a segment with surface charge density σ_m in solution S ($j = S$) or in its pure fluid state i ($j = i$) is determined by

$$\ln \Gamma_{i/j}^t(\sigma_m^t) = -\ln \left\{ \sum_s^{nhb, OH, OT} \sum_{\sigma_n} p_j^s(\sigma_n^s) \Gamma_{i/j}^s(\sigma_n^s) \exp \left[\frac{-\Delta W(\sigma_m^t, \sigma_n^s)}{RT} \right] \right\}, \quad (6)$$

where $\Delta W(\sigma_m^t, \sigma_n^s)$ describes the electrostatic interaction between surface segment of type t with screening charge density σ_m and surface segment of type s with screening charge density σ_n . It is calculated by

$$\Delta W(\sigma_m^t, \sigma_n^s) = c_{ES} (\sigma_m^t + \sigma_n^s)^2 - c_{hb}(\sigma_m^t, \sigma_n^s) (\sigma_m^t - \sigma_n^s)^2, \quad (7)$$

with the electrostatic interaction coefficient $c_{ES}/(\text{kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^4 \cdot \text{e}^{-2}) = 6525.69 + 1.4859 \cdot 10^8 / (T/\text{K})^2$ and hydrogen bonding interaction coefficients

$$c_{\text{hb}}(\sigma_m^t, \sigma_n^s)/(\text{kcal}\cdot\text{mol}^{-1}\cdot\text{\AA}^4\cdot\text{e}^{-2}) = \begin{cases} 4013.78 & \text{if } s = t = OH \text{ and } \sigma_m^t \cdot \sigma_n^s < 0 \\ 932.31 & \text{if } s = t = OT \text{ and } \sigma_m^t \cdot \sigma_n^s < 0 \\ 3016.43 & \text{if } s = OH, t = OT \text{ and } \sigma_m^t \cdot \sigma_n^s < 0 \\ 0 & \text{otherwise.} \end{cases} \quad (8)$$

The residual contribution was taken from preceding work on COSMO-SAC without modification or parameter optimization. Details can be found in Ref. [19].

In the development of the COSMO-SAC model, the dispersion contribution to the charging Gibbs energy for solute i in solvent j $\Delta G_{i/j}^{*dsp}$ was estimated by using a first-order mean field approximation to consider all possible pairwise interactions between the atoms in different molecules [17]. Because the difference of this contribution in its pure fluid state (i/i) and in a mixture (i/S) is small, the dispersion contribution to the activity coefficient $\ln \gamma_{i/S}^{dsp}$ is also small and was assumed to be zero until now in the COSMO-SAC model. However, it is shown in the present study that this small dispersion contribution does influence the accuracy of fluid phase behavior prediction significantly.

In this study, the molecular simulation tool for thermodynamic properties *ms2* [12] was used to study the contribution of the dispersive interactions to the activity coefficient. The role of the dispersive interaction was quantified by a series of molecular simulations for binary mixtures composed of Lennard-Jones model fluids (summarized in Table 1). This type of model mixtures was chosen because it contains only repulsive and dispersive interactions (the residual term becomes zero). As listed in Table 1, all Lennard-Jones fluids considered in this study have the same size and shape (spheres with a constant size parameter σ) in order to study the dispersion contribution in the COSMO-SAC (2010) model (the combinatorial terms become

zero). Different binary Lennard-Jones model mixtures, where the ratio of energy parameters $\varepsilon_1/\varepsilon_2$ was varied from 1.2 to 1.8, were simulated to study the effect of different strengths of the dispersive interaction on the non-ideality of the mixture.

The molecular simulation results for the excess Gibbs energy for binary mixtures of Lennard-Jones fluids are shown in Figure 1. These simulation results can be described by the one-constant Margules equation

$$\frac{G^{ex}}{RT} = Ax_1x_2 \quad , \quad (9a)$$

with constant A determined from [43,44]

$$A = w \cdot \left[\frac{1}{2}(\varepsilon_1 + \varepsilon_2) - \sqrt{\varepsilon_1\varepsilon_2} \right] \quad , \quad (9b)$$

where $w = 0.275$; ε_1 and ε_2 are the interaction energy parameters of the two Lennard-Jones model components as summarized in Table 1. Since the one-constant Margules equation can describe these model systems that are dominated by dispersive interaction, it was used to consider the contribution of the dispersive interaction to the activity coefficient in the COSMO-SAC model. Only binary mixtures were regarded in this work, but it is straightforward to extend the Margules equation to multicomponent mixtures [3,5,45]. For binary mixtures containing the components 1 and 2 , the activity coefficient due to the dispersion contribution for substances 1 and 2 are then

$$\ln \gamma_1^{dsp} = Ax_2^2 \quad , \quad (10a)$$

$$\ln \gamma_2^{dsp} = Ax_1^2 \quad , \quad (10b)$$

where x_i is the mole fraction of component i in the liquid phase and the constant A was determined from the molecular dispersion parameters ε_1 and ε_2 via Eq. (9b) with

$$w = \begin{cases} -0.275, & \text{if (a) water + } hb \text{ - only - acceptor} \\ & \text{(b) COOH + } nhb \text{ or } hb \text{ - donor - acceptor} \\ & \text{(c) water + COOH} \\ 0.275, & \text{otherwise,} \end{cases} \quad (11)$$

where *hb*-only-acceptor denotes substances that are able to form a hydrogen bond by accepting a proton from its neighbor, such as ethers, esters, ketones and nitro compounds; *hb*-donor-acceptor is substance that is able to form hydrogen bonds by either providing a proton or accepting a proton from its neighbors, such as alcohols and amines; COOH indicates substances with a carboxyl group, such as carboxylic acids and benzoic acids.

