



# Modifications to the Exchange Energy in Cosmo-Sac Model for Improving the Accuracy of Infinite Dilution Activity Coefficient Prediction of Ionic Liquid Systems

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Research Article

## Abstract

A new approach for improving the accuracy of infinite dilution activity coefficient of organic solutes in ionic liquids using COSMO-SAC was investigated in this research. The accuracy of Infinite Dilution Activity Coefficient (IDAC) of solutes in ionic liquids determined by the original COSMO-SAC model has been improved by modifying the model and fitting the adjustable parameters with experimental data from National Institute of Standards and Technology (NIST). The exchange energy expression was modified by including segment interaction parameters  $C_1$  and  $C_2$  to account for the charges on cations and anions, as well as the non-electrostatic contribution  $C_{ne}$  to ascertain its effect on the systems. The standard segment surface area,  $a_{eff}$ , standard surface area in Staverman–Guggenheim equation,  $q$ , standard volume in Staverman–Guggenheim equation,  $r$ , segment interaction parameters  $C_1$  and  $C_2$ , and the non-electrostatic contribution,  $C_{ne}$ , were fitted to 414 experimental data points using least square curve fitting program in Matlab. The data points were composed of 39 solutes, 10 cations and 11 anions in a temperature range from 288.15 to 395.95K. The optimal values for the parameters  $a_{eff}$ ,  $q$ , and  $r$  in the modified model from this work are  $7.649 \text{ \AA}^2$ ,  $236.61 \text{ \AA}^2$  and  $3.111 \text{ \AA}^3$ , respectively. Values of the hydrogen bonding interaction coefficient and hydrogen bonding interaction cut-off charge,  $C_{hb}$  and  $\sigma_{hb}$  remain  $85580 \text{ kcal mol}^{-1} \text{ \AA}^4 e^{-2}$  and  $8.4 \times 10^{-3} 0.0084 e \text{ \AA}^{-2}$  respectively, as in the original model. The values of parameters  $C_1$ ,  $C_2$  and  $C_{ne}$  have been determined to be  $3.415 \times 10^{-14}$ , 1.278 and  $5.06 \times 10^{-2}$ , respectively. The calculated IDAC results agree with the experimental data within the Average Relative Deviation (ARD) deviation of 20.71%, hence can be used for screening purposes of ionic liquids. The model from this work performs best for solutes with low polarity. Among the solutes used in this work, the model performed best for Alkynes, with ARD of 5.91%, while the poorest result was recorded for Water with ARD of 98.75%. The ARD of IDAC from 29 data points which were not included in the parameter optimization was computed using the modified model to be 18.07%. In terms of Henry's law constant calculation for  $\text{CO}_2$  in ionic liquids, the ARD of COSMO-SAC model from this work is 17.2% for 17 data points, as against that from COSMO-SAC 2010 which is 9.8%. Henry's law constant for  $\text{CO}_2$  in the ionic liquids 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][TF2N]) and in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TF2N]) was also in good agreement with the experimental values at temperatures below the critical temperature of  $\text{CO}_2$ .

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## Keywords

COSMO-SAC; Exchange Energy; Infinite Dilution Activity Coefficient; Ionic Liquid; Segment Interaction.

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## 1. Introduction

Ionic liquids (ILs) are salts that have melting points below  $100^\circ\text{C}$  as described by Lei *et al.*,(2017). They are wholly composed of cations and anions. Ionic liquids have received much attention over the last two decades due to their unique properties such as low vapour pressure, tunability, solvation properties for organic and inorganic compounds, etc.

Ionic liquids have several industrial applications. The applications include alkylation of hydrocarbons, capture of pollutant gases, hydrogenation, performance additives in coating pigments and fuels, use as solvents, etc., as discussed by Greer *et al.*,(2020).

Walter *et al.*,(2021) described activity coefficient of a compound ( $\gamma_i$ , where  $i$  refers to the compound) as a measure of non-idealities in liquid systems composed of two or more chemical species. Infinite dilution activity coefficient (IDAC),  $\gamma_i^\infty$ , also known as limiting activity coefficient is the limiting value of the activity coefficient of a solute when its concentration tends towards zero.

$$\lim(\gamma_i)_{x \rightarrow 0} = \gamma_i^\infty \quad (1)$$

Activity coefficients at infinite dilution provide a useful tool for calculating Henry's Law constant and other applications like solvent selection in extraction processes, as described by Brouwer *et al.*,(2019).

IDAC for gaseous and liquid mixtures can be calculated using several methods, such as, UNIFAC (Dong *et al.*, 2020), ASOG (Robles and Cisternas, 2015), NRTL (Lin *et al.*, 2021), UNIQUAC (Normawati *et al.*, 2016) or COSMO-SAC (Lin and Sandler, 2002) models. The COSMO-SAC approach has a major advantage over the other methods in terms of simplicity in that the calculations only require the knowledge of a structural formula and certain model parameters which is available in the relevant literature (Xiong *et al.*, 2014).

The solubility of CO<sub>2</sub> in various ionic liquids using Henry's law constant to determine the capacity of the various ionic liquids to absorb CO<sub>2</sub> was studied by Nadir *et al.*, (2022). Several authors (Anand *et al.*, 2018, Shah *et al.*, 2012, Tianhao *et al.*, 2021, Dong *et al.*, 2019) have reported mixed results for IDAC prediction of ionic liquid systems. Anand *et al.*, (2018) reported that the COSMO-SAC model is more accurate in predicting IDAC of IL-free systems, indicating that this method still requires validation and further development.

