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Characterization of bis(fluorosulfonyl)imide based ionic liquids by gas chromatography

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1 **Introduction**

2 Ionic liquids were found to be efficient solvents for different numerous separation problems
3 present in industrial processes.

4 This last decade, environmental laws impose a strong reduction of industrial discharge but
5 also enforce a “zero discharge” policy for certain pollutants that are known or suspected to be
6 persistent bioaccumulative. In chemical industry, the main separation and purification
7 processes are based on liquid–liquid extraction. This technique easy to implement has the
8 main drawback to use volatile and toxic organic solvents. In view of the current situation,
9 industrials and scientists have to rethink industrial manufacturing processes. One key should
10 be the use of cleaner extraction solvents in future extraction processes. Ionic liquids can be
11 described as the LEGO Molecules for Chemists while their physico-chemical properties are
12 adjustable by choosing an appropriate set of ions. [1-2] Nevertheless, this family of solvents
13 has also some disadvantages such as high viscosity, thermal instability and especially
14 significant toxicity. [3] Indeed, it is now well established that numerous ILs are toxic in nature
15 and their toxicities strongly depend on their structure. It was found that the anion has not an
16 important impact excepted for [Tf₂N]. [4-5] ILs with long alkyl chain length have significant
17 toxicity that may be reduced by introducing functional polar groups to this chain. From
18 toxicology and microbial degradation points of view, pyridinium ILs are more environmental
19 friendly than imidazolium ILs.

20 The use of ILs still required physico-chemical properties measurement for a better
21 understanding of these solvents in solution but also the implementation of new quantitative
22 properties-structure relationships. Our team have determined the activity coefficients at
23 infinite dilution of solutes dissolved in several 1,3-dialkylimidazolium [6–16],
24 tetraalkylammonium [17-18], N-alkylpyridinium [16], N,N-dialkylpyrrolidinium [19-20],
25 N,N-dialkylpiperidinium [14,15], tetraphosphonium [21,22], N-alkylquinuclidinium [23], and

1 1,2,3-tris(diethylamino)- cyclopropenylum [24] ILs. Our previous contributions
2 demonstrated that numerous ILs could replace conventional fluids in desulfurization or
3 denitrogenation processes in petroleum industry but also in liquid-liquid extraction of organic
4 compounds from various media. For example, bis (trifluoromethylsulfonyl)imide,
5 hexafluorophosphate and bis(fluorosulfonyl)imide based ILs were found to be efficient for the
6 extraction phenols [25-27], phenolic acids [28], carbohydrates [29-30], caprolactam [31],
7 furfural [32-33], other organic compounds [34-35] from aqueous solution and the recovery of
8 rare earth elements (36). Domanska et al have demonstrated that ILs such as trihexyl-
9 tetradecyl- phosphonium tricyanomethanide [P_{6,6,6,14}][TCM] [37], 1-decyl-3-
10 methylimidazolium tetracyanoborate [DMIM][TCB] [38],
11 dimethyldodecylphenoxyethylammonium dicyanamide [N_{1,1,12,20Ph}][DCA] and
12 dimethyldodecylphenoxyethylammonium bis{(trifluoromethyl)sulfonyl}imide [N_{1,1,12,20Ph}]
13 [Tf₂N] [39] present a specific interest for the extraction of butanol from aqueous solution.

14
15 In this work, activity coefficients of organic compounds and water in 1-butyl-1-
16 methylpyrrolidinium bis(fluorosulfonyl)imide [BMPyr][FSI], N propyl N
17 methylpyrrolidinium bis(fluorosulfonyl)imide [PrMPyr][FSI], 1-ethyl-1-methylimidazolium
18 bis(fluorosulfonyl)imide [EMIM][FSI] and 1-methyl-1-propylpiperidinium
19 bis(fluorosulfonyl)imide [MPrPip][FSI] were measured by inverse gas chromatography in a
20 range of temperature from 323.15 K to 373.15K. The molecular structures of these ILs studied
21 in this work are given in Table 1. To our knowledge, only one chromatographic study was
22 published on this family of ionic liquids [40]. Experimental data were compared with results
23 obtained using COSMO-RS. Then, experimental gas-to-IL partition coefficients were
24 correlated using the Linear Solvation Energy Relationship.