The molecular dispersion parameter $\varepsilon_{Molecule}$ for real molecules was determined from an atomic contribution approach

$$\varepsilon_{Molecule} = \frac{1}{N_{Atom}} \sum_{j=1}^n \varepsilon_j N_j, \quad (12)$$

where ε_j is the dispersion parameter of atom j , N_j the number of type j atoms, n the total number of atoms in the molecule and N_{Atom} the total number of atoms for which the dispersion parameter is not zero. Currently, only hydrogen atoms were excluded in N_{Atom} , if they are not bound to oxygen, nitrogen and fluorine atoms. This treatment is similar to the coarse-grained modeling in molecular simulations where the effect of a hydrogen atom is taken into account through other heavier atoms connected to it. The average of the atomic dispersion parameter over all atoms of a molecule, instead of the sum of it, is used to determine the molecular dispersion parameter for a molecule because we wish not to include the size effects, which has already been taken into account by the Staverman-Guggenheim combinatorial term. For example, the molecular dispersion parameter of n-hexane would be twice larger than that of n-propane when the sum of the dispersion interactions was used. This dispersion term

was then too large and deteriorated the prediction accuracy. Our choice of the one-constant Margules equation, which is appropriate for equally sized molecules, also helps exclude the effects from molecular size and shape differences in the dispersion term.

The values of the atomic dispersion parameter ε_j , as summarized in Table 2, were optimized here to a large set of experimental vapor-liquid equilibrium (VLE) data of binary mixtures. Detail discussion is given below.

3. Computational details and parameter optimizations

The computational details and all parameter values for the residual and combinatorial contributions are the same as those for the COSMO-SAC (2010) model, details are given in Ref. [19]. The freely available cosmo-file database (VT-database) containing over 1400 compounds from Liu's group at Virginia Tech [46,47] was used in this work. However, the cosmo-files of some compounds in the VT-database were updated by Sandler's group at the University of Delaware and were used in this work. It should be noted that the VT-database was established using the quantum mechanical program DMol3 in Materials Studio, including the COSMO solvation calculation [22,23]. Different quantum mechanical packages provide different cosmo-files (output from COSMO calculations) and often the accuracy of the predictions may become worse when cosmo-files from other quantum mechanical packages are used [48-50]. Therefore, it is recommended that a re-optimization of the COSMO-SAC parameters may be necessary in such cases.

The calculation of the dispersion contribution to the activity coefficient was as follows: First, the molecular dispersion parameter $\varepsilon_{Molecule}$ was obtained from Eq. (12).

Then, the activity coefficient due to the dispersion contribution was determined for both components in the binary mixture from Eqs. (9) to (11).

In this study, only substances composed of carbon, hydrogen, nitrogen, oxygen, chlorine and fluorine atoms were considered. Because an atomic contribution approach was used to estimate the molecular dispersion parameter for real molecules, a total of 13 global parameters was introduced in the COSMO-SAC-dsp model. In addition, the type of hybridization was considered for carbon, nitrogen and oxygen atoms. Hydrogen atoms were taken into account only when they are bound to oxygen, nitrogen or fluorine atoms, i.e. if they are capable to form a hydrogen bond. These 13 global parameters were obtained from optimization to experimental VLE data using the following objective function

$$Obj = \left\{ \frac{1}{M} \sum_{j=1}^M \left[\left(\frac{P_j^{\text{calc}} - P_j^{\text{expt}}}{P_j^{\text{expt}}} \right)^2 + (y_{1,j}^{\text{calc}} - y_{1,j}^{\text{expt}})^2 \right] \right\}^{1/2}, \quad (13)$$

where M is number of VLE data points, P the vapor pressure and y_1 the vapor phase mole fraction of component 1 in the mixture; the superscripts calc and expt indicate the calculated results and the experimental data, respectively. All experimental VLE data were retrieved from the DECHEMA Chemistry Data Series [51-53].

The parameter optimization of these 13 global parameters was carried out as follows: First, the ten dispersion parameters for carbon, nitrogen, oxygen, chlorine and fluorine were optimized to experimental VLE data for 219 non-hydrogen-bonding (*nhb*) binary systems. Once these parameters were optimized, they were fixed in the subsequent optimization of the remaining parameters. Second, the dispersion parameters of H(OH) and H(NH) were optimized to experimental VLE data for 170 binary systems which contain hydrogen-bonding (*hb*) interactions, but no water or carboxylic acids. Finally, 52 binary VLE systems containing water and carboxylic

acids were used to optimize the dispersion parameters of H(water/COOH). All binary systems used in this optimization are summarized in the Supplementary Material and the values of these global atomic dispersion parameters are listed in Table 2.

4. Results and discussions

In this study, VLE data and infinite dilution activity coefficient data were used to validate the COSMO-SAC-dsp model. VLE data for a total of 441 binary mixtures, containing 1308 isotherms, in the temperature range from 207.92 K to 553.15 K and pressure range from 0.084 kPa to 6.87 MPa, were considered. These data were retrieved from the DECHEMA Chemistry Data Series [51-53]. The infinite dilution activity coefficient data were taken from the literature [54-66]. They consist of 2385 data points (966 binary mixtures) in the temperature range from 238.2 K to 453.2 K. These systems can be categorized into two types: *nhb* and *hb* systems. Systems where one or both components have at least one hydroxyl (OH) group (including water and carboxylic acids) or amine (NH and NH₂) group were considered as *hb* systems; the others are *nhb* systems. It should be noted that exclusively VLE data were used in the optimization of the dispersion parameters.