Shah *et al.*, (2012) tried to correlate the experimental IDAC data by varying C<sub>hb</sub> in the COSMO-SAC 2002 model. Their efforts were unsuccessful, until they used the 2007 model, which has a more fundamentally sound expression for hydrogen bonding.

In recent studies, attempts have been made to develop a hybrid model which combines the ease of IDAC prediction offered by the COSMO-SAC model with the relatively high prediction accuracy of the UNIFAC model, called COSMO-UNIFAC model (Dong *et al.*, 2019, Ruisong *et al.*, 2020, Dong *et al.*, 2019). While this approach gives higher accuracy in terms of IDAC calculations, a drawback is that the functional group parameters of new compounds needed for IDAC prediction need to be obtained from a regression. The regression can be done using IDAC obtained from COSMO-SAC.

In this work, the Conductor-like Screening Model-Segment Activity Coefficient (Lin and Sandler, 2002) model was reparametrized for IDAC predictions of solutes in ILs at different temperatures using experimental data from the NIST database. The result from the reparametrized model was compared with the experimental data by calculating the average relative deviation (ARD) of the modified model from the experimental data. The aim of this work is to develop a new method of improving the accuracy of the COSMO-SAC 2002 model to predict the IDAC of solutes in ionic liquids without splitting the sigma profiles of species based on hydrogen bonding, as was done in more recent models (Xiong *et al.*, 2014).

## 2. COSMO-SAC Theory

In the COSMO-SAC model (Lin and Sandler, 2002), the surface of each molecule is divided into segments and the screening charge density corresponding to each segment is calculated. This three-dimensional charge distribution is projected on a two-dimensional histogram by calculating the probability of finding a segment having a screening charge density  $\sigma$ . This probability distributions  $p_i(\sigma)$ , also known as sigma profiles, are unique to each molecule.

$$p_i(\sigma) = \frac{A_i(\sigma)}{A_i} \quad (2)$$

where  $A_i(\sigma)$  is the surface area of specie with a charge density of value  $\sigma$ ;  $A_i$  is the total surface area of species  $i$ . For a mixture, the  $\sigma$ -profile,  $p_s(\sigma)$ , is determined from the area-weighted average of contributions from all the components present in the mixture. This is given as

$$p_s(\sigma) = \frac{\sum_i x_i A_i p_i(\sigma)}{\sum_i x_i A_i} \quad (3)$$

where  $x_i$  is the mole fraction of component  $i$  in the mixture. Since different surfaces have different number of segments, the following algorithm is used to obtain apparent screening charges  $\sigma_m$  to be used in the original COSMO-SAC model:

$$\sigma_m = \frac{\sum_n \sigma_n^* \frac{r_n^2 r_{eff}^2}{r_n^2 + r_{eff}^2} \exp\left(-\frac{d_{mn}^2}{r_n^2 + r_{eff}^2}\right)}{\sum_n \frac{r_n^2 r_{eff}^2}{r_n^2 + r_{eff}^2} \exp\left(-\frac{d_{mn}^2}{r_n^2 + r_{eff}^2}\right)} \quad (4)$$

where  $\sigma_n^*$  is the original, non-averaged, surface charge of the  $n$ -th segment given in elementary charge  $e$  coming directly from the COSMO file,  $r_n = (a_n/\pi)^{0.5}$ ,  $r_{av} = 0.5 \text{ \AA}$ , and  $d_{mn}$  is the distance (in  $\text{\AA}$ ) between the centres of the surface segments  $n$  and  $m$  in  $\text{\AA}$ . The sigma profiles of the various components are used in a thermodynamic model to calculate the activity coefficients of the components in a solution. The self-energy of a segment pair  $E_{pair}$  necessary for the calculation of the segment activity coefficient contains contributions from the electrostatic interactions  $E_{mf}$ , the hydrogen-bonding interactions  $E_{hb}$  and non-electrostatic interaction,  $E_{ne}$ .

$$E_{pair}(\sigma_m, \sigma_n) = E_{mf}(\sigma_m, \sigma_n) + E_{hb}(\sigma_m, \sigma_n) + E_{ne}(\sigma_m, \sigma_n) \quad (5)$$

The non-electrostatic energy is assumed to be a constant  $C_{ne}$  term.

$$E_{pair}(\sigma_m, \sigma_n) = \frac{\alpha'}{2} (\sigma_m + \sigma_n)^2 + C_{hb} \max[0, \sigma_{ac} - \sigma_{hb}] \min[0, \sigma_{don} - \sigma_{hb}] + C_{ne} \quad (6)$$

Where  $\sigma_{hb} = 0.0084 e \text{ \AA}^{-2}$ ,  $\sigma_{acc} = \max(\sigma_m, \sigma_n)$  and  $\sigma_{don} = \min(\sigma_m, \sigma_n)$ .  $\alpha'$  is a constant for the misfit energy calculated from the surface area of a standard segment as follows:

$$\alpha' = \frac{0.64 \times 0.3 \times a_{eff}^{1.5}}{\epsilon_o} \quad (7)$$

$$\epsilon_o = 2.395 \times 10^{-4} \text{ (Permittivity of free space)}$$

It is assumed that the non-electrostatic energy pair cancel out,  $C_{ne}$  becomes zero and the exchange energy  $\Delta W$  becomes.

$$\Delta W(\sigma_m, \sigma_n) = \frac{\alpha'}{2} (\sigma_m + \sigma_n)^2 + C_{hb} \max[0, \sigma_{ac} - \sigma_{hb}] \min[0, \sigma_{don} - \sigma_{hb}] \quad (8)$$

Table 1: Values of parameters in COSMO-SAC 2002.

