On the volatility of aromatic hydrocarbons in ionic liquids: Vapor-liquid equilibrium measurements and theoretical analysis

Emilio J. González[a], José Palomar[b],[*] Pablo Navarro[c], Marcos Larriba[b], Julián García[d], and Francisco Rodríguez[d]

[a]*Departamento de Ingeniería Química Industrial y del medioambiente, Universidad Politécnica de Madrid, E-28006 Madrid, Spain*
[b]*Sección de Ingeniería Química (Dpto. Química Física Aplicada), Universidad Autónoma de Madrid, E–28049 Madrid, Spain.*
[c]*CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal*
[d]*Department of Chemical Engineering, Complutense University of Madrid, E–28040 Madrid, Spain.*

[*] To whom correspondence should be addressed. Tel.: +34 91 497 6938

E-mail address: pepe.palomar@uam.es (Jose Palomar).

Abstract

The use of ionic liquids (ILs) as solvent in the liquid-liquid extraction of aromatic compounds is one of their most studied applications. Nevertheless, the recovery of the extracted hydrocarbons has been much less investigated, being a required task to complete the global separation process. Taking into account the negligible vapor pressure of the ILs, this step could be easily carried out by flash distillation, which requires the study of vapor-liquid equilibrium (VLE). In order to study this topic deeper, in this work a systematic analysis of the VLE and vapor-liquid-liquid equilibrium (VLLE) data for {aromatic hydrocarbon + IL} binary mixtures was carried out, from both an experimental and computational point of view. For that, new experimental VLE and VLLE data of 24 {toluene + IL} binary mixtures were

measured at 323.15 K using a technique based on the static headspace gas chromatography (HS-GC), providing relevant information on the toluene retained in the liquid depending on the cation/anion structure of the IL in the mixture. Furthermore, the quantum chemical Conductor-like Screening Model for Real Solvents (COSMO-RS) method was applied to better understand the structure-property relationship determining the phase behavior of {aromatic hydrocarbon + IL} binary systems. First, the suitability of COSMO-RS to predict VLE and VLLE data of {toluene + IL} binary mixtures was evaluated by comparison to 225 experimental data at 323.15 K, including 24 different ILs over the whole composition range. Valuable conclusions were achieved respect to the molecular model of IL needed to adequately predict VLE and VLLE data of the {aromatic hydrocarbon + IL} binary mixtures. Once the computational approach was stated, COSMO-RS methodology was used to analyze the influence of the intermolecular interactions between the toluene and the IL component on the phase behavior of their mixtures. As a result, COSMO-RS was demonstrated as a useful tool for the rational design of ILs with optimized properties for the separation of aromatic + aliphatic hydrocarbon binary mixtures, considering both liquid-liquid extraction and solvent regeneration steps.

Keywords: Ionic liquids; toluene; aromatic hydrocarbons, VLE; HS-GC; COSMO-RS

1. Introduction

To date, the use of ionic liquids (ILs) as solvents in the liquid-liquid extraction of aromatic hydrocarbons is one of the most studied applications in the field of the separation processes, as evidenced by the large number of references that can be found in the literature. Most of the works are based on the experimental determination of liquid-liquid equilibrium (LLE) data for {aliphatic + aromatic + IL} ternary systems, after which the ability of the ILs to extract aromatic hydrocarbons is evaluated through the selectivity and solute distribution ratio values [1-20]. In most cases, experimental LLE data are also correlated using thermodynamic models, mainly the NTRL equation. Usually, the aromatic compounds studied are

benzene, toluene, ethylbenzene and xylene isomers [3,5,6,11,15-18] while the aliphatic hydrocarbons include linear alkanes (such as hexane, heptane, and octane), and cycloalkanes (such us cyclohexane and cyclooctane) [11,18]. Regarding hydrocarbon mixtures, the most common is that composed of heptane and toluene, which has been widely considered as model to study this kind of systems [1,2,4,7,9,12-14,19,20]. Concerning the ILs applied as extraction solvents, those based on the imidazolium and pyridinium cationic families have been broadly explored, mainly in combination with bis(trifluormethylsulfonyl)imide (NTf2-) [5.6,8,9,11,15] although other anions including borate [12], phosphate [16] alkylsulfate [1,2,20], sulfonate [19], nitrate [10], or cyano [3,7,13] have been recently proposed. Many of these studies were focused on evaluating the effect of the cation substituents on the LLE. In particular, the initial goal was to analyze the impact of the alkyl chain length [2,8,9,10-15,20] on the phase equilibrium behavior; nevertheless, recent studies have also addressed the effect of including functional groups as hydroxyl-, benzyl-, or allyl-, in order to design functionalized ILs for selective separation of aromatic and aliphatic hydrocarbons [5-7]. Furthermore, the current trend is towards studying more complex mixtures such as quaternary systems or synthetic gasoline models [21-24] as well as using binary mixtures of ILs as solvent [23-25].

In general, the results obtained are quite promising, but they also indicate that the extraction capacity of the ILs as solvents is strongly affected by their ionic structure. Due to their high aromatic character, imidazolium- and pyridinium-based ILs have been the most studied ILs in the extraction of aromatics. In general, the typical substituents of these cations consist of alkyl groups, although new functional groups such as benzyl, vinyl or hydroxyethyl are being incorporated, which opens new opportunities [5,6]. For instance, Ebraimi et al. [6] concluded that the addition of a hydroxyethyl group to imidazolium cation significantly enhances the performance of the ionic liquid in terms of selectivity. An increase in the length of the alkyl chains in imidazolium or pyridinium based-ILs caused a rise in the aromatic distribution ratios but the opposite effect was observed in the values of aromatic/aliphatic selectivities [8-14].

The anion structure also has a significant effect on the extraction properties of ILs in the separation of aromatic hydrocarbons from aliphatic phase. High values of aromatic distribution ratios were obtained employing ILs formed by the NTf_2, BF_4, FAP, and $FeCl_4$ anions [9,12,16,18], whereas quite large aromatic/aliphatic selectivities were observed for ILs composed of hexafluorophosphate (PF_6), tris(pentafluoroethyl)trifluorophosphate (FAP), hydrogen sulfate (HSO_4), tricyanomethanide (TCM), dicyanamide (DCA), tetrathiocyanatocobaltate ($Co(SCN)_4$) or thiocyanate (SCN) anions [2,4,5,15-20,22].

Despite the significant work made in this field to date, the above mentioned works are specifically focused on the liquid-liquid extraction process, leaving aside the recovery of the hydrocarbons from the IL-rich phase (extract). Since ILs have negligible vapor pressures, the selective separation of the extracted hydrocarbons from the IL is considered easily performed by evaporation [26]. However, the vapor-liquid-liquid phase behavior of hydrocarbon + IL mixture may mainly determine the capital investment and operating costs [27, 28]. Therefore, new information – both experimental and theoretical – concerning the vapor liquid equilibrium (VLE) and the vapor-liquid-liquid equilibrium (VLLE) of the {aliphatic + aromatic + IL} systems is of a great interest, in order to improve our understanding of this field.