4.1 Vapor-liquid equilibrium results

The introduced dispersion parameters were obtained from fitting to all VLE data in this study, but it is nonetheless interesting to discuss the descriptive performance of the COSMO-SAC-dsp model. Its accuracy was evaluated using the average absolute relative deviation in vapor pressure (AARD-*P*) and average absolute deviation in vapor phase mole fraction (AAD-*y*₁)

$$\text{AARD} - P (\%) = \sum_{i=1}^N \frac{1}{N} \left(\sum_{j=1}^M \frac{1}{M} \left| \frac{P_{i,j}^{\text{calc}} - P_{i,j}^{\text{expt}}}{P_{i,j}^{\text{expt}}} \right| \times 100\% \right), \quad (14a)$$

$$\text{AAD} - y_1 (\%) = \sum_{i=1}^N \frac{1}{N} \left(\sum_{j=1}^M \frac{1}{M} |y_{1,i,j}^{\text{calc}} - y_{1,i,j}^{\text{expt}}| \times 100\% \right), \quad (14b)$$

where M is the number of data points on an isotherm of a binary mixture; N is the number of isotherms of a binary mixture for which experimental data were considered. For some binary systems, experimental data were available for numerous isotherms in the database, such as for benzene + cyclohexane or water + methanol. Averaging over all isotherms for a binary mixture was done to avoid the overrepresentation of such systems in the overall deviation. In this work, the modified UNIFAC model [67] was used as a baseline reference. Table 3 summarizes the overall deviations with respect to VLE data from three different models. Modified UNIFAC is the most accurate, with the lowest AARD- P and AAD- y_1 of 3.44% and 1.53%, but only 411 out of 441 binary VLE systems were considered because of the missing parameter issue. The overall AARD- P and AAD- y_1 from the COSMO-SAC-dsp model are 5.11% and 2.12%, respectively, which are 25% and 12% lower than the overall AARD- P and AAD- y_1 of the COSMO-SAC (2010) model. This significant improvement was observed for both *nhb* and *hb* systems. As listed in Table 3, the overall AARD- P and AAD- y_1 for *nhb* systems from the COSMO-SAC-dsp model are 3.51% and 1.45%, respectively, those from the COSMO-SAC (2010) model are 4.33% and 1.56%. For *hb* systems, the overall AARD- P and AAD- y_1 from the COSMO-SAC-dsp model are 6.68% and 2.78%, respectively, those from the COSMO-SAC (2010) model are 9.18% and 3.26%. Overall, the results from the COSMO-SAC-dsp model are significantly better than those from the COSMO-SAC (2010) model for both *nhb* and *hb* systems.

Figure 2 shows VLE phase diagrams of four exemplary binary mixtures, which

cover a wide variety of substances: alkanes, ketones, aldehydes, acetates, aromatics and fluoro-compounds. In these cases, the COSMO-SAC (2010) model underestimates the non-ideality of the mixtures. After considering the dispersion contribution, the COSMO-SAC-dsp model can describe these systems very well and often has a similar accuracy as the modified UNIFAC model. The COSMO-SAC-dsp model is clearly more accurate than the COSMO-SAC (2010) model, especially for systems containing fluoro-compounds. As summarized in Table 4, the overall AARD- P and AAD- y_1 from the COSMO-SAC-dsp model were significantly reduced in comparison to the COSMO-SAC (2010) model. It is worth mentioning that modified UNIFAC has a severe issue of missing parameters for this type of systems (only three out of 15 binary mixtures can be described). Therefore, the COSMO-SAC-dsp model can be particularly useful for this type of mixtures.

For *hb* systems, also a significant improvement was achieved as illustrated in Fig. 3. In analogy to the findings above, the COSMO-SAC (2010) model usually underestimates the non-ideality of mixtures which can be improved by considering the dispersive interactions in mixtures. However, it should be noted that the COSMO-SAC (2010) model sometimes overestimates the non-ideality of mixtures, especially for systems containing water or small carboxylic acids [three types of systems with $w = -0.275$ in Eq. (11)]. A possible explanation for this phenomenon is that the molecular structure and molecular surface screening charges from quantum mechanical and COSMO calculations cannot represent these molecules in these mixtures or under certain concentration or temperature conditions. For example, it has been experimentally shown that acetic acid forms dimers or chain fragments in the liquid phase [68,69], so using only acetic acid monomers in VLE calculations is not sufficient. Chen et al. [70] proposed a theoretically based route to better describe

systems containing acetic acid. In the present study, we propose an empirical way, considering dispersive interaction with $w = -0.275$ for these complex systems. For mixtures of acetic acid + *nhb* compounds, an improvement was achieved as shown in Fig. 3(c) without significantly influencing predictions for mixtures of acetic acid + *hb* compounds as illustrated in Fig. 3(d).