Parameters	Meaning	Values
$a_{\text{eff}}$	Standard segment surface area	$7.50 \text{ \AA}^2$
$C_{\text{hb}}$	hydrogen bonding interaction coefficient	$8.558 \times 10^4 \text{ kcalmol}^{-1} \text{ \AA}^4 \text{ e}^{-2}$
$\sigma_{\text{hb}}$	hydrogen bonding interaction cut-offcut-offcut-off charge	$0.0084 \text{ e\AA}^{-2}$
$q$	standard surface area in Staverman–Guggenheim equation	$79.53 \text{ \AA}^2$
R	standard volume in Staverman–Guggenheim equation	$66.69 \text{ \AA}^3$

Source: Xiong *et al.*,(2014).

Table 1 shows the adjustable model parameters used in COSMO-SAC 2002. Han *et al.*,(2018) improved the accuracy of the COSMO-RS model for predicting the IDAC of solutes in ionic liquids by optimizing the adjustable parameters of COSMO-RS. They obtained significant improvements compared to the original COSMO-RS models. The objective function was the average relative deviation, and it was minimized to obtain new values for the model parameters. The objective function, OF, is expressed as follows:

$$OF = \min \left\{ \frac{1}{N} \sum_i^N \left| \frac{\gamma_i^{\infty, \text{exp}} - \gamma_i^{\infty, \text{calc}}}{\gamma_i^{\infty, \text{exp}}} \right| \right\} \quad (9)$$

where  $\gamma_i^{\infty, \text{exp}}$  and  $\gamma_i^{\infty, \text{calc}}$  are the experimental and calculated activity coefficients of solute  $i$  in ILs at infinite dilution.  $N$  is the number of data points.

### 3. Modifications made in this work

The eCOSMO-SAC model proposed by Shu *et al.*,(2011) is a modification of COSMO-SAC 2002 for electrolytes. In this work, an expression like the exchange energy used in eCOSMO-SAC was used. Another addition made in this work is the non-electrostatic contribution,  $C_{\text{ne}}$  hitherto assumed to cancel out from the expression. This was done to test its effect in systems containing Ionic liquids.

$$\Delta W(\sigma_m, \sigma_n) = C_1 \cdot \frac{\alpha'}{2} (\sigma_m + \sigma_n)^2 + C_2 \cdot C_{\text{hb}} \max[0, \sigma_{\text{ac}} - \sigma_{\text{hb}}] \min[0, \sigma_{\text{do}} - \sigma_{\text{hb}}] + C_{\text{ne}} \quad (10)$$

It is assumed that the segment interaction parameters  $C_1$  and  $C_2$  should compensate for the molecular forces in the system.

Ionic liquids are composed of cation and anion. The cations and anions are treated as separate entities in the computations of this work; hence the system is Ternary, i.e., solute – cation - anion. However, in laboratory experiments, ionic liquid is treated as a single entity, hence the system is binary, i.e., solute and IL.

It has been found that the derivation by Klamt (2012) that converts the IDAC from computational format ( $\gamma_{i,x \rightarrow 0}^{\text{tern}}$ ) to laboratory format ( $\gamma_i^{\text{bin}}$ ) further improves the accuracy of the predicted results.

$$\gamma_i^{\text{bin}} = 0.5 \gamma_{i,x \rightarrow 0}^{\text{tern}} \text{ (Infinite Dilution only)} \quad (11)$$

Equation (11) has been incorporated into the modified COSMO-SAC model.

### 4. Computational Details

Figure 1 shows the process flow diagram of the work. DMol3, a module in BIOVIA’s Materials Studio was used to carry out the geometry optimization of the molecules. The chemical structures used in geometry optimization were obtained from PubChem, ChemSpider and NISTwebbook. In carrying out the geometry optimization, the quality and functional were set to ‘fine’ and GGA/VWN-BP, respectively (GGA represents the generalized gradient approximation, and VWN-BP represents the Becke – Perdew version of the Volsko – Wilk – Nusair functional). The DNP basis was set to v4.0.0 as described by Mullins *et al.*,(2006). The same settings in were followed in the energy calculation to create the COSMO file with the addition of COSMO environment keywords (See Appendix file for DMol input files). It should be noted that the charges set for solutes, cations and anions during the geometry optimization and energy calculation are 0, 1 and -1, respectively. Also, the ‘spin unrestricted’ was checked in the case of the ions. The sigma profiles were then created using the sigma average program provided on the Virginia Tech University website (VT Sigma Profile Databases, 2008). Note that the units of acosmo, vcosmo, and segment areas generated by Materials Studio version 2017 are in atomic unit (au) and must be converted to Angstrom (Å) by multiplying by 0.5292, to obtain accurate sigma profile calculation with this programme.