Although enough information on VLE for systems involving ILs can be found in the literature [4, 29-48] these works mainly report experimental data for ionic liquid mixed with polar solvents such as alcohols or water. The number of experimental VLE data concerning mixtures containing hydrocarbons and ILs has substantially increased in recent years but it remains scarce [4,39-48]. As it is known, this information data can be obtained using dynamic or static methods. In general, the experimental VLE determination of totally miscible mixtures is usually conducted by isobaric and dynamic methods. Nevertheless, since ILs are quite viscous and their mixtures with hydrocarbons are rarely miscible over the whole composition range -what could complicate the mixing process- the use of a static and isothermal determination is a good option. In the particular case of the aromatic recovery from ILs, this is not the miscibility but it is the high concentration of the IL that implies a clear benefit of static techniques instead

of dynamic ones. Accordingly, a static and isothermal method based on the headspace – gas chromatography (HS-GC) technique [49] was used in this work to obtain the experimental VLE data for systems containing hydrocarbons and ILs. This technique also requires a smaller quantity of sample than dynamic methods, which accelerates the equilibrium and drastically reduces the chemicals consumption. This latter is very important taking into account the high current price of the ILs. In the last years, we have published several works concerning the experimental determination of VLE data for systems containing *n*-heptane, toluene and ILs [4, 43-48] using this technique in a satisfactory way. These works report VLE data using both pure ILs (tricyanomethanide-, or dicyanamide, or thiocyanate-, or bis(trifluomethylsulfonyl)imide-based ILs), and IL/IL or IL/inorganic salt mixtures as mass agent. The obtained results show that: i) the presence of ILs results in a considerable enhancement of the relative volatility of *n*-heptane from toluene.; ii) the relative volatilities achieved using mixture of ILs as mass agent are intermediate between those achieved using pure ILs; iii) the use of IL/inorganic mixtures as entrainer does not get improve the high relative volatility of *n*-heptane from toluene achieved with pure ILs. Although this information is very useful, it is not enough to establish general conclusions for ILs in general, being necessary to evaluate a higher and more representative sample of ILs to get more knowledge about the phase behavior of these systems.

In the research on IL potential application, one main first stage is the selection of the cation-anion combination, which confers the required properties to the IL solvent. In this context, *a priori* computational methods capable of predicting thermodynamic data of IL-based systems may be of great utility. The quantum-chemical approach COSMO-RS has demonstrated to present a general suitability to describe thermodynamic properties in systems containing ILs [50], including gas-liquid (GLE) [51-54], vapor-liquid (VLE) [55-59], liquid-liquid (LLE) [60-65] and solid-liquid (SLE) [66-70] equilibrium data. In fact, COSMO-RS has been applied with success to predict the LLE [62,63,65,71-74] and VLE diagrams

[27, 75-77] involved in the separation of {aliphatic + aromatic} systems by using IL as extracting agents. Predictions from COSMO-based models have been recently applied to the conceptual design of the two main unit operations –liquid-liquid extraction and vacuum distillation- proposed to separate aromatic and aliphatic hydrocarbons with ILs [27,28,75]. These studies indicated the convenience of considering both separation stages when selecting the best IL as extracting solvent and, as consequence, the importance of the availability of LLE and VLE data. An additional advantage of the physically-founded COSMO-RS theory is that it provides a better understanding of the fluid system behavior from a molecular point of view. For example, excess enthalpy (H^E) predicted by COSMO-RS has been demonstrated a valuable thermodynamic property to analyze the mixture behavior of ILs with organic compounds. Relationships between H^E values and GLE, VLE, LLE and SLE data have been systematically established [51,52,65,66,67,73,78]. Since COSMO-RS method estimates the contribution of the intermolecular interactions between the components to the excess enthalpy of the mixture, this theoretical information can be consistently used to design ILs with desired properties for specific applications [51-53, 65,79], *i.e*. ILs that minimize the energy expenses of solvent regeneration stage.

The main goal of this work is to perform a systematic study of the VLE of {aromatic hydrocarbon + IL} binary mixtures, to accomplish this relevant information required for the potential development of new separation process of {aromatic + aliphatic} hydrocarbon mixtures based on IL extracting solvents. For this purpose, firstly, new experimental VLE data for 24 {toluene + IL} binary mixtures were measured at 323.15 K by HS-GC. Although this work is mainly focused on the VLE region, experimental data were obtained in a wide composition range, including the saturation zone in which two liquid-phases (VLLE) are observed. Toluene was taken as a reference of aromatic hydrocarbon. The toluene – IL interaction is a simple but useful approach to understand the aromatic – IL interactions in the phase behavior. In fact, several works have used this simplified model to study the phase behavior - LLE and VLE - of this kind of mixtures [2,4,7,9,12-14, 43-47]. The ILs included in this work was selected -among those commonly

proposed based on their favorable LLE data- to evaluate the effect of the ionic structure (cation, anion and substituents) on the VLE of {toluene + ionic liquid) mixtures [1-16]. For that, a total of 24 ILs were included, involving several pyridinium and imidazolium-based cations with borate- (BF_4), cyano- (SCN, DCA), imide- (NTf_2), sulfate- (ESO_4, MSO_4, HSO_4) and sulfonate- (MSO_3) based anions. Secondly, COSMO-RS simulations were carried out to complement the analysis of VLE phase behavior of {toluene + IL}. As preliminary step, COSMO-RS capacity to predict VLE and VLLE data of the mixtures of interest was validated by comparison to the experimental data reported in this work, evaluating two alternative molecular models (ion-pair and independent ions) to simulate the IL compound in the mixture. Once the computational approach was validated and confirmed that provide a good description of the experimental VLE/VLLE data, COSMO-RS method was applied to find a theoretical justification of the observed experimental trends. The changes of the volatility of toluene in the binary mixture with the IL structure were successfully analyzed in terms of the different intermolecular interactions between the IL and the aromatic compound. Current systematic study provides new insights on the phase behavior of {aromatic compound + IL} mixture, relevant for the design of the separation process of extracted components by distillation, stage needed for the required IL solvents regeneration and aromatic product purification.

2. Materials and methods:

2.1. Chemicals

All ILs used in this work were supplied by Iolitec GmbH (Germany) and toluene was purchased from Sigma-Aldrich. The abbreviation, name, CAS number and specifications of the chemicals included in this article are reported in Table 1. All of them were used as received without any further

treatment. In order to avoid water absorption, chemicals were stored in a desiccator in their original tightly closed bottles and the handling of the ILs was made in a glove box filled with dry nitrogen.

2.2. Apparatus and procedure

In the present work, isothermal VLE data for {toluene + ionic liquid} binary mixtures have been measured at T = 323.15 K using the HS-GC technique aforementioned introduced. Specifically, an Agilent GC 7890A equipped with a flame ionization detector (FID) and an HP-5 Agilent column is coupled to an Agilent HS 7697A injector that uses a loop system to extract the vapor sample. Additional details are available in our previous work [43]. Key parameters for Agilent GC 7890A are reported in Table 2.

Binary mixtures containing toluene and each ionic liquid were prepared by mass over a wide composition range, including the immiscible region. For this, a Mettler Toledo XS 205 balance with a precision of ± 10^{-5} g was used. Firstly, the ionic liquid and then toluene were added into 20.0 mL vials. The final volume in feed was fixed in 1.0 mL to facilitate the evaporation of toluene and to reduce the equilibration time. Once the vial was sealed, the mixture was vigorously mixed using a Labnet Vortex Mixer and then inserted in the oven of the HS injector at 323.2 K for 2 h. After the phase equilibrium was reached, a vapor sample was taken by the sampling device of the HS injector and, then, the toluene peak area (A_i) is obtained by GC for each experiment.