4.2 Infinite dilution activity coefficient predictions

The infinite dilution activity coefficient γ^∞ usually represents the highest deviation from the ideal solution and is important for chemical processes design. This type of data is thus a good candidate to evaluate the predictive power of the COSMO-SAC-dsp model. The overall deviations of the predicted results from the experimental data were calculated as follows

$$\text{Error} = \sum_{i=1}^N \frac{1}{N} \left| \ln \gamma_i^{\infty, \text{calc}} - \ln \gamma_i^{\infty, \text{expt}} \right|, \quad (15)$$

where N is the number of data points. The modified UNIFAC model [67] was again used as the baseline reference for comparison. As listed in Table 5, the modified UNIFAC model provides the lowest deviations for *nhb* systems, but the COSMO-SAC-dsp model exhibits the lowest deviations for *hb* systems. It has been shown in prior work [71] that the modified UNIFAC model has larger deviations for infinite dilution activity coefficients of both water in alkanes (including cyclic alkanes) and alkanes in water. Figure 4 compares the predicted $\ln \gamma^\infty$ from the COSMO-SAC-dsp model and the COSMO-SAC (2010) model. For both *nhb* and *hb* systems, the COSMO-SAC (2010) model provides good predictions, but on average it underestimates $\ln \gamma^\infty$, especially for higher values of $\ln \gamma^\infty$, cf. Fig. 4(b). The COSMO-SAC-dsp model leads to slightly higher values for $\ln \gamma^\infty$ in case of *nhb*

systems and reduces the overall deviations by 25%. In case of *hb* systems, the predicted $\ln \gamma^\infty$ from the COSMO-SAC-dsp model are shifted up if $w = 0.275$ in Eq. (11) or shifted down if $w = -0.275$. The overall deviations for *hb* systems were reduced by 45%.

Furthermore, as listed in Table 5, a total of 1621 $\ln \gamma^\infty$ data (861 binary mixtures) were considered as a validation dataset since these binary mixtures were not included in the training set for parameter optimization. For *nhb* systems, the accuracy of COSMO-SAC-dsp for the validation dataset and for the whole dataset is similar; for *hb* systems, the accuracy of COSMO-SAC-dsp for the validation dataset is slightly worse than that for the whole dataset. However, a significant improvement was still observed, a reduction of 26 % in overall error when comparing with that of COSMO-SAC (2010). This again supports that considering the dispersive interactions in the COSMO-SAC-dsp model can improve its predictive accuracy.

It is useful to quantify the relative contribution to the activity coefficient from different terms of the COSMO-SAC-dsp model. Some examples are listed in Table 6: The experimental $\ln \gamma^\infty$ values included in this study range from -1.347 (methyl ethyl ketone in chloroform) to 23.384 (1-octadecanol in water) and the contribution from the dispersion term ranges from -0.876 to 0.796. For binary mixtures of alkanes + alkanes, the most important contribution is from the combinatorial term, while the dispersion term has a contribution of zero. The residual contribution dominates for most other binary mixtures, except for those having relatively small $\ln \gamma^\infty$ values within the range of the dispersion term. This is consistent with the physics that the dispersive interaction is usually weaker than the electrostatic interaction.

5. Conclusions

A contribution considering the dispersive interactions in mixtures was introduced into the COSMO-SAC (2010) model, denoted as COSMO-SAC-dsp model, to improve its accuracy for VLE and the infinite dilution activity coefficient. This dispersion term is based on molecular simulation data from classical model force fields for binary mixtures, where the dispersive interactions were varied. For binary mixtures, dispersion was described with the one-constant Margules equation where the constant is determined from the molecular dispersion parameter of the components. Furthermore, an atomic contribution method is proposed to calculate the dispersion parameter for a given molecule. A total of 13 global parameters was introduced into the COSMO-SAC-dsp model and all of them were obtained from regression to a large set of binary VLE data from experiments. This dispersion term significantly improves the accuracy of predictions of the infinite dilution activity coefficient for both non-hydrogen-bonding and hydrogen-bonding systems. The extension of this method to multicomponent systems is straightforward and is underway.

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Supplementary Material

Supplementary material associated with this article can be found in the online version.

Tables

Table 1. Summary of simulated binary mixtures of Lennard-Jones model fluids with $\varepsilon_1/k_B = 100$ and $\sigma_1 = \sigma_2$ and the parameter A of the one-constant Margules equation

ε_2/k_B (K)	$\varepsilon_1/\varepsilon_2$	A
83.333	1.2	0.102
71.428	1.4	0.324
62.500	1.6	0.592
55.556	1.8	0.875

Table 2. Values of the global atomic dispersion parameters of the**COSMO-SAC-dsp model**

Atom type	ε_{Atom}/k_B (K)
C (sp3)	115.7023
C (sp2)	117.4650
C (sp)	66.0691
-O-	95.6184
=O	-11.0549
N (sp3)	15.4901
N (sp2)	84.6268
N (sp)	109.6621
F	52.9318
Cl	104.2534
H (OH)	19.3477
H (NH)	141.1709
H (water/COOH)	58.3301

Table 3. Comparison of overall deviations of vapor–liquid equilibrium predictions from different predictive methods

	COSMO-SAC-dsp		COSMO-SAC (2010)		N^a	Mod. UNIFAC (1998)		
	N^a	AARD- P (%)	AAD- y_1 (%)	AARD- P (%)		AAD- y_1 (%)	AARD- P (%)	AAD- y_1 (%)
<i>nhb</i>	219	3.51	1.45	4.33	1.56	197 ^b	2.23	0.96
<i>hb</i>	222	6.68	2.78	9.18	3.26	214 ^b	4.55	2.06
Overall	441	5.11	2.12	6.77	2.42	411 ^b	3.44	1.53

a. Number of binary mixtures considered in this study. It should be noted that for a given binary mixture data on several isotherms may have been used.

b. Fewer binary mixtures were considered in case of modified UNIFAC due to missing parameters.