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2. Experimental Methods

2.1. Ionic liquid synthesis and solute probes

1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide [BMPyr][FSI], N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide [PrMPyr][FSI], 1-ethyl-1-methylimidazolium bis(fluorosulfonyl)imide [EMIM][FSI] and 1-methyl-1-propylpiperidinium bis(fluorosulfonyl)imide [MPrPip][FSI] were purchased from Solvionic with a purity of 99.9% (mass percent). Test solutes were purchased from Sigma-Aldrich at a purity 99.5% (mass percent) and were used without further purification.

2.2. Vibrating-tube densimeter and density measurement

Densities of the ILs were measured using an Anton Paar DMATM 4500 M digital vibrating-tube densimeter in the temperature range from 293.15 to 393.15 K at atmospheric pressure. The detailed procedure was given in our previous work [6-9]. All experimental data are given in Table 2.

2.3. Chromatographic instrumentation and experimental procedures

Thermodynamic properties at infinite dilution were determined using procedures described in previous works [6-9]. In summary, the measurements were conducted by using a Bruker 450 gas chromatograph equipped with a heated on-column injector, a thermal conductivity detector (TCD) and a flame ionization detector (FID). The injector and detector temperature was fixed at 250°C. Helium carrier gas flow rate was measured using an Alltech Digital Flow Check Mass Flowmeter. The temperature of the oven was measured with a Pt 100 probe and controlled to within 0.1 K. Retention data were collected and treated with Galaxie software.

1 The preparation of the packed columns was described in detail in our previous articles
2 [1-20]. Packed columns of 1-meter length containing between 30 and 50% IL stationary phase
3 coated onto an 80–100 mesh Chromosorb WHP support material were prepared by a rotary
4 evaporation method. Briefly, IL was dissolved in ethanol in the presence of a precise mass of
5 Chromosorb WHP. Ethanol was then removed from the mixture using rotary evaporation. The
6 support was equilibrated at 343 K under vacuum during 6 h. Then, the conditioning of the
7 packed columns was performed at 373 K over 12 h using a gas flow rate of 20 cm³ min⁻¹. The
8 estimated uncertainty for activity coefficients was 3%, taking into account the possible
9 uncertainties in determining the retention data, the solute thermodynamic properties, and the
10 column loading.

11

12 **3. Theoretical Basis for Thermodynamic Quantities**

13 Retention data were used to calculate the activity coefficient at infinite dilution of
14 solute 1 in IL 2 ($\gamma_{1,IL}^\infty$) using the following expression [41-43]:

$$15 \quad \ln \gamma_{1,IL}^\infty = \ln \left(\frac{n_{IL} RT}{V_N P_1^o} \right) - P_1^o \cdot \frac{B_{11} - V_1^o}{RT} + \frac{2B_{13} - V_1^\infty}{RT} \cdot J \cdot P_o \quad (1)$$

16 where n_{IL} is the mole number of the IL stationary phase component inside the column, R is the
17 ideal gas constant, T denotes the temperature of the oven, V_N is the net retention volume, B_{11}
18 refers to the second virial coefficient of the solute in the gaseous state at temperature T , B_{13}
19 represents the mutual virial coefficient between the solute 1 and the carrier gas helium
20 (denoted 3), and P_1^o is the probe vapor pressure at temperature T .

21 The gas-to-IL partition coefficients K used in the LSER model were calculated from
22 activity coefficients at infinite dilution using Eq. 2:

23

$$K = \frac{RT}{\gamma_{1,IL}^{\infty} P_1^0 V_{IL}} \quad (2)$$

2

3 From the $\gamma_{1,IL}^{\infty}$ values, the partial molar excess enthalpy, $\Delta H_1^{E,\infty}$ and entropy at infinite dilution

4 $\Delta S_1^{E,\infty}$ can be calculated assuming a van't Hoff relation holds:

5

$$\ln \gamma_{1,IL}^{\infty} = \frac{\Delta G_1^{E,\infty}}{RT} = \frac{\Delta H_1^{E,\infty}}{RT} - \frac{\Delta S_1^{E,\infty}}{R} \quad (3)$$

7

8 It follows from Eq. (3) that if the logarithm of the activity coefficient at infinite dilution is

9 plotted against $1/T$, a straight line having a slope of $\Delta H_1^{E,\infty} / R$ and an intercept of $\Delta S_1^{E,\infty} / R$

10 is obtained.