For all experiments included in this work, the vapor composition is pure toluene, whereas the partial pressure (p_i) of toluene was calculated as follows [49]:

$$p_i = \frac{p_i^0 \cdot A_i}{A_i^0} \quad (1)$$

where A_i^0 is the peak area developed by 1.0 mL of pure toluene in feed at the same equilibration temperature of 323.2 K, and p_i^0 denotes the saturated vapor pressure of toluene taken from the literature [80].

Finally, the toluene and IL liquid mole fractions (x_i) for each of the {toluene + ionic liquid} systems were calculated as follows:

$$x_i = \frac{z_i \cdot F - \left(P_i \cdot V_G / R \cdot T\right)}{\sum_{i=1}^{2}\left(z_i \cdot F - \left(P_i \cdot V_G / R \cdot T\right)\right)} \quad (2)$$

where z_i denotes the mole fraction of the component i in the VLE feed (1 for toluene, and 2 for the IL), F is the molar amount of the feed, and V_G refers to the vapor (headspace) volume of the vial, which was 19.0 mL for all runs done.

Given the high price of the ILs and taking into account the results obtained in previous works concerning the recovery and reuse of ILs [4,5], the experimental data were obtained using fresh and recovered IL. The regeneration of the IL was carried out following the same procedure previously published [4]. Briefly, the IL was regenerated in a Büchi Glass Oven B-585 connected to a Büchi Vacuum Pump V-700 for 36 h at (363 ± 1) K, 100 kPa, and 50 rpm. The purity of the recovered IL was tested by comparison of the density and viscosity values of fresh and recovered IL.

2.3. Computational Details

COSMO-RS calculations were carried out following a multistep procedure. First, the software Gaussian09 [81] was used for the quantum-chemical calculation to generate the COSMO files for each compound studied. For this purpose, the molecular geometry for each compound was optimized at B3LYP/6-31++G** computational level in the ideal gas phase. Vibrational frequency calculations were performed to confirm the presence of an energy minimum. Ion-pairs [CA] and independent ions [C+A] were used as molecular model to simulate IL compounds in COSMO-RS calculations. Once the molecular models were optimized, Gaussian09 was used to compute the COSMO files. The ideal screening charges

on the molecular surface for each species were calculated by the continuum solvation COSMO model using the BVP86/TZVP/DGA1 level of theory. Subsequently, the COSMO files were used as an input in the COSMOthermX [82] code to calculate the thermodynamic properties, as LLE data, activity coefficients of the components and excess enthalpy of the mixtures. In COSMO-RS model, the excess enthalpy (H^E) of a binary mixture is obtained by the algebraic sum of three contributions associated to electrostatic-*misfit* (*MF*), Van der Waals (*vdW*) and hydrogen bond (*HB*) intermolecular interactions. According to our chosen quantum method, we used the corresponding parameterization (BP_TZVP_ C21_0108) that is required for the calculation of physicochemical data and that contains the intrinsic parameters of COSMOtherm.

3. Result and discussion

3.1. Experimental VLE and VLLE data for {toluene+ IL} mixtures

In order to carry out a systematic study about the effect of the ionic liquid structure on the phase behavior of {toluene (1) + ionic liquid (2)} binary mixtures, VLE and VLLE data were experimentally measured at 323.2 K using the above described HS-GC technique. The obtained results are reported in Table 3 and the corresponding *p-x* diagrams are plotted in Figures S1-S4, available as Supporting Information. For comparison purpose, VLE data for the system {toluene (1) + [EMim][DCA] (2)} taken from the literature [43] were also included in Table 3. In order to facilitate the analysis and interpretation of the results, a simplified *p-x* diagram, in which only the most representative systems were included, is plotted in Figure 1, for illustrative purpose. Experimental VLE (miscible regions) and VLLE (immiscible regions) data show that the ionic liquid structure (cation, anion and substituents) has a significant effect on the phase behavior of the studied {toluene + ionic liquid} binary systems. For one side, the partial vapor pressure (*i.e.* the volatility) of the aromatic compound in the mixture evolves from a practically

ideal behavior ([OMim][NTf_2] in Figure 1) (toluene activity coefficient equal to 1) to a strongly positive deviation from Raoult's law ([EMim][SCN] in Figure 1), progressively increasing the toluene volatility of the mixture. On the other hand, all the studied {toluene + ionic liquid} binary systems present an immiscible region (VLLE area in Figure 1), in agreement with previously reported LLE data of this kind of systems, which usually show partial miscibility [2,8,9]. This immiscible zone -which is directly related to the solubility of toluene in the ILs- strongly depends on the chemical nature of the IL. A general trend is observed: the partial miscibility of toluene in IL decreases when increasing the partial pressure of toluene in the mixture; this is, in {toluene + ionic liquid} mixtures with higher positive deviations from ideal behavior. The *p-x* diagrams for the mixtures studied in this work are strongly affected by the anion nature (Figure S4), highlighting the dominant role played by the anion on the phase equilibria. Small anion with polar character (as $[SCN]^-$) decreases the solubility of toluene in IL. On the other hand, the cation also seems to play an important role in the VLE and VLLE behaviors of {toluene + ionic liquid} system, as can be seen in Figure 1, and Figures S1-S3. In fact, the immiscibility region is slightly greater for imidazolium than pyridinium-based IL (Figures 1 and S3) and decreases when the alkyl chains increase in size and number (Figure 1 and Figures S1-S2).

Since VLE behavior will determine the recovery stage of the aromatic hydrocarbons from IL-rich phase obtained in the previous extraction stage by distillation, the analysis of the VLE data is crucial for better understanding this step and designing the most appropriate global process. In order to perform a quantitative analysis of the IL structure effects, the VLE behavior of {toluene (1) + ionic liquid (2)} binary systems was evaluated at fixed toluene composition of $x_1 = 0.1$ and 323.15 K. This molar fraction of aromatic compound was selected for two main reasons: all the studied systems show VLE diagram for this composition and it represents the typical aromatic content expected in the extract stream [83,84]. Figures 2-3 depict the partial vapor pressure (p_1) and the activity coefficient (γ_1) of the toluene in the

studied mixtures with IL at of x_1 = 0.1 and 323.15 K. The activity coefficients of toluene (γ_1) were estimated using the Raoult´s law for non-ideal solutions:

$$p_1 = x_1 \cdot \gamma_1 \cdot p_1^0 \quad (3)$$

where p_1^0 is the vapor pressure of pure toluene at 323.15 K. Therefore, at the fixed values of composition and temperature, p_1 and γ_1 are related by an unique proportional constant of 1.23 bar. Therefore, p_1 and γ_1 are reference thermodynamic parameters of the aromatic hydrocarbon volatility in the {toluene (1) + ionic liquid (2)} binary systems.

The effect of the anion and cation head group on the VLE can be analyzed and discussed from Figure 2. As can be observed, the toluene volatility in the mixture with IL is strongly affected by the anion, presenting in all cases positive deviation from ideality and increasing in the order: $[NTf_2]$ < [DCA] < [TFES] < $[ESO_4]$ < [SCN] < $[MSO_4]$ < $[BF_4]$ < $[MSO_3]$ < $[HSO_4]$. On the other hand, the partial pressure of toluene in the imidazolium-based IL [BMim][BF_4] is found slightly higher than that measured in [$^1B^3$Mpy][BF_4], related to a less ideal mixture.