The solute (1) – IL (2) system, which is actually a binary system in real life, was treated as a ternary system of solute (1) – IL-cation (2) – IL-anion (3) in our computations as suggested by Lin and Sandler (2002). Therefore, the final IDAC values computed must be converted to correspond with real life binary systems by multiplying it by 0.5. The segment interaction parameters ( $C_1$  and  $C_2$ ), the non-electrostatic contribution ( $C_{\text{ne}}$ ) and other adjustable parameters in the original COSMO-SAC model were fitted to experimental data using lsqcurvefit function in MATLAB. The dataset consists of 414 data points of experimental IDAC values made up of 38 solutes, 10 cations and 11 anions. Table 2 shows the solutes, cations and anions used in the reparametization. All the experimental data points were obtained from the NIST IL Thermo database (Retrieved from <https://www.nist.gov/mml/acmd/trc/ionic-liquids.database>). For more on the data points please check table B2 in the appendix.

The fitting was done in a systematic manner. First, the original COSMO-SAC was fitted with the experimental data for  $a_{\text{eff}}$ ,  $C_{\text{HB}}$ ,  $q$  and  $r$  and  $\sigma_{\text{hb}}$ . The model was then modified with the new parameters and fitted for  $a_{\text{eff}}$ ,  $q$ ,  $r$ ,  $C_1$ ,  $C_2$ , and  $C_{\text{ne}}$  in a separate run.

The model was then validated using a fresh set of data points not used in the reparametization. Figure 1 is the process flow chart of the methodology used in this work.

Table 1: Solutes, cations and anions used for the reparametization of the modified COSMO-SAC model.

	SOLUTES		IL CATIONS	IL ANIONS
ethyl ethanoate	vinyl acetate	dichloromethane	1-butyl-3-methyl-imidazolium	Tetrafluoroborate
propane-2-ol	pyridine	thiophene	1-butyl-4-methyl-pyridinium	Chloride
acetonitrile	tetrahydrofuran	pentanal	1-butyl-1-methyl-pyrrolidinium	dimethylphosphate
methanol	1-nitropropane	butanal	1-ethyl-3-methyl-imidazolium	Ethanesulfonate
propan-1-ol	acetone	heptanal	Ethylpyridinium	ethyl sulfate
ethanol	1,3-dimethylbenzene	methyl propanoate	1-hexyl-3-methyl-imidazolium	methanesulfonate (mesylate)
trichloromethane	1,4-dimethylbenzene	methyl pentanoate	1,3-dimethyl-imidazolium	methyl sulfate
tetrachloromethane	1,2-dimethylbenzene	methyl heptanoate	1-octyl-3-methyl-imidazolium	hexafluorophosphate bis(trifluoromethylsulfonyl)- amide
pentan-2-one	ethylbenzene	hexanal	1-ethyl-2,3-dimethylimidazolium	Octylsulfate
butanone	toluene	propanal	pyridinium	methoxyethylsulfate
water	benzene	methyl hexanoate		
1-hexyne	1-heptyne	methyl butanoate		
1,4-dioxane	styrene			

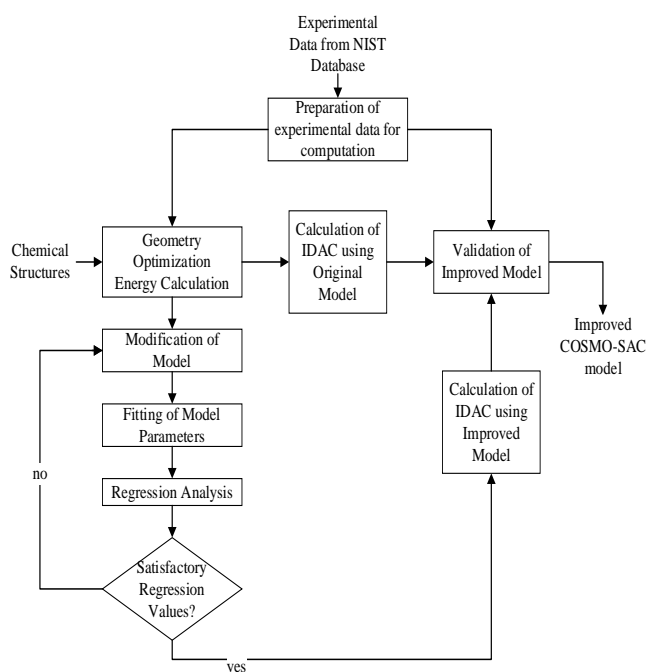


Figure 1: Process flow chart of the work

## 5. Results and Discussion

### 5.1 Sigma Profiles and Polarity

The sigma profile and segment activity coefficient were divided into three areas by two vertical lines,  $\sigma = -0.0082 \text{ e}/\text{\AA}^2$  and  $\sigma = +0.0082 \text{ e}/\text{\AA}^2$ , as described by Hou *et al.*, (2019). The middle part is the non-hydrogen bond region.

The left side of  $\sigma = -0.0082 \text{ e}/\text{\AA}^2$  is the H-bond donor region, and the right side of  $\sigma = +0.0082 \text{ e}/\text{\AA}^2$  is the H-bond acceptor region. The  $\sigma$ -profiles for the IL cations and anions generated in this work are shown in Figures 2 and 3.

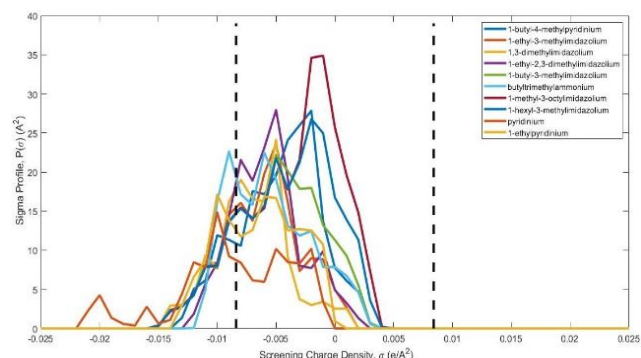


Figure 2: Sigma profile of cations used in this work.