11 The solubility parameter of the ionic liquid, δ_2 , can be calculated using the following

12 equation [43]:

13

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^{\infty}}{RT} \right) = \left(\frac{2 \delta_2}{RT} \right) \times \delta_1 - \frac{\delta_2^2}{RT} \quad (4)$$

15 Where χ_{12}^{∞} characterizes interactions between the solute and the stationary phase, δ_1 and δ_2

16 are solubility parameters of the solute and of the ionic liquid, respectively. If the left-hand

17 side of the equation (4) is plotted against δ_1 , a straight line having a slope of $2\delta_2 / RT$ and an

18 intercept of $-\delta_2^2 / RT$ is obtained. The solubility parameter of the ionic liquid, δ_2 , can be

19 calculated from the slope or the intercept of the straight line.

20

21 **3.1 Linear Solvation Energy Relationship Model.**

22

23 Linear Solvation Energy Relationship (LSER) model developed by Abraham et al. is a useful

24 tool for the characterization of stationary phases and their interaction with solutes. [45-48]

25 The original version of LSER model thermodynamic properties related to Gibbs free energy.

1 In this study, retention data are used to calculate the gas-to-IL partition coefficients, K . The
2 most recent representation of the LSER model is given by Eq. (5):

$$3 \log K_L = c_{IL} + e_{IL} \cdot E + s_{IL} \cdot S + a_{IL} \cdot A + b_{IL} \cdot B + l_{IL} \cdot L \quad (5)$$

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6 The capital letters represent the solutes properties and the lower case letters the
7 complementary properties of the ionic liquids. The solute descriptors are the excess molar
8 refraction **E**, dipolarity/ polarizability **S**, hydrogen bond acidity basicity, **A** and **B**,
9 respectively, the gas-liquid partition coefficient on n-hexadecane at 298 K, **L**. These solute
10 descriptors of about 4000 were measured using experimental procedure or calculated using
11 group contribution. [45-52] The coefficients c_{IL} , e_{IL} , s_{IL} , a_{IL} , b_{IL} and l_{IL} are not simply fitting
12 coefficients, but they reflect complementary properties of the solvent phase. All solute
13 descriptors used in this work are given in Table 1S supporting information.

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16 **4. Results and Discussion**

17 **4.1 Activity coefficients at infinite dilution**

18 The γ_i^∞ values of selected organic compounds and water in the four bis(fluorosulfonyl)imide
19 based ILs are given in Tables 3-6. The behavior of solutes with [FSI] based ILs are quite
20 similar than those observed in previous works on other ILs. In homologous series, the
21 solubility of compounds decreases with an increase of the chain length. In this work, this
22 trend is observed with alkanes or alkanols. Then, the solubility of solutes is related to their
23 polarity and their capacity to form hydrogen bond. Compounds containing nitro functionals
24 group (see nitroalkanes), cyano group (acetonitrile), carbonyl group, dioxane tetrahydrofuran
25 and pyridine have a good solubility in [FSI] based ILs. As expected, the lowest solubility in

1 [FSI] based ILs is observed with the heaviest apolar compounds, tetradecane at 323K (
2 $\gamma_i^\infty=570.25$ in N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide, 362.56 in 1-butyl-
3 1-methylpyrrolidinium bis(fluorosulfonyl)imide at 333.15K, 501.54 in 1-methyl-1-
4 propylpiperidinium bis(fluorosulfonyl)imide at 323.15K and 1135.03 in 1-ethyl-1-
5 methylimidazolium bis(fluorosulfonyl)imide. Figure 1 presents activity coefficients at infinite
6 dilution of benzene, 1-propanol, thiophene, butanone and water in [EMIM][FSI] studied in
7 this work. The solubility of alkanes, alkenes, alcohols and water increases with an increase of
8 temperature. The opposite trend is observed with the other polar compounds studied in this
9 work. [Tf₂N] and [FSI] anions are two anions with quite similar structures. From previous
10 works [19,53], we can conclude that the solubility of organic compounds is more important in
11 dialkylimidazolium [Tf₂N] than in dialkylimidazolium [FSI]. The tendency is reversed with 1-
12 Alkyl-1-methylpyrrolidinium cations. As expected, an increase of the alkyl chain length
13 increases the hydrophobicity of ILs. This behavior is observed with dialkylpyrrolidinium
14 based ILs. [19-20] Activity coefficients of various organic compound on 1-butyl-1-
15 methylpyrrolidinium bis(fluorosulfonyl)imide were published recently by the team of
16 Domanska [40]. A deviation of about 16% is observed between data published previously and
17 this work at 353.15K. The largest deviations are observed with light alkanes. In all cases,
18 γ_i^∞ values measured in this work are smaller than those measured by Domanska and
19 Karpinska. This difference may be explained by the different purity of the ionic liquid used in
20 both studies. Full data are given in Table 2S.