The influence of the substituent of the cation on the VLE of {toluene (1) + ionic liquid (2)} binary systems for x_1 = 0.1 at T = 323.15 K is plotted in Figure 3. This figure shows that the number of substituents, their length, and their position have also impact on the VLE of these systems, but in a much less extent. Regardless of type of ILs studied, the vapor pressures and the activity coefficients slightly increase when decreasing the number of substituents or their length. For the isomer ionic liquids, the values of the vapor pressure of toluene in the mixture increase in the order: [$^1B^4$Mpy][BF_4] >[$^1B^3$Mpy][BF_4] >[$^1B^2$Mpy][BF_4].

Current results indicate that the selection of the optimal ILs for aromatic-aliphatic separation by liquid-liquid extraction should consider carefully the VLE behavior in the system, since it will be determinant in the efficiency and energy duty of the aromatic recovery/ solvent regeneration stage by distillation.

Distribution ratio (D) of aromatic compound between aliphatic-rich and IL-rich immiscible liquid phases and aromatic/aliphatic selectivity (α_{12}) of IL are thermodynamic parameters generally used to evaluate the extractive properties of ILs [3,23]. Higher D values ensure higher separation capacity and, consequently, better aromatic recovery performance in extraction column; whereas higher selectivity allows obtaining extract stream less contaminated in aliphatic and, closely related, lower energy expenses in solvent regeneration stage to obtain an aromatic product with desired purity [27,28]. A higher aromatic volatility in IL-rich phase also contributes to economize the solvent regeneration stage by distillation [75]. The experimental results obtained in this work allow obtaining a deeper insight on the extractive properties of ILs for the global aromatic-aliphatic separation process. As can be seen in Figure 4 (see experimental data from bibliography in Table S1 of Supporting Information), the volatility of toluene (1) in the binary mixture with IL (2) (for $x_1 = 0.1$ at $T = 323.15$ K) follows similar trend than the toluene selectivity in the aromatic-aliphatic-IL ternary mixture; on the contrary, the toluene volatility decreases for ILs with higher aromatic extractive capacity. These results illustrate the complexity of selecting suitable ILs for aromatic-aliphatic separation. Thus, searching for ILs which promotes higher immiscibility with aliphatic compounds would contribute to obtain aromatic product of higher purity with lower operating costs; whereas using higher separation capacity as IL design criteria would allow using lower solvent flow, what reduces the capital cost but also the operating costs in both extraction and regeneration stages.

3.2. Analysis of the VLE data by COSMO-RS methodology

In this section, a theoretical analysis of the VLE and VLLE data in {toluene (1) + ionic liquid (2)} binary systems was performed by COSMO-RS method, in order to obtain a deeper insight on the phase behavior from a molecular point of view. As first stage, the predictability of COSMO-RS approach regarding VLE and VLLE data of studied {toluene + ionic liquid} systems was validated. For this purpose two different molecular models were considered to simulate the IL component in the mixtures: i) Independent ions model (C+A) where the cation and anion are optimized independently and, as consequence, describes the IL as two charged species, with highly polarized functional groups, and does not introduce any cation-anion interaction. C+A molecular model has been applied with success to describe the thermodynamic properties of IL with compounds with relatively high polarity (ammonia [79], acetone [78], water [56], and alcohols [58]); and ii) Ion-pair molecular model (CA), where cation and anion are optimized as a whole considering the one cation with one anion. CA model has been generally probed more useful to describe IL-based systems involving non-polar compounds or gases (as aromatics [52,73,75], alkenes [53], CO_2 and N_2, [51]). In order to evaluate COSMO-RS predictions, the experimental *p* values of VLE data of the 24 studied {toluene + ionic liquid} binary systems were systematically compared to calculated *p* values by linear regression (Table 4; for more information see Table S2 in Supporting Information). Figure 5 compares the VLE COSMO-RS predictions using C+A and CA model for the {toluene (1) + ionic liquid (2)} binary systems studied in this work. As can be seen, both COSMO-RS approaches predict reasonably the experimental trends. However, C+A model generally overestimates, whereas CA model underestimates, the volatility of the toluene in the mixture. In addition, Figure 5 shows different COSMO-RS reliability to describe the VLLE of studied system using C+A and CA models. As can be seen, C+A and CA COSMO-RS approaches predict, respectively, higher and lower immiscible ranges of toluene in IL than experimental evidences. This conclusion is more evident with those systems presenting higher positive deviation from ideality. It can be concluded that C+A model overestimates the polar character of the IL and, consequently, the repulsive intermolecular interactions

with non-polar toluene compound, increasing the volatility of the later. In contrast, using CA model implies obtaining just the opposite effect: the charge compensation due to cation-anion interactions describes a less unfavorable mixing behavior of IL and toluene than what showed experimental measurements. A more quantitative analysis is obtained from statistical parameters collected in Table 4. As can be seen, the mean percentage error (MPE) are clearly lower -globally and for each systems- using CA model (global MPE: 22 %) in COSMO-RS than using C+A model (global MPE: 57%). In addition, the square correlation coefficients (R^2) from calculated-experimental *p* data linear regression using CA molecular model in COSMO-RS calculations are higher than 0.99 in most of studied cases, whereas R^2 in the 0.73-0.97 are obtained using C+A model. As consequence, following COSMO-RS analysis will be performed using ion-pair molecular model (CA) of IL, as a more adequate approach to describe the properties of aromatic hydrocarbon + IL binary mixtures.

In several previous studies [51,52,65,75,79], GLE and VLE data of IL + common compounds were successfully related to excess enthalpy (H^E) of the mixture, what implied that enthalpic term determine the properties of this kind of systems. One main advantage of COSMO-RS is that provides the contributions of the different intermolecular interactions to the H^E values, then allowing understanding the phase-behavior from a molecular point of view. Figure 6 compares the equilibrium pressure (as thermodynamic reference of toluene volatility) for x_1 = 0.1 and equimolar excess enthalpy (H^E) of the studied {toluene (1) + ionic liquid (2)} binary systems, both calculated by COSMO-RS at T = 323.15 K using CA molecular model. As can be seen, the strong positive deviation from ideality observed in these aromatic-IL systems can be clearly related to endothermicity of the mixture; *i.e.* to the repulsive intermolecular interactions of the components in the mixture or the loss of favorable interactions from the pure compounds to the mixture. {Toluene + ionic liquid} systems with higher vapor pressure are those presenting strong unfavorable polar interactions or loss of attractive hydrogen-bond (HB) interactions between the ionic component and the non-polar aromatic component. In fact, these systems with high *p*

value involve ILs presenting anion and/or cation with strong HB acceptor and/or donor groups, which confer higher polarity to IL and the capacity to form cation-anion hydrogen bonds. These {toluene + ionic liquid} systems with higher toluene volatility will be easier separated by distillation; however, is should be emphasized that corresponds to those with ILs presenting lower aromatic separation capacity but higher aromatic/aliphatic selectivity. In contrast, ILs with less polar character (composed by a big anion with delocalized charge and a cation with long alkyl chains and absence of acidic groups) allows {toluene + ionic liquid} mixtures with near ideal VLE behavior, what implied higher efforts in the solvents regeneration stage of the separation process, but correspond with IL presenting favorable separation capacity.