The shape and range for all the studied cations are similar. Their  $\sigma$ -profiles contains one main peak located in the non-hydrogen bond region, reaching the H-bond donor region (figure 2). Similarly, the shape and range for all the studied anions are also similar. They contain one main peak in the non-hydrogen bond region, reaching the H-bond acceptor region (figure 3). The similarity in shape and range of cations and anions is an indication that the ions have similar polarity and the ability to form hydrogen bonds.



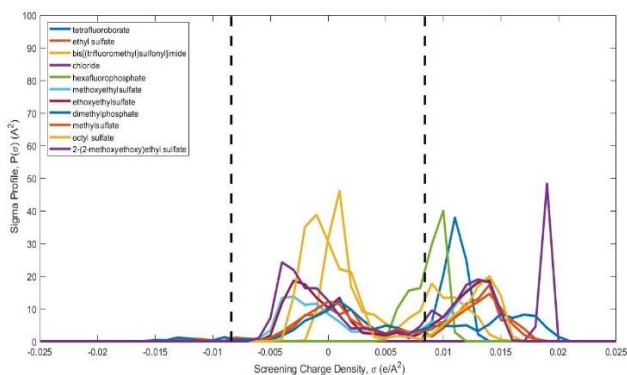


Figure 3: Sigma profiles of anions used in this work.

The  $\sigma$ -profiles of solutes are from the Virginia Technology (VT) university sigma profile database (VT Sigma Profile Databases, 2008). They are broadly classified as polar and non-polar in this work. The  $\sigma$ -profiles of some representative polar solutes (figures 4 and 5) and non-polar solutes (figures 6 and 7) are provided.

Polar compounds generally have portions of their sigma profile in both the hydrogen donor and hydrogen acceptor regions of the  $\sigma$ -profiles. Alcohols, in particular (figure 4) have peaks in the non-hydrogen donor region and a small of the  $\sigma$ -profile in the hydrogen donor zone and hydrogen acceptor zone. Water is another example of a polar compound. It has  $\sigma$ -profiles distributed in all the three regions of the sigma profile.

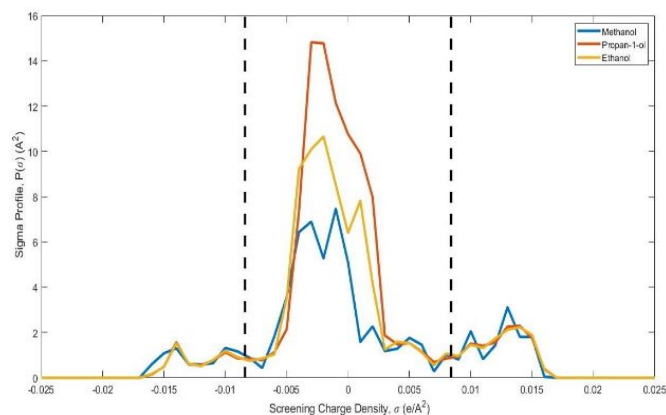


Figure 4: Sigma profiles of alkanols

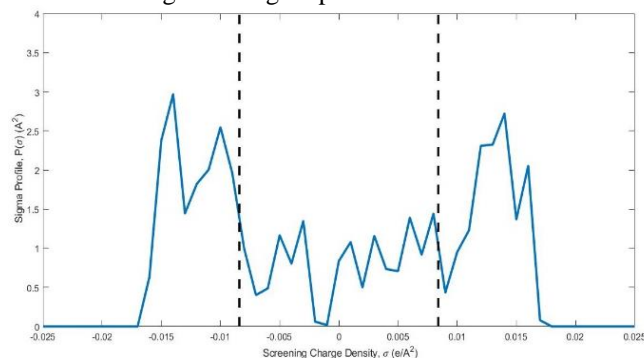


Figure 5: Sigma Profile of water

The  $\sigma$ -profiles of weak-polar compounds lie almost completely in the non-hydrogen bonding region. Hydrocarbons generally exhibit this kind of  $\sigma$ -profile. For example, 1-heptyne and 1-hexyne in figure 6 have a very small part of the  $\sigma$ -profiles lying in the acceptor and donor regions. 1,3 dimethylbenzene, benzene, styrene and thiophene in Figure 7 have  $\sigma$ -profiles almost completely in the non-hydrogen bonding region.