21 The partial molar excess Gibbs free energy $\Delta G_1^{E,\infty}$, enthalpy $\Delta H_1^{E,\infty}$ and entropy $\Delta S_1^{E,\infty}$ at
22 infinite dilution for 51 solutes in [FSI] ionic liquids at 323.15 K are given in Tables 3S-5S.
23 [FSI] based ILs behave similarly than other [Tf₂N] based ILs. [6,7] Indeed, numerous binary
24 mixtures {organic compound+[FSI] IL} present a positive deviation from Raoult's. Few
25 exceptions are observed with light ketones (acetone and 2-butanone) and acetonitrile for all

1 [FSI] ILs and 1,4- dioxane, chloroform, dichloromethane, nitromethane, thiophene and
 2 tetrahydrofuran excepted for [EMIM]. The largest negative values of $\Delta G_1^{E,\infty}$ (negative
 3 deviations from Raoult's law) was found for acetonitrile (-1.81 kJ·mol⁻¹ for [PrMPyr][FSI], -
 4 1.73 kJ·mol⁻¹ for [EMIM][FSI], 1.64 kJ·mol⁻¹ for [BMPyr][FSI] and -1.53 kJ·mol⁻¹ for
 5 [MPrPip][FSI]). As expected, the largest positive deviations ($\Delta G_1^{E,\infty} > 0$) are obtained with
 6 alkanes (17.05 kJ·mol⁻¹ for [PrMPyr][FSI], -18.9 kJ·mol⁻¹ for [EMIM][FSI], 16.7 kJ·mol⁻¹ for
 7 [MPrPip][FSI]). The positive $\Delta H_1^{E,\infty}$ values observed with alkanes, alkenes, alkynes, CCl₄,
 8 trimethylamine and water indicates that these compounds have no particular affinity with
 9 [FSI] based ILs. Then, the positive $T\Delta S_1^{E,\infty}$ values observed with alcohols and water confirm
 10 their weak interaction with the IL.

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13 **4.2 Selectivity and capacity**

14 The selectivity $s_{12}^\infty = \gamma_{13}^\infty/\gamma_{23}^\infty$ and capacity $k_2^\infty = 1/\gamma_{23}^\infty$ of ILs studied in this work but
 15 also others published in the literature [53-67] are presented in Table 7 for separation problems
 16 of organic compounds from aqueous solution such as thiophene (1)/water (2) , benzene
 17 (1)/water (2), Acetone (1)/water (2), 1-butanol (1)/water (2), acetonitrile (1)/water (2) and
 18 pyridine (1)/water (2) at 323.15 K. In the case of the extraction of thiophene from aqueous
 19 solution, the s_{12}^∞ values obtained with ILs range from 0.22 to 12.01 while the k_2^∞ values vary
 20 between 0.79 ([BMPYR][FAP]) to 1.55 ([EMIM][FAP]). It seems to be difficult to propose a
 21 relationship between selectivity and the cation. Indeed, the s_{12}^∞ values obtained increase
 22 according to [EMIM]<[PrMPyr]<[BMPyr]<[MPrPip] with [FSI] ILs, [BMPyr]< [EMIM]
 23 with [FAP] ILs and [BMPyr]<[MPrPip] with [Tf₂N]. Analysis of results concerning the
 24 separation of benzene from aqueous solution shows that the worst performing ILs is
 25 [EMIM][SCN] ($s_{12}^\infty = 0.08$ and $k_2^\infty = 0.29$) and the more efficient appears to be

1 [EMIM][FAP] ($s_{12}^{\infty} = 12.89$ and $k_2^{\infty} = 1.66$) in term of selectivity and [EMIM][FSI] ($s_{12}^{\infty} =$
2 2.8 and $k_2^{\infty} = 1.75$) in term of capacity. [FSI] ILs present the largest selectivity values with
3 the separation problems related to acetone and acetonitrile.