4. Conclusions

In this work, a systematic experimental and theoretical analysis of the vapor-liquid equilibrium of {aromatic hydrocarbon (toluene) + ionic liquid} binary mixtures (24 different ILs; 225 experimental data at 323.15 K) has been performed in order to contribute to the knowledge of ILs as extractive solvent in aromatic-aliphatic separation. COSMO-RS method predictability for VLE and VLLE data of toluene-IL systems was evaluated, proposing a computational approach (based on ion-pair molecular model for IL) which provides valuable predictions of toluene volatility in a wide sample of included ILs. Experiments and calculations reveal that the volatility of toluene in the binary mixture with IL strongly depends on the nature of the anion and, in a minor extent, the cation involved. In all cases, VLE diagram of toluene-IL system show positive deviation from ideality (Raoult's law), being this behavior determined by the loss of favorable hydrogen-bond and electrostatic intermolecular interactions when mixing the IL with the aromatic compound. Clear relationships are found between the volatility of toluene in the binary mixture with IL and the reported toluene distribution coefficient (opposite trend) and selectivity (same trend) in aromatic-aliphatic-IL ternary mixtures. It implies that the design of IL

with optimized extractive properties should carefully consider their effects on extraction and regeneration stages of aromatic-aliphatic separation process.

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Table 1. Abbreviation, name, CAS number and specifications of the pure ionic liquids

Abb.	*Name*	*CAS number*	*Specifications*		
			Purity, in mass fraction	*Halides*[b]	*Water content*[c]
[Bpy][NTf_2]	1-butylpyridinium bis(trifluoromethylsulfonyl)imide	187863-42-9	> 0.99	< 100 ppm	< 100 ppm
[Eim][NTf_2]	1-ethylimidazolium bis(trifluoromethylsufonyl)imide	353239-10-8	> 0.99	< 100 ppm	< 200 ppm
[EMim][NTf_2]	1-ethyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide	174899-82-2	> 0.99	< 100 ppm	< 200 ppm
[EMMim][NTf_2]	1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsufonyl)imide	174899-90-2	> 0.98	< 100 ppm	< 300 ppm
[PMim][NTf_2]	1-methyl-3-propylimidazolium bis(trifluoromethylsufonyl)imide	216299-72-8	> 0.99	< 100 ppm	< 200 ppm
[BMim][NTf_2]	1-butyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide	174899-83-3	> 0.99	< 100 ppm	< 100 ppm
[BMMim][NTf_2]	1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsufonyl)imide	350493-08-2	> 0.99	< 100 ppm	< 200 ppm
[HMim][NTf_2]	1-hexyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide	382150-50-7	> 0.99	< 100 ppm	< 100 ppm
[OMim][NTf_2]	1-methyl-3-octylylimidazolium bis(trifluoromethylsufonyl)imide	178631-04-4	> 0.99	< 100 ppm	< 100 ppm
[EMim][BF_4]	1-ethyl-3-methylimidazolium tetrafluoroborate	143314-16-3	> 0.98	< 2%	< 1000 ppm
[BMim][BF_4]	1-butyl-3-methylimidazolium tetrafluoroborate	174501-65-6	> 0.99	< 1000 ppm	200 ppm
[Bpy][BF_4]	1-butylpyridinium tetrafluoroborate	203389-28-0	> 0.99	< 100 ppm	< 300 ppm
[^{1}B^{2}Mpy][BF_4]	1-butyl-2-methylpyridinium tetrafluoroborate	286453-46-1	> 0.98	< 100 ppm	< 200 ppm
[^{1}B^{3}Mpy][BF_4]	1-butyl-3-methylpyridinium tetrafluoroborate	597581-48-1	> 0.99	< 100 ppm	< 500 ppm
[^{1}B^{4}Mpy][BF_4]	1-butyl-4-methylpyridinium tetrafluoroborate	34952-33-0	> 0.99	< 100 ppm	< 300 ppm
[Hpy][BF_4]	1-hexylpyridinium tetrafluoroborate	474368-70-2	> 0.99	< 100 ppm	< 200 ppm
[EMim][MSO_3]	1-ethyl-3-methylimidazolium methanesulfonate	145022-45-3	> 0.99	< 100 ppm	< 100 ppm
[EMim][HSO_4]	1-ethyl-3-methylimidazolium hydrogensulfate	412009-61-1	> 0.98	< 100 ppm	< 300 ppm
[EMim][MSO_4]	1-ethyl-3-methylimidazolium methylsulfate	516474-01-4	> 0.99	< 100 ppm	< 500 ppm
[EMim][ESO_4]	1-ethyl-3-methylimidazolium ethylsulfate	342573-75-5	> 0.99	< 100 ppm	< 100 ppm
[EMim][TFES]	1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate	880084-63-9	> 0.99	< 100 ppm	< 100 ppm
[EMim][DCA]	1-ethyl-3-methylimidazolium dicyanamide	370865-89-7	> 0.98	< 2%	< 2000 ppm
[EMim][SCN]	1-butyl-3-methylimidazolium thiocyanate	331717-63-6	> 0.98	< 2 %	< 1000 ppm
[BMim][SCN]	1-butyl-3-methylimidazolium thiocyanate	334790-87-0	> 0.98	< 2%	< 2000 ppm

[a] Nuclear Magnetic Resonance
[b] Ion Chromatography
[c] Karl Fischer

Table 2. Key parameters for Agilent GC 7890A

Inlet	523.2 K, 100:1 split
Detector	573.2 K, FID
Carrier Gas	He 3X, supplied by Praxair
Column	Agilent HP-5, 30 m x 0.32 mm x 0.25 µm
Oven	348.2 K

Table 3. Experimental VLE and VLLE data for {toluene (1) + ionic liquid (2)} Binary Systems at 323.15 K[a]

x_1	p/ kPa	x_1	p/ kPa	x_1	p/ kPa
{toluene (1) + [BMim][BF_4] (2)}		{toluene (1) + [BMim][NTf_2] (2)}		{toluene (1) + [PMim][NTf_2] (2)}	
0.0060	0.3	0.0112	0.2	0.0112	0.2
0.0765	3.5	0.1174	1.9	0.1106	2.0
0.1574	6.4	0.2239	3.7	0.2146	4.0
0.2236	8.4	0.3131	5.4	0.2988	5.7
0.3507	12.0	0.4707	8.5	0.4444	8.5
0.4136	12.2	0.5269	9.6	0.5102	9.7
0.5278	*12.3*	0.6428	11.5	0.6302	11.8
0.6260	*12.3*	0.7234	12.3	0.7096	12.3
1.0000	*12.3*	*1.0000*	*12.3*	*1.0000*	*12.3*
{toluene (1) + [BMMim][NTf_2] (2)}		{toluene (1) + [Bpy][BF_4] (2)}		{toluene (1) + [Eim][NTf_2] (2)}	
0.0122	0.2	0.0061	0.3	0.0107	0.3
0.1231	1.9	0.0748	3.7	0.1024	2.7
0.2328	3.8	0.1538	7.1	0.1945	5.2
0.3241	5.4	0.2113	9.2	0.2812	7.1
0.4776	8.2	0.3434	12.3	0.4240	10.0
0.5451	9.5	*0.4093*	*12.2*	0.4836	10.9
0.6627	11.5	*0.5251*	*12.0*	0.5932	12.3
0.7396	12.3	*0.6248*	*12.3*	*0.6884*	*12.3*
1.0000	*12.3*	*1.0000*	*12.3*	*1.0000*	*12.3*
{toluene (1) + [EMim][BF_4] (2)}		{toluene (1) + [Bpy][NTf_2] (2)}		{toluene (1) + [EMim][ESO_4] (2)}	
0.0069	0.3	0.0130	0.2	0.0064	0.4
0.0657	5.4	0.1166	1.8	0.0759	4.5
0.1300	10.2	0.2208	3.5	0.1514	8.0
0.1943	12.1	0.3103	4.9	0.2227	11.2
0.3186	*12.0*	0.4617	7.7	0.3541	12.1
0.3760	*12.3*	0.5245	8.8	*0.4187*	*12.1*
0.4856	*12.3*	0.6355	10.8	*0.5330*	*12.2*
0.5881	*12.2*	0.7279	12.3	*0.6292*	*12.3*
1.0000	*12.3*	*1.0000*	*12.3*	*1.0000*	*12.3*
{toluene (1) + [EMim][HSO_4] (2)}		{toluene (1) + [EMim][MSO_3] (2)}		{toluene (1) + [EMim][MSO_4] (2)}	
0.0034	2.0	0.0055	0.7	0.0052	0.5
0.0584	11.5	0.0657	6.5	0.0683	5.7
0.1378	11.8	0.1323	11.5	0.1384	10.7
0.2062	12.1	0.2004	12.3	0.2063	12.3
0.3108	*12.3*	*0.3229*	*12.5*	*0.3355*	*12.3*
0.3703	*12.4*	*0.3910*	*12.3*	*0.3940*	*12.3*
0.4892	*12.4*	*1.0000*	*12.3*	*0.5111*	*12.4*
0.6182	*12.4*			*0.6083*	*12.2*
1.0000	*12.3*			*1.0000*	*12.3*
{toluene (1) + [$^1B^2$Mpy][BF_4] (2)}		{toluene (1) + [$^1B^3$Mpy][BF_4] (2)}		{toluene (1) + [$^1B^4$Mpy][BF_4] (2)}	
0.0071	0.3	0.0065	0.2	0.0049	0.1
0.0812	3.9	0.0755	2.4	0.0843	2.6