Table 4. Comparison of overall deviations of vapor–liquid equilibrium predictions for systems containing fluoro-compounds

	N^a	AARD- P (%)	AAD- y_1 (%)
COSMO-SAC-dsp	15	4.92	3.37
COSMO-SAC (2010)	15	9.87	3.71
Mod. UNIFAC (1998)	3 ^b	4.57	2.03

- a.* Number of binary mixtures considered in this study. It should be noted that for a given binary mixture data on several isotherms may have been used.
- b.* Fewer binary mixtures were considered in case of modified UNIFAC due to missing parameters.

Table 5. Comparison of overall deviations of infinite dilution activity coefficient predictions

	<i>nhb</i>		<i>hb</i>	
	N^a	Error ^{<i>b</i>}	N^a	Error ^{<i>b</i>}
COSMO-SAC-dsp	1411 (651) ^{<i>c</i>}	0.199	348 (210) ^{<i>c</i>}	0.455
	1923 (728)	0.192	462 (238)	0.336
COSMO-SAC (2010)	1923 (728)	0.255	462 (238)	0.624
Mod. UNIFAC (1998)	1923 (728)	0.104	419 (224) ^{<i>d</i>}	0.496

- a.* Number of infinite dilution activity coefficient data points considered in this study. The number of binary mixtures is given in parentheses.
- b.* Error was determined from Eq. (15).
- c.* Number of infinite dilution activity coefficient data points for binary mixtures that are not included in parameter optimization.
- d.* Fewer infinite dilution activity coefficient data were considered in case of modified UNIFAC due to missing parameters.

Table 6. Comparison of various contributions to $\ln \gamma^\infty$

Solute	Solvent	T (K)	$\ln \gamma_i^{\infty, \text{expt}}$	$\ln \gamma_i^{\infty, \text{calc}}$	$\ln \gamma_i^{\infty, \text{calc}}$	$\ln \gamma_i^{\text{res}}$	%	$\ln \gamma_i^{\text{comb}}$	%	$\ln \gamma_i^{\text{dsp}}$	%
				COSMO-SAC -dsp	COSMO-SAC (2010)						
n-pentane	n-heptane	293.15	0.000	-0.032	-0.032	0.0001	-0.4%	-0.0317	100.4%	0.0000	0.0%
n-pentane	n-tetracosane	298.15	-0.300	-0.611	-0.611	0.0012	-0.2%	-0.6123	100.2%	0.0000	0.0%
n-pentane	benzene	298.15	0.713	0.793	0.793	0.8001	100.8%	-0.0075	-0.9%	0.0009	0.1%
n-pentane	1,2-dichloroethane	298.15	1.504	1.198	1.189	1.2032	100.4%	-0.0146	-1.2%	0.0098	0.8%
1,1-dichloroethane	1,1,1-trichloroethane	328.2	0.058	0.076	0.076	0.0787	103.6%	-0.0032	-4.2%	0.0004	0.5%
n-pentane	acetonitrile	298.15	2.845	3.310	3.200	3.3610	101.6%	-0.1610	-4.9%	0.1095	3.3%
n-pentane	acetone	298.15	1.637	1.473	1.141	1.1924	81.0%	-0.0513	-3.5%	0.3317	22.5%
benzene	triethylamine	323.5	0.247	0.281	0.201	0.2426	86.3%	-0.0413	-14.7%	0.0799	28.4%
1-pentene	ethylbenzoate	313.2	0.668	0.131	0.079	0.1426	109.0%	-0.0632	-48.3%	0.0514	39.3%
isoprene	methylethylketone	293.15	0.405	0.207	-0.020	-0.0206	-9.9%	0.0003	0.1%	0.2277	109.8%
toluene	ethylacetate	298.2	0.285	0.205	-0.009	-0.0185	-9.0%	0.0094	4.6%	0.2145	104.4%
chloroform	n-hexane	301	0.457	0.314	0.291	0.3346	106.7%	-0.0434	-13.8%	0.0224	7.1%
acetone	1-butanol	298	0.924	0.582	0.529	0.5548	95.4%	-0.0255	-4.4%	0.0525	9.0%
n-pentane	ethanol	298	2.197	2.020	1.736	1.8569	91.9%	-0.1214	-6.0%	0.2845	14.1%
benzene	water	298	7.800	8.166	7.370	8.4222	103.1%	-1.0519	-12.9%	0.7955	9.7%
n-pentane	water	298.15	11.552	11.694	10.951	12.3241	105.4%	-1.3733	-11.7%	0.7429	6.4%
1-octadecanol	water	298.15	23.341	22.694	22.114	29.9470	132.0%	-7.8329	-34.5%	0.5793	2.6%
n-heptane	acetic acid	298	3.157	3.206	4.081	4.3649	136.2%	-0.2835	-8.8%	-0.8758	-27.3%

Figure Caption

Figure 1. Comparison of the dimensionless excess Gibbs energy from molecular simulation (\diamond : $\varepsilon_1/\varepsilon_2 = 1.2$; \circ : $\varepsilon_1/\varepsilon_2 = 1.4$; Δ : $\varepsilon_1/\varepsilon_2 = 1.6$; \square : $\varepsilon_1/\varepsilon_2 = 1.8$) and the one-constant Margules equation with a constant A as determined by Eq. (9b) (---: $\varepsilon_1/\varepsilon_2 = 1.2$; -·-: $\varepsilon_1/\varepsilon_2 = 1.4$; ---: $\varepsilon_1/\varepsilon_2 = 1.6$; —: $\varepsilon_1/\varepsilon_2 = 1.8$).