4 As shown in table 7, the largest values of selectivity for the most separation problems studied
5 in this work were obtained with [EMIM][FSI]. ILs constitutes of [FSI] anion and an
6 appropriate cation should be potentially suitable solvents for the separation of the organic
7 compounds from water in comparison with other ILs.

8

9 **4.3 COSMO-RS model.**

10 Klamt and his coworkers modified the dielectric continuum solvation methods used in
11 quantum chemical to propose the conductor-like screening model (COSMO). The conductor-
12 like screening model for real solvents (COSMO-RS) is the extension of COSMO beyond the
13 dielectric limits. This approach combines statistical thermodynamics and the COSMO
14 quantum chemical calculations to evaluate thermodynamic properties. [69-72] The power of
15 COSMO-RS is its good ability to predict the thermodynamic properties of compounds
16 without the need of experimental data. The COSMO-RS model was found to be suitable for
17 the estimation of physico-chemical properties of pure ILs, deep eutectic solvents but also their
18 phase diagrams with organic solvents [84-87]. In this study, all calculations were performed
19 using the *COSMOtherm* package [73] purchased from COSMOlogic GmbH & Co. KG
20 (Leverkusen, Germany). The conformations and COSMO files of bis(fluorosulfonyl)imide
21 anion, 1-ethyl-3-methylimidazolium, N-propyl-N-methylpyrrolidinium, 1-butyl-1-
22 methylpyrrolidinium, 1-methyl-1-propylpiperidinium and all the solutes come from
23 *COSMObaseIL* and *COSMObase BP_TZVP_FINE_COSMO_C30_1601* compilation,
24 respectively. Activity coefficients at infinite dilution of organic compounds and water in the
25 four [FSI] ILs studied in this work were predicted using COSMO-RS in the range of

1 temperature from 323.15 K to 373.15 K. All results are presented in Table 6S-9S. The
2 predictive power of COSMO-RS model is evaluated through the average absolute relative
3 deviation (AARD) and the root mean square error (RMSE) defined as:

$$4 \quad AARD = \frac{100}{N} \times \sum_{i=1}^N \left| 1 - \frac{\gamma_i^{\infty,calcd}}{\gamma_i^{\infty,exp}} \right| \quad (6)$$

$$7 \quad RMSE = \sqrt{\frac{1}{N} \times \sum_{i=1}^N (\gamma_i^{\infty,calcd} - \gamma_i^{\infty,exp})^2} \quad (7)$$

8
9 AARD and RMSE values obtained for all solutes and selected families of compounds in the
10 four ILs studied are given in Table 8. Results obtained on bis(fluorosulfonyl)imide ILs are of
11 the same magnitude as those obtained on other families of ILs. [87] The best results are
12 obtained with [MPPip][FSI] with an AARD of 18.52%. Nevertheless, it is important to
13 mention that $\gamma_{1,IL}^{\infty}$ values of dichloromethanes are poorly predicted (AARD = 201.09%).
14 Concerning [FSI] ILs, large AARD is observed with aromatics and dichloroalkanes. Figure 2
15 shows that COSMO-RS approach is not efficient for the prediction of $\gamma_{1,IL}^{\infty}$ of heavy apolar
16 compounds.

17 Conformations of molecules also play an important role in the quality of COSMO-RS
18 prediction. In Cosmotherm, bis(fluorosulfonyl)imide anion has 1 conformer while [EMIM],
19 [MPPyr] and [BMPyr] cations are represented by 3, 2 and 2 conformers, respectively.
20 Therefore, an IL is represented as a mixture of different IL molecule conformers in COSMO-
21 RS. The impact of the cation and the solute conformations on the prediction of $\gamma_{1,IL}^{\infty}$ of
22 selected solutes are presented in Table 10S. Analysis of results led to the conclusion that the
23 best predictions are obtained when the most stable conformation of the cation is used.