0.1608	6.5	0.1642	4.9	0.1648	4.8
0.2373	9.2	0.2337	6.9	0.2401	6.8
0.3650	12.3	0.3698	10.0	0.3786	9.9
0.4348	*12.1*	0.4293	11.5	0.4368	11.1
0.5390	*12.4*	0.5370	12.3	0.5424	12.1
0.6567	*12.1*	*0.6350*	*12.3*	*0.6486*	*12.3*
1.0000	*12.3*	*1.0000*	*12.3*	*1.0000*	*12.3*
{toluene (1) + [EMim][NTf_2] (2)}		{toluene (1) + [EMim][TFES] (2)}		{toluene (1) + [EMMim][NTf_2] (2)}	
0.0092	0.2	0.0082	0.2	0.0070	0.1
0.1045	2.3	0.0825	4.4	0.1104	2.2
0.1999	4.4	0.1647	7.7	0.2104	4.3
0.2842	6.2	0.2407	10.2	0.2922	5.9
0.4308	9.2	0.3727	12.1	0.4465	8.9
0.4961	10.6	*0.4453*	*12.0*	0.5079	10.0
0.6059	12.0	*0.5491*	*12.0*	0.6347	11.7
0.6972	12.3	*0.6699*	*12.3*	0.7099	12.3
1.0000	*12.3*	*1.0000*	*12.3*	*1.0000*	*12.3*
{toluene (1) + [HMim][NTf_2] (2)}		{toluene (1) + [Hpy][BF_4] (2)}		{toluene (1) + [OMim][NTf_2] (2)}	
0.0146	0.2	0.0078	0.2	0.0134	0.1
0.1292	1.7	0.0915	2.7	0.1436	1.6
0.2440	3.5	0.1816	5.1	0.2665	3.3
0.3323	4.9	0.2562	7.0	0.3636	4.7
0.4883	7.8	0.3939	10.1	0.5196	7.6
0.5522	9.0	0.4551	11.0	0.5846	8.8
0.6589	11.2	0.5735	12.3	0.6872	10.7
0.7422	12.2	*0.6683*	*12.4*	0.7675	12.1
1.0000	*12.3*	*1.0000*	*12.3*	*1.0000*	*12.3*
{toluene (1) + [EMim][SCN] (2)}		{toluene (1) + [BMim][SCN] (2)}		{toluene (1) + [EMim][DCA] (2)}[b]	
0.0066	0.5	0.0056	0.3	0.0092	0.4
0.0312	2.3	0.0386	1.6	0.0350	1.7
0.0617	4.3	0.0764	3.0	0.0664	3.2
0.0915	6.3	0.1130	4.4	0.1204	5.9
0.1256	8.4	0.1493	5.7	0.1616	8.0
0.1339	8.7	0.1856	7.0	0.2360	10.2
0.2239	12.4	0.2531	9.1	0.3796	11.4
0.3139	*12.6*	0.3501	11.4	0.4405	11.6
0.3720	*12.4*	*0.4092*	*12.4*	0.5520	11.9
0.4781	*12.5*	*0.5223*	*12.4*	0.6500	12.0
0.5818	*12.3*	*0.6260*	*12.4*	*0.7367*	*12.2*
1.0000	*12.3*	*1.0000*	*12.3*	*1.0000*	*12.3*

[a] Standard uncertainty (u) were u(x) = 0.0001 and u(P) = 0.1 kPa
[b] From ref. [43]

Table 4. Statistical results obtained from comparison of experimental and predicted VLE data

Family	Anion	Cation	C+A model				CA model			
			N	*Linear regression*[a]		MPE(%)[b]	*N*	*Linear regression*[a]		MPE (%)[b]
				R^2	SD			R^2	SD	
Imidazolium	$[NTf_2]$	[Eim]	7	0.73	3.3	83.2	7	0.99	1.3	12.5
		[EMim]	7	0.87	1.9	51.5	7	0.99	1.5	14.5
		[EMMim]	8	0.92	1.4	37.7	8	0.99	1.5	13.6
		[PMim]	8	0.90	1.6	46.8	8	0.99	1.6	9.9
		[BMim]	8	0.91	1.5	41.8	8	0.99	1.6	12.9
		[BMMim]	8	0.94	1.3	31.2	8	0.99	1.0	12.0
		[HMim]	8	0.93	1.3	41.1	8	0.99	1.5	12.7
		[OMim]	8	0.94	1.2	39.1	8	0.99	1.3	12.4
		[Bpy]	8	0.89	1.7	53.5	8	0.96	1.0	25.6
	$[BF_4]$	[EMim]	4	0.80	3.1	38.3	4	0.99	3.2	38.3
		[BMim]	5	0.90	2.0	39.1	5	0.99	1.4	17.8
	$[MSO_3]$	[EMim]	4	0.95	1.5	24.9	4	0.93	5.0	61.4
	$[MSO_4]$	[EMim]	4	0.99	0.6	8.9	4	0.97	4.4	53.6
	$[ESO_4]$	[EMim]	5	0.94	1.6	24.1	5	0.94	1.9	36.7
	$[HSO_4]$	[EMim]	4	0.96	1.2	22.9	4	0.68	4.2	46.9
	[SCN]	[EMim]	7	0.76	3.4	73.6	7	0.79	2.7	37.5
		[BMim]	9	0.73	3.7	83.6	9	0.99	2.4	34.7
	[DCA]	[EMim]	10	0.83	3.9	126.9	6	0.99	1.9	27.6
	[TFES]	[EMim]	5	0.97	3.5	41.6	5	0.99	1.5	28.4
Pyridinium	$[BF_4]$	[Bpy]	5	0.73	3.6	83.9	5	0.99	1.8	23.4
		[Hpy]	7	0.72	3.4	82.1	7	0.99	0.5	8.8
		$[^1B^2Mpy]$	5	0.90	2.0	39.1	5	0.99	1.4	17.8
		$[^1B^3Mpy]$	7	0.82	2.7	66.8	7	0.99	1.7	16.3
		$[^1B^4Mpy]$	7	0.80	2.9	81.1	7	0.99	0.5	15.9