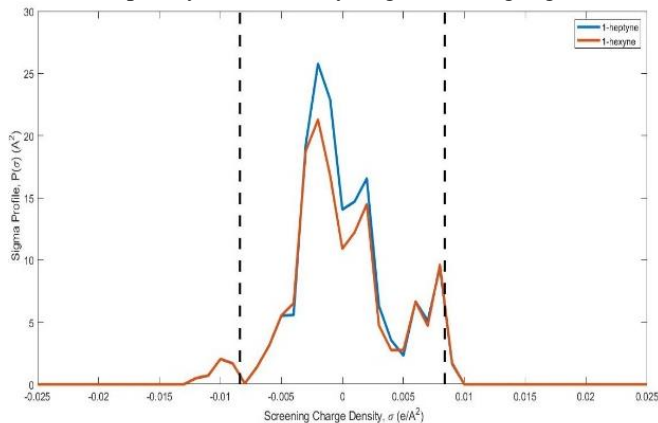


Figure 6: Sigma profiles of 1-heptyne and 1-hexyne

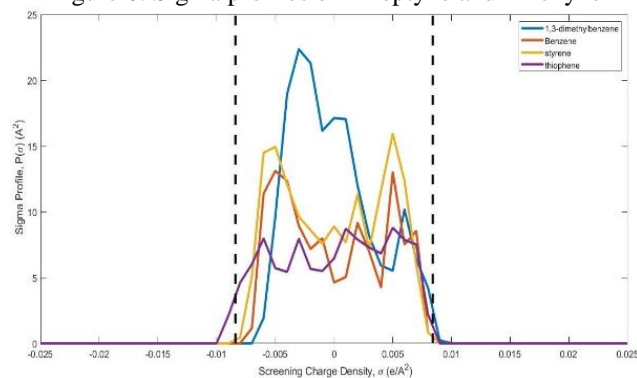


Figure 7: Sigma profiles of aromatics

## 5.2 Optimization and Regression

Figure 8 is the parity plot of experimental data to the predicted results using the original COSMO-SAC model. The original COSMO-SAC model gave poor predictions as compared to the experimental values. The ARD of the original model for 414 data points was found to be 6959%. This is mainly since the original COSMO-SAC model parameters were not fitted with experimental data for ionic liquid systems. Moreover, the original COSMO-SAC model was not robust enough to account for the hydrogen bonds and other inter-atomic and inter-molecular forces. The need to modify the model became clear if further reduction in ARD was to be expected, hence the modification of the original model as seen in equation (9).

Table 3: Optimization of modified COSMO-SAC model

Parameters	$a_{eff}(\text{\AA}^2)$	$C_{HB}(\text{kcal}\text{\AA}^4\text{mole}^{-1}\text{e}^{-2})$	$Q(\text{\AA}^2)$	$r(\text{\AA}^3)$	$\sigma_{HB}(\frac{\text{e}}{\text{\AA}})$	$C_1$	$C_2$	$C_{ne}$
Initial	7.50	85580	79.53	66.69	$8.4 \times 10^{-3}$	0.10	1.20	0.10
Optimal	7.65	85580	236.61	3.11	$8.4 \times 10^{-3}$	$3.415 \times 10^{-14}$	1.278	$5.06 \times 10^{-2}$

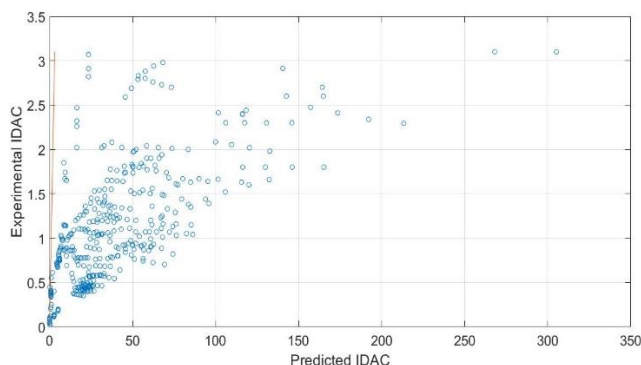


Figure 8: Comparison between experimental data and predicted results by the original COSMO-SAC model

In fitting the modified model,  $C_{hb}$  and  $\sigma_{hb}$  were made constants as they did not change after parameter optimization. Hence, only  $a_{eff}$ ,  $q$ ,  $r$ ,  $C_1$ ,  $C_2$ , and  $C_{ne}$  were optimized (Table 3). Significant improvements were observed as an ARD of 21% was obtained, as seen in the regression table (Table 4).

Table 4: Regression for COSMO-SAC model

Model	$R^2$	$R^2_{adj}$	RMSE	ARD (%)
Original COSMO-SAC	0.024	0.012	0.685	6959
Modified COSMO-SAC	0.916	0.915	0.20	21

The same data points were used in the reparametrization presented in figures 8 and 9 (The full data used in this work can be found in the appendix file file). Figure 8, in comparison with figure 9, shows a better fitting of the predicted IDAC values (blue circles) and experimentally determined IDAC (orange line). This clearly indicates an improvement in accuracy of the model because of our modifications. Therefore, the optimal values of  $a_{eff}$ ,  $q$ ,  $r$ ,  $C_1$ ,  $C_2$ , and  $C_{ne}$  to be used in the modified model from this work can be found in Table 3.

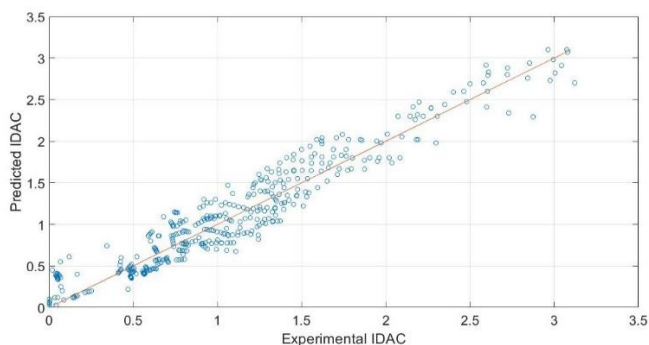


Figure 9: Parity plot for predicted (blue circles) IDAC from the optimized model.