24

1 **4.4 Solubility parameters.** The solubility parameters δ_2 of the four ionic liquids studied in
 2 this work are listed in Table 9. It was found that temperature has no a significant influence on
 3 δ_2 . Therefore, δ_2 values given in Table (9) are average values obtained between 323.15 and
 4 373.15 K. Analysis of results show that the solubility parameters of [FSI] based ILs decrease
 5 in the following order: [EMIM] > [PrmPyr] > [BmPyr] > [MPrPip]. This suggests that
 6 solubility parameter values are directly related to the size of the ILs. According to
 7 Marciniak's works [89-90], solubility parameter values of ILs vary from 17.9 MPa^{1/2} for
 8 [OMIM][Cl] to 30.7 MPa^{1/2} for [BMPIP][SCN]. In this work, the highest value of δ_2 was
 9 observed with the [EMIM] cation, while the minimum was obtained with [MPrPip]. This
 10 confirms a significant influence of the cation on the solubility parameters. From the δ_2 values,
 11 standard enthalpy of vaporization ($\Delta_{vap}H$) at 298 K were estimated using equation (8):

$$13 \quad \delta_2 = \sqrt{\frac{\Delta_{vap}H - RT}{v}} \quad (8)$$

14 Where v is the molar volumes of the IL determined from densities given in Table 2. The
 15 calculated $\Delta_{vap}H$ values from retention data but also from molecular dynamic are listed in
 16 Table 9. [88] [PrmPyr] [FSI], [BmPyr] [FSI] and [MPrPip] [FSI] have quite similar $\Delta_{vap}H$
 17 values and [EMIM] cation presents a lowest average $\Delta_{vap}H$ value of 140.4 kJ·mol⁻¹. The
 18 difference observed between experimental values and those calculated from molecular
 19 dynamic for [PMPyr][FSI] and [EMIM][FSI] are 9.2 and 5.8 kJ·mol⁻¹, respectively.

21 **4.5 LSER characterization.**

22 The gas-to-IL partition coefficients K_L of solutes in ILs required for the LSER model were
 23 calculated using equation 2. All data are presented in Table 11S-14S. The coefficients c_{IL} , e_{IL} ,
 24 s_{IL} , a_{IL} , b_{IL} and l_{IL} coefficients describing the ILs obtained by multiple linear regression of

1 log K_L of organic compounds are given in Table 10. Large squared correlation coefficients
2 (R^2) and Fischer F-statistic values with small deviation (SD) indicate that LSER correlations
3 are able to estimate log K of organic compounds in these four [FSI] ILs. The quality of
4 correlations obtained for the four ILs studied in this work at 323.15 K is illustrated in Figure
5 3.

6 Analysis of LSER characterization of the four ionic liquids studied in this work points out that
7 the dipolarity (s_{IL}) and hydrogen bond basicity (a_{IL}) are quite similar for these four [FSI] ILs.
8 This observation indicates that the cation and the alkyl chain length have weak impact on the
9 basic character and the polarity of [FSI] ILs. The polarizability expressed by the e_{IL} parameter
10 in LSER model is strongly sensitive to the structure of the IL. As an example, changing 1-
11 methyl-1-propylpiperidinium by 1-butyl-1-methylpyrrolidinium leads to a Δe_{IL} of 0.115. The
12 hydrogen bond acidity of bis(fluorosulfonyl)imide based ILs is also strongly depending on the
13 structure of the solvent. Results indicate that the highest hydrogen-bond acidity value is
14 observed with imidazolium based ionic liquid. In this work, the acidity of FSI ILs decreases
15 according to [EMIM]>[MPrPip]> [PrMPyr]> [BMPyr]. It can be noted that b_{IL} parameter
16 values are inversely proportional to the alkyl chain length. The l_{IL} parameter values of ILs are
17 ranking to their size: [MPrPip]> [BMPyr]> [PrMPyr]> [EMIM]. The increasing of the
18 temperature in gas chromatography reduces the retention times of solutes and their
19 interactions with the stationary phase (here IL). Figure 4 shows that there are linear
20 relationships between LSER parameters and the temperature. Therefore, we can propose
21 temperature dependent LSER model in which c_{IL} , e_{IL} , s_{IL} , a_{IL} , b_{IL} and l_{IL} can be expressed as
22 followed:

23

$$24 \quad x = x_0 \times T + x_1 \quad (9)$$

25

1 The constants x_0 and x_1 for each LSER coefficients are given for the four ILs studied in this
2 work in Table 11. Low standard deviation on logarithm of partition coefficients obtained
3 using the temperature dependent LSER model indicates that these correlations could be used
4 to predict logK of volatile organic compounds not taken into account in the databank.