[a] R^2 : Square correlation coefficient; SD: Standard deviation. [b] MPE: Mean percentage error

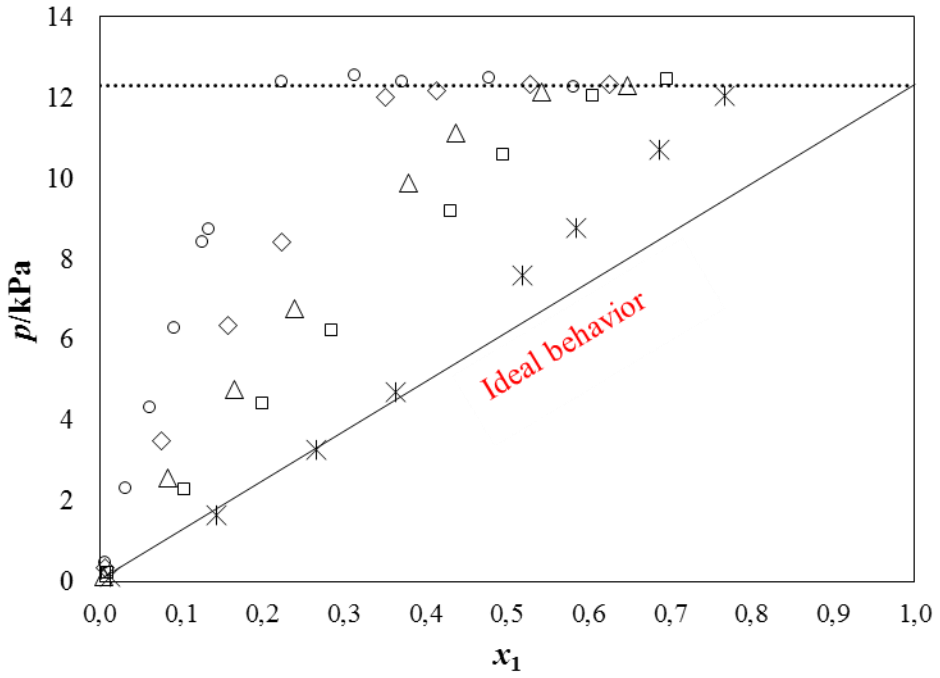

Figure 1. VLE and VLLE data for {toluene (1) + ionic liquid (2)} binary systems at T = 323.15 K. Symbols: (○) [EMim][SCN]; (◇) [BMim][BF_4]; (△) [$^1B^4$Mpy][BF_4]; (□) [EMim][NTf_2]; (∗) [OMim][NTf_2]. Dashed line shows the vapor pressure of toluene at T = 323.15 K.

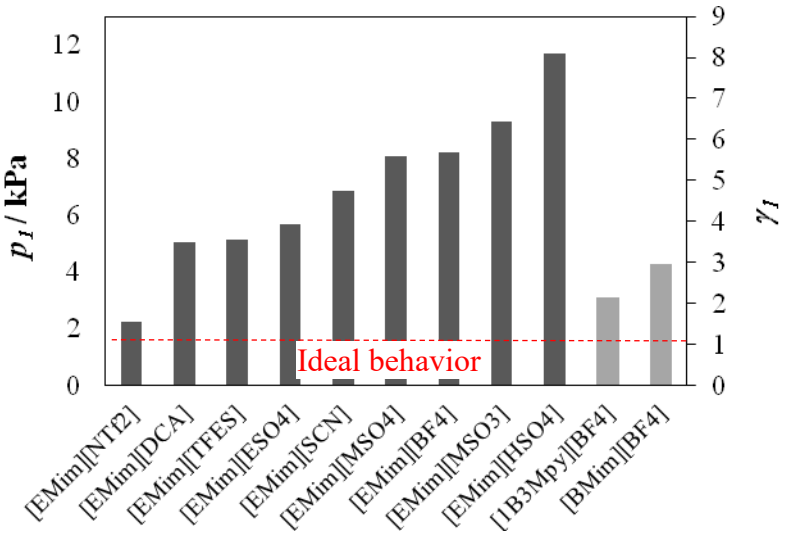

Figure 2. Effect of the nature of the anion and cation head group on the VLE for {toluene (1) + ionic liquid (2)} binary systems for x_1 = 0.1 at T = 323.15 K.

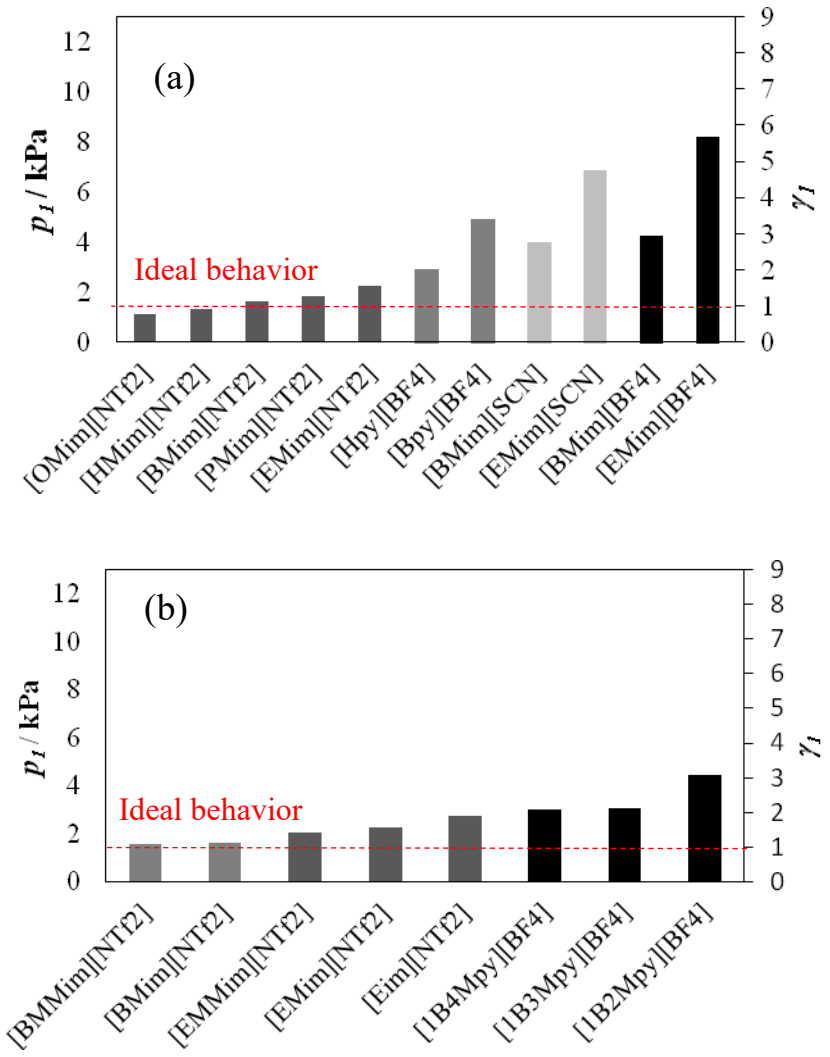

Figure 3. Effect of the substituents on the VLE of {toluene (1) + ionic liquid (2)} binary systems for x_1 = 0.1 at T = 323.15 K. (a) length; (b) number and position.