Figure 2. Comparison of vapor-liquid equilibria from COSMO-SAC-dsp (—), COSMO-SAC (2010) (-·-) and modified UNIFAC (---) for non-hydrogen-bonding systems: (a) n-butane (1) + acetone (2), (b) butanal (1) + n-heptane (2), (c) methyl acetate (1) + benzene (2) and (d) trifluoromethane (1) + isobutene (2). The results from modified UNIFAC are not shown in (d) because of the missing parameter issue.

Figure 3. Comparison of vapor-liquid equilibria from COSMO-SAC-dsp (—), COSMO-SAC (2010) (-·-) and modified UNIFAC (---) for hydrogen-bonding systems: (a) n-hexane (1) + ethanol (2), (b) cyclohexylamine (1) + N,N-dimethylformamide (2), (c) cyclohexane (1) + acetic acid (2) and (d) ethanol (1) + acetic acid (2). The results from COSMO-SAC (2010) are not shown in (c) because it failed for this system.

Figure 4. Comparison of prediction of infinite dilution activity coefficient from COSMO-SAC-dsp (\circ) and COSMO-SAC (2010) (Δ) with experimental data for (a) non-hydrogen-bonding systems and (b) hydrogen-bonding systems.

Figures

Figure 1.

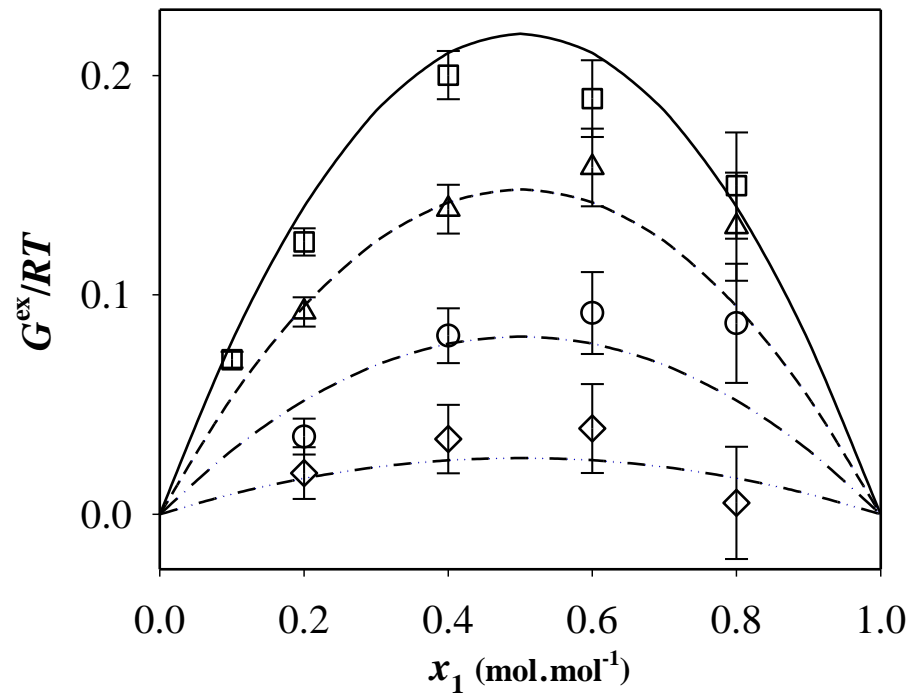


Figure 2.