The segment interaction parameters  $C_1$  and  $C_2$  are empirical parameters.  $C_1$  is included in the model to account for the Coulombic force, which is the sum of electrostatic and van der Waals interactions on ionic liquid. Interestingly, the value of  $C_1$  which is  $3.415 \times 10^{-14}$  is close to the value of coulombic constant for ionic liquids, as proposed by Shi *et al.*, (2017). The physical significance of  $C_2$  is unclear, but it serves as a scaling factor for the hydrogen bonding coefficient  $C_{hb}$ .

In terms of parameter magnitude, the values of the optimal parameters suggest that the electrostatic term in the model contributes little or is insignificant to this model. The charges on cations and anions of IL are generally delocalized over the surface of the ion. Indeed, it appears to be one of the necessary conditions for ionic liquids that no polarity hotspots are present since this would lead to aggregation of ions and subsequently to crystallization (Klamt, 2005). Thus, for IL systems, it appears that electrostatic interaction does not play a major role. However, this is not the case for polarity, as shall be seen in the next section.

Non-electrostatic interactions play a role in the form of long-range intermolecular force. In the original work published by Lin and Sandler (2002) it was assumed that the non-electrostatic interactions cancel out.  $C_{ne}$  was introduced to test this assumption and evaluate the physical importance of the term. The value of  $C_{ne}$  shows that the contribution of the non-electrostatic term is small but does not cancel out.

### 5.3 ARD based on Solute Chemical Groups

A closer look at the ARD for the modified model for the various chemical groups indicates that although the ARD for the model is 21%, the ARD of the solutes differs with the chemical group (figure 10). In terms of the lowest ARD, alkynes, nitriles, and aromatics have the lowest ARD, while pyridine, alcohol and water had the highest ARD.

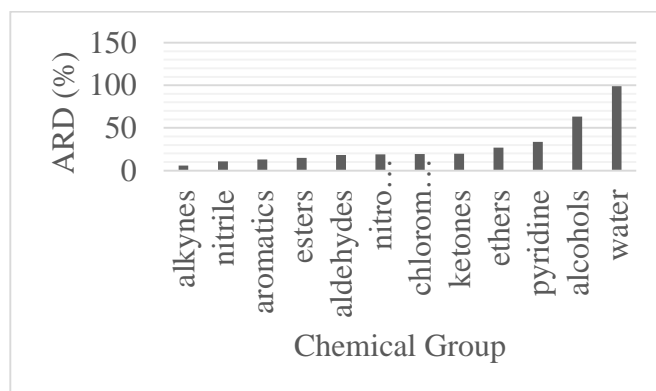


Figure 10: ARD for the various chemical groups used in the curve fitting.

Chemical groups have generally been known to have varying polarity ranking, as described by Ophardt (2003). It can be seen

from the polarity ranking of some organic solutes used in this work (figure 11) that there is a relationship between the ARD of the solutes and polarity. It appears that solutes with higher polarity have a higher ARD and lower prediction accuracy with this model, while those with lower polarity have a lower ARD and higher prediction accuracy.



Figure 11: Polarity ranking and increasing prediction accuracy of solutes in this work.

## 6. Validation of Modified Model

### 6.1 IDAC of new systems

To validate the modified model, the ARD of 29 data points which were not included in the parameter optimization, formed using 1 new cation, 1 old cation and 2 new anions (Table 5), was computed using the modified model. The ARD value of 18.07% indicates (Table 6) that the model can better handle other ionic liquid systems not included in the parameter optimization with a more reasonable level of accuracy than the original COSMO-SAC 2002. Unfortunately, the  $R^2$  and  $R^2_{adj}$  are not so good.

One reason for the poor regression values might be the insufficient robustness of the model in terms of hydrogen-hydrogen and hydrogen-non-hydrogen bonding, like is seen in other modified models (e.g., COSMO-SAC 2010). It will be interesting to see the effect of implementing the strategy used in this work for other modified models with more elaborate hydrogen and non-hydrogen interaction modelling. However, this work is limited in scope to COSMO-SAC 2002, as explained in the introduction. For more details on the data points used in the validation, please check the appendix file.

Table 5: Cations, anions and solutes used in the validation of the modified model

SOLUTES	IL CATIONS	IL ANIONS
ethyl ethanoate	1-butyl-1-methyl-pyrrolidinium	tetracyanoborate
dichloromethane	1-butyl-1-methyl-pyrrolidinium	tetracyanoborate
1,3-dimethylbenzene	1-butyl-1-methyl-pyrrolidinium	tetracyanoborate
Ethylbenzene	1-ethyl-3-methylimidazolium	mesylate
acetone	1-ethyl-3-methylimidazolium	mesylate
butanone	1-ethyl-3-methylimidazolium	mesylate
benzene	1-ethyl-3-methylimidazolium	mesylate

Table 6: Summary of ARD (%) for the validation

MODEL	DATA POINTS	$R^2$	$R^2_{adj}$	RMSE	ARD (%)
COSMO-SAC (2002)	29	0.3424	0.1630	204.204	3248.88
Modified COSMO-SAC	29	0.396	0.231	1.569	18.07

### 6.2 Henry's Constant

Henry's constant computed using the COSMO-SAC model from this work was compared to experimental values, as well as the values from COSMO-SAC 2010, as reported by Lee *et al.*, (2015) and the result is graphically shown in figure 12.