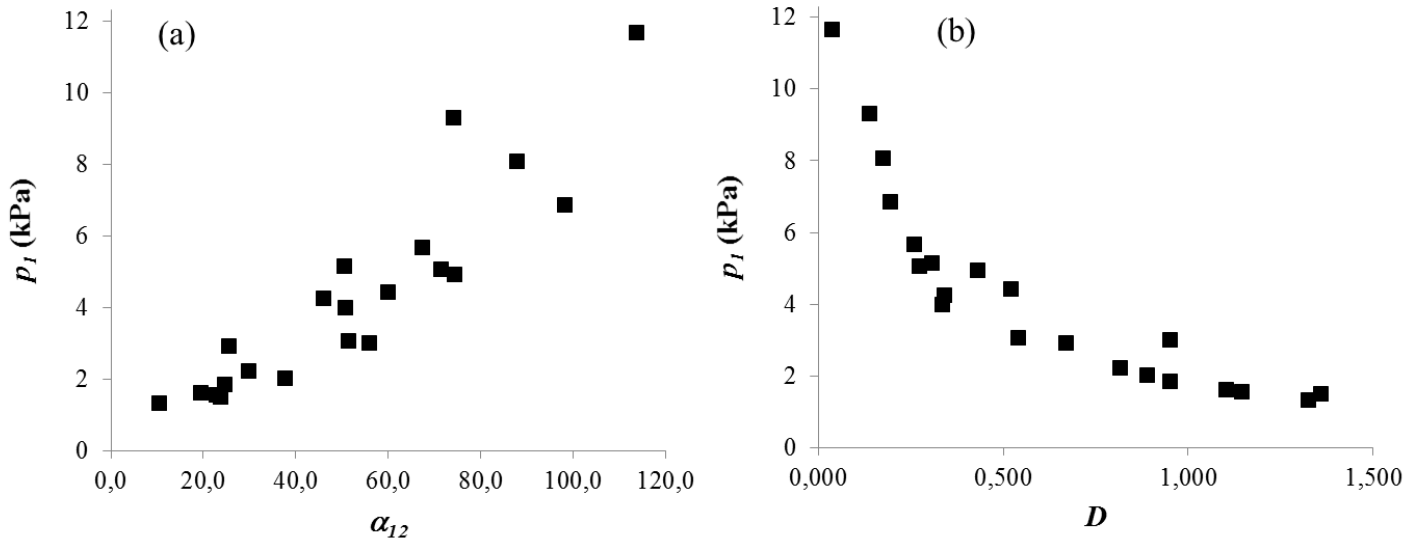

Figure 4. VLE (p_1) data *vs* LLE data of {toluene (1) + ionic liquid (2)} binary systems for $x_1 = 0.1$ at $T =$ 323.15 K. (a) Toluene/heptane selectivity (α_{12}); (b) Toluene partition coefficient (D).

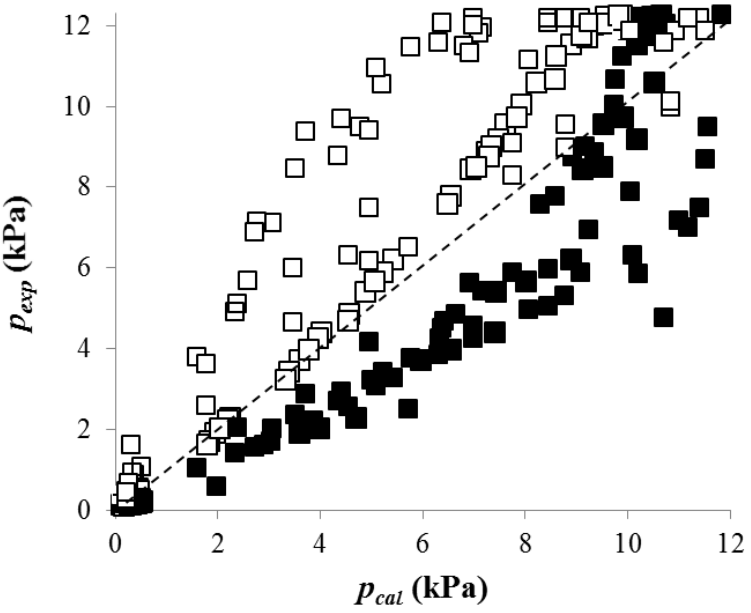

Figure 5. Experimental *vs* calculated pressures for {toluene + ionic liquid} binary systems at $T = 323.15$ K, using C+A (black symbols) and CA (white symbols) molecular models in COSMO-RS calculations.

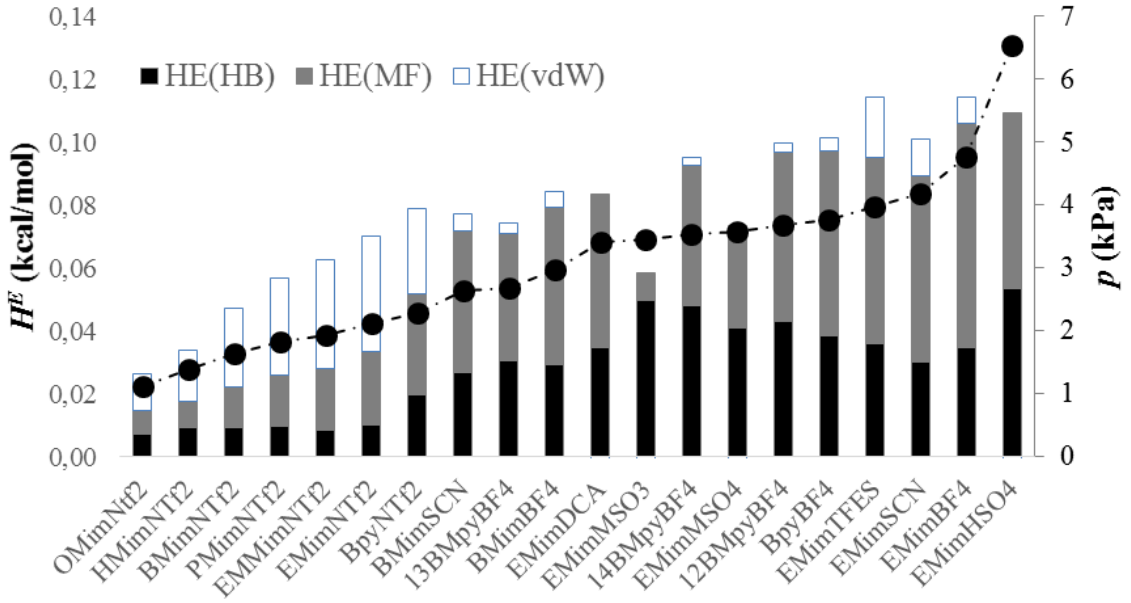

Figure 6. Toluene volatility (*p* of VLE isotherm diagram) for $x_1 = 0.1$ and equimolar excess enthalpy (H^E) of {toluene (1) + ionic liquid (2)} binary systems calculated by COSMO-RS at $T = 323.15$ K using CA molecular model.