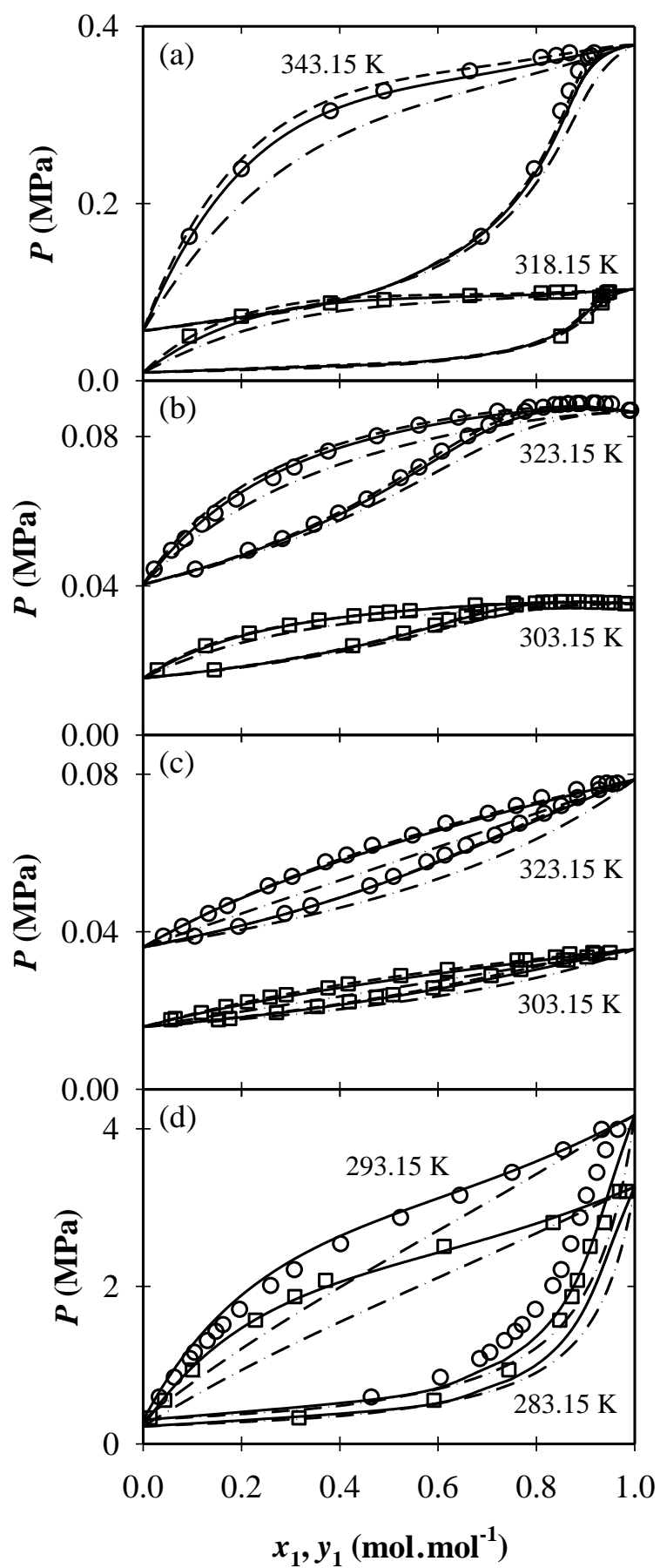


Figure 3.

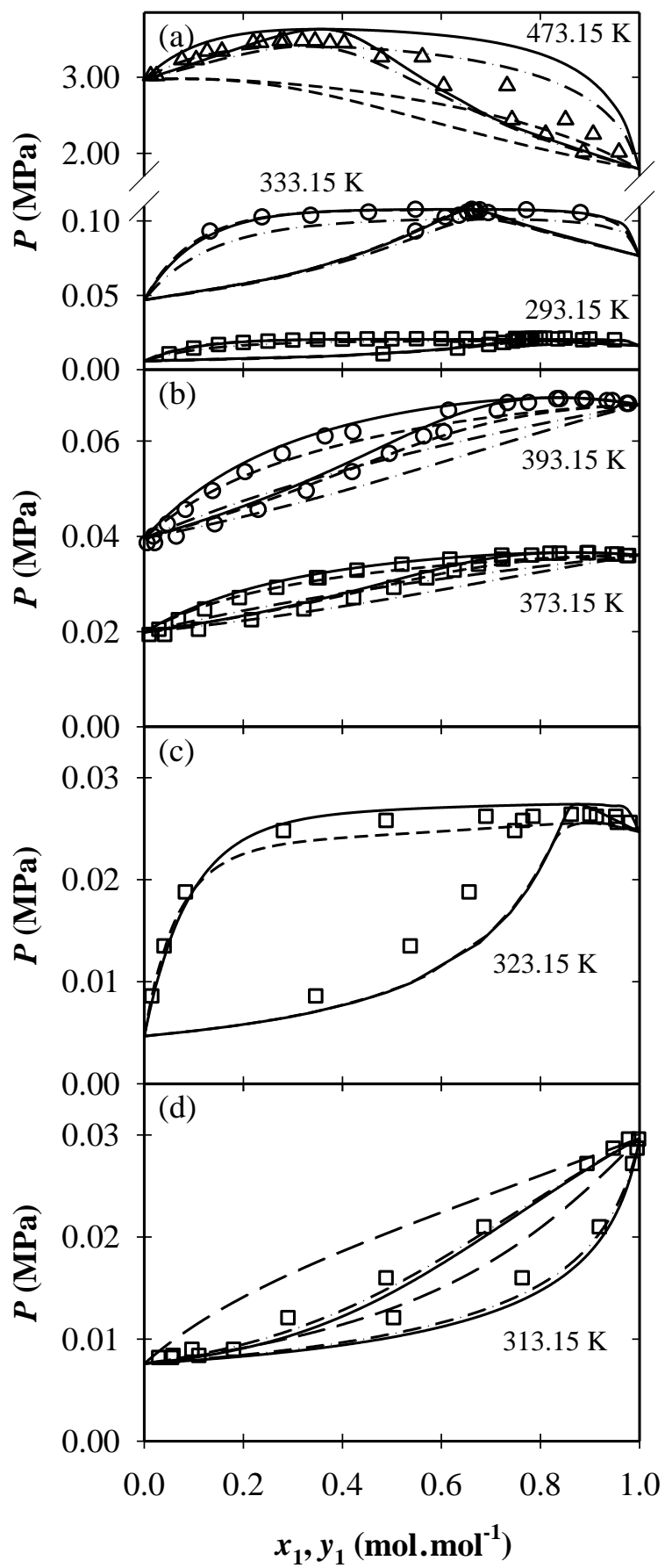


Figure 4(a)