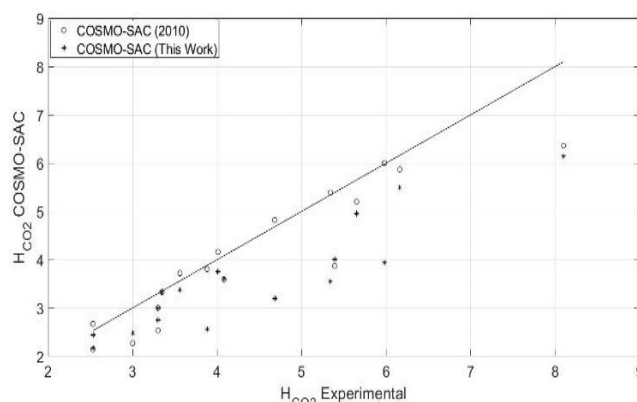


Figure 12: Experimental and COSMO-SAC predicted (this work and COSMO-SAC 2010) plot of Henry's constant.

Although COSMO-SAC 2010 has a different hydrogen bonding model, it was observed that the accuracy of the model from this work was not very far off from that of COSMO-SAC 2010. The COSMO-SAC model from this work has ARD value of 17.2% for 17 data points, as against COSMO-SAC 2010 which has ARD of 9.8%.

It is important to note that CO<sub>2</sub> is not among the systems used to fit the new model parameters of the COSMO-SAC model from this work. The modified model was tested for Henry's law constant for CO<sub>2</sub> in the ionic liquids BMIM-TF<sub>2</sub>N and EMIM-TF<sub>2</sub>N (figures 13 and 14 respectively) between 280 to 500K. The model performs reasonably well at temperatures below the critical temperature of CO<sub>2</sub>, which is 304.15K (31°C). The model tested for temperatures above the critical temperature of CO<sub>2</sub> clearly shows a significant deviation from the experimental values, as seen in figures 13 and 14.

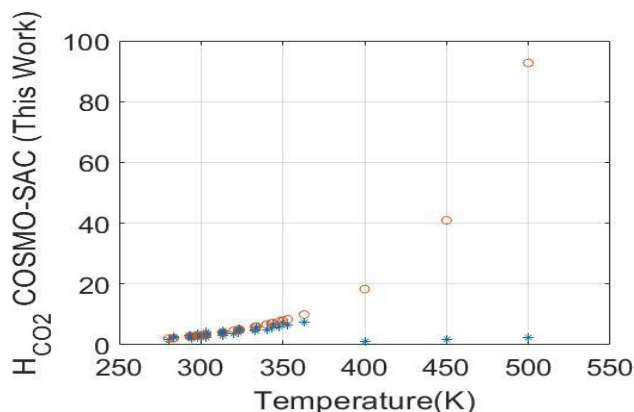


Figure 13: Experimental (blue asterisk) and predicted (this work, red circles) Henry's constant versus temperature for CO<sub>2</sub> in BMIM-TF<sub>2</sub>N

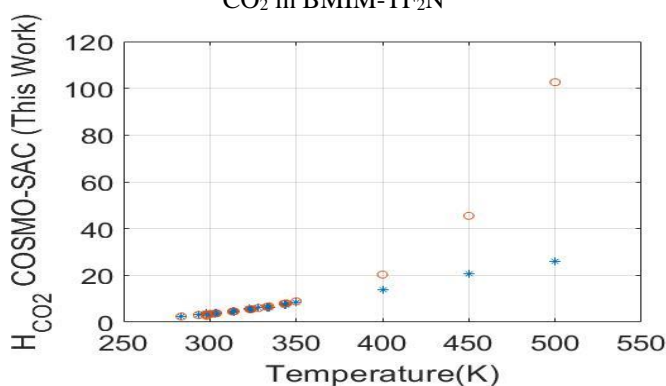


Figure 14 Experimental (blue asterisk) and predicted (this work, red circles) Henry's constant versus temperature for CO<sub>2</sub> in EMIM-TF<sub>2</sub>N

## 7. Conclusion

Modifying the exchange energy of COSMO-SAC 2002 model and fitting the model parameters with experimental data improves the accuracy of COSMO-SAC for binary systems of solute in ionic liquid. The optimal values for the parameters  $a_{eff}$ ,  $q$ , and  $r$  in the modified model from this work have been determined to be  $7.649 \text{ \AA}^2$ ,  $236.61 \text{ \AA}^2$  and  $3.111 \text{ \AA}^3$ , respectively. Values of  $C_{hb}$  and  $\sigma_{hb}$  remain 85580 and  $8.4 \times 10^{-3}$  respectively as in the original model. The parameters  $C_1$ ,  $C_2$  and  $C_{ne}$  introduced to the model have been determined to be  $3.415 \times 10^{-14}$ , 1.278 and  $5.06 \times 10^{-2}$  respectively.

The COSMO-SAC model from this work has a lower ARD of 21% as compared to 6959% from the original COSMO-SAC model. Furthermore, validation of the modified model with new data points not used in the reparametization shows that the model can be used for predicting IDAC of ionic liquid systems not included in the model reparametization, especially when the solutes have low polarity.

The model has a higher accuracy for solutes that have lower polarity, such as hydrocarbons than for those that have higher polarity like water and alcohols.

The COSMO-SAC model from this work gives a reasonable estimate of Henry's constant for CO<sub>2</sub> in the ionic liquids BMIM-TF<sub>2</sub>N and EMIM-TF<sub>2</sub>N below the critical temperature of CO<sub>2</sub>.

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