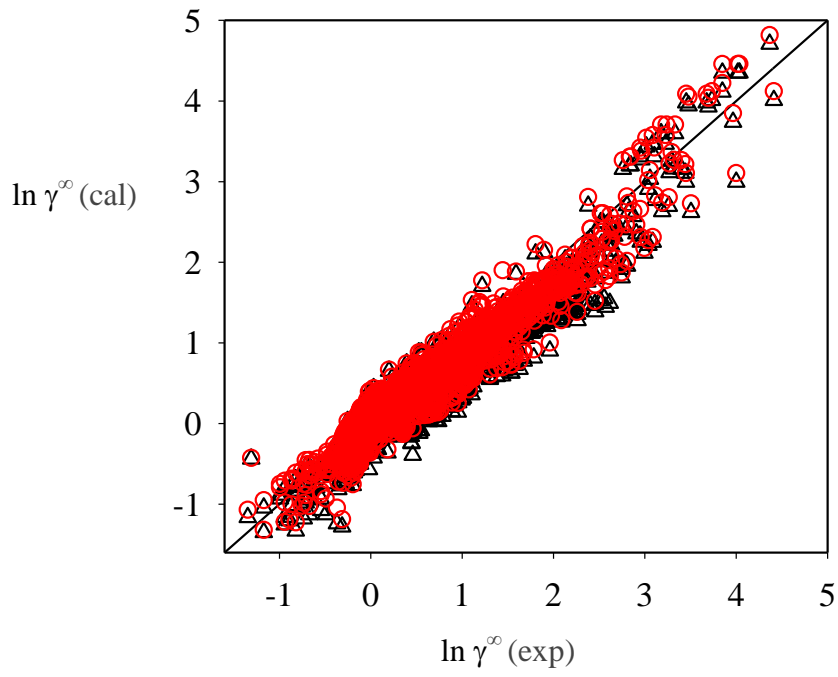
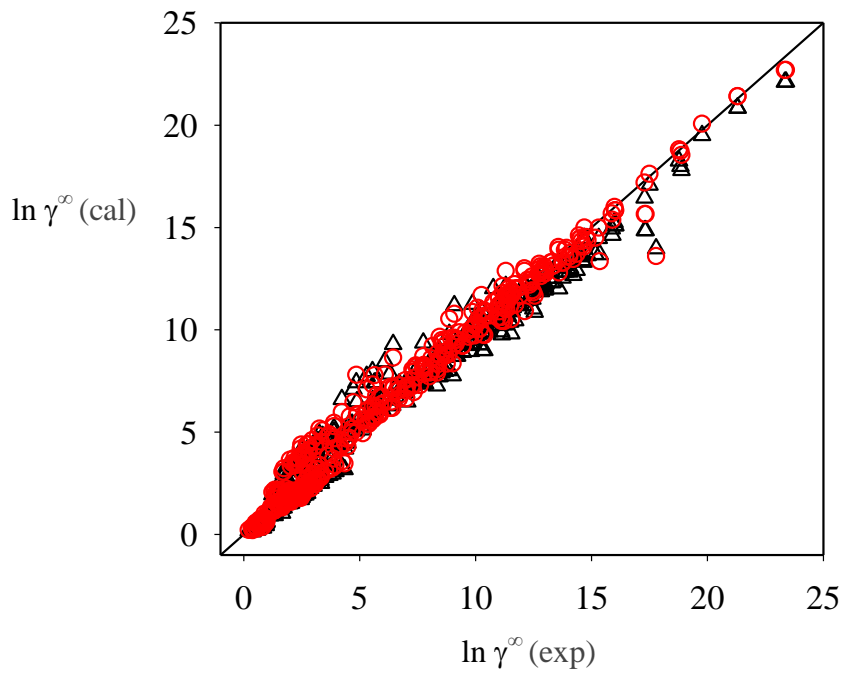


Figure 4(b)



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Corrigendum

Corrigendum to <'Considering the dispersive interactions in the COSMO-SAC model for more accurate predictions of fluid phase behavior'>

<[Fluid Phase Equilibria 367 (2014) 109–116]>

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The authors regret that some errors were found in the above article.

1. The value of w is incorrect and four passages in the text should be revised:

(a) On page 111, third line of the left column:

“where $w = 0.275$ ” should be revised to “where $w = \pm 0.27027$ ”

(b) On page 111, Eq. (11) should also be revised to:

$$w = \begin{cases} -0.27027, & \text{if (a) water + } hb \text{ - only - acceptor} \\ & \text{(b) COOH + } nhb \text{ or } hb \text{ - donor - acceptor} \\ & \text{(c) water + COOH} \\ 0.27027, & \text{otherwise,} \end{cases} \quad (11)$$

(c) On page 113, third paragraph:

“... [three types of systems with $w = -0.275$ in Eq. (11)] ... In the present study, we propose an empirical way, considering dispersive interaction with $w = -0.275$ for these complex systems.”

should be revised to:

“... [three types of systems with $w = -0.27027$ in Eq. (11)] ... In the present study, we propose an empirical way, considering dispersive interaction with $w = -0.27027$ for these complex systems.”

(d) On page 114, at the end of the first paragraph on the left column:

“In case of hb systems, the predicted $\ln\gamma^\infty$ from the COSMO-SAC-dsp model are shifted up if $w = 0.275$ in Eq. (11) or shifted down if $w = -0.275$.”

should be revised to:

“In case of hb systems, the predicted $\ln\gamma^\infty$ from the COSMO-SAC-dsp model are shifted up if $w = 0.27027$ in Eq. (11) or shifted down if $w = -0.27027$.”

2. On page 112, Table 2:

“H (water/COOH)” should be revised to “H (water)”

3. The overall error of COSMO-SAC-dsp for *hb* systems in predicting the infinite dilution activity coefficient is incorrect and two should be revised:
 - (a) On page 114, Table 5:

The overall error of COSMO-SAC-dsp for *hb* systems should be revised from “0.336” to “0.487”.
 - (b) On page 114, last sentence of the first paragraph on the left column:

“The overall deviations for *hb* systems were reduced by 45%.”
should be revised to:
“The overall deviations for *hb* systems were reduced by 22%.”

The authors would like to thank Andreas Klamt at COSMOlogic GmbH & Co. KG and Jürgen Rarey at DDBST GmbH for pointing out these errors. The authors would like to apologise for any inconvenience caused.

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