5 In Table 12, LSER parameters of ILs studied in this work and published in the literature
6 [11,12,14,74,75,77,79-83] are given at 323K. The LSER parameters of ILs are ranged
7 $0 < e_{IL} < 0.86$; $0 < s_{IL} < 5.15$; $0.91 < a_{IL} < 7.27$; $0 < b_{IL} < 1.81$ and $0.35 < l_{IL} < 1.51$. Compared to the
8 scales of LSER parameters, we can conclude that [FSI] ILs are moderately polar and basic (
9 e_{IL} , s_{IL} and a_{IL} of about 0.25, 2.5 and 2.2, respectively). It is also important to note that
10 [FSI] ILs have low acidity.

11

12 **5. Conclusion**

13 In this work, four [FSI] based ILs namely 1-butyl-1-methylpyrrolidinium
14 bis(fluorosulfonyl)imide, N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide, 1-ethyl-
15 1-methylimidazolium bis(fluorosulfonyl)imide and 1-methyl-1-propylpiperidinium
16 bis(fluorosulfonyl)imide were characterized using inverse gas chromatography.

17 Thermodynamic properties at infinite dilution (γ_i^∞ , $\Delta G_1^{E,\infty}$, $\Delta H_1^{E,\infty}$ and $\Delta S_1^{E,\infty}$) calculated
18 from retention data for 51 solutes in these ILs allow having a better understanding of solute-
19 IL interactions. LSER analysis have shown that the dipolarity and hydrogen bond basicity of
20 [FSI] ILs are not affected by the cation and/or the alkyl chain length. However, the
21 polarizability is strongly sensitive to the structure of the IL. The predicted γ_i^∞ values by
22 COSMO-RS model are in good agreement with our experimental data for light compounds. It
23 must be pointed out that the best results are obtained with the lowest energy conformations of
24 the cation and of the solute. In the end, [FSI] based ILs appear to be efficient solvents for the
25 extraction polar organic compounds from aqueous solution.

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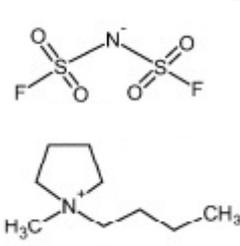
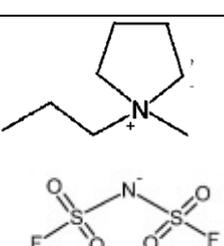
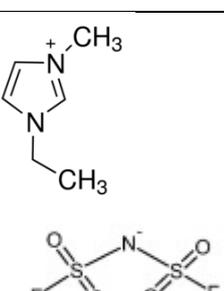
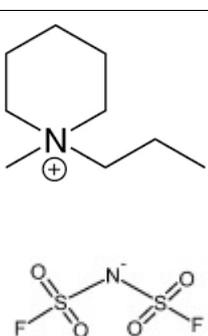
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5

- 1 **Table 1.** Investigated ionic liquids: structure, name and abbreviation of name, molar mass,
 2 purification method and purity.

Structure	Name, Abbreviation	$M/(g \cdot mol^{-1})$	Purif.method	Mass fraction purity/water content (mass fraction)
	1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide [BMPyr][FSI] Solvionic	322.39	323 K under vacuum during 24h	99.5% / $124 \cdot 10^{-6}$
	N propyl N methylpyrrolidinium bis(fluorosulfonyl)imide [PrMPyr][FSI] Solvionic	308.37	323 K under vacuum during 24h	99.5% / $135 \cdot 10^{-6}$
	1-ethyl-1-methylimidazolium bis(fluorosulfonyl)imide [EMIM][FSI] Solvionic	291.30	323 K under vacuum during 24h	99.5% / $104 \cdot 10^{-6}$
	1-methyl-1-propylpiperidinium bis(fluorosulfonyl)imide [MPrPip][FSI] Solvionic	322.35	323 K under vacuum during 24h	99.5% / $112 \cdot 10^{-6}$

3

1 **Table 2.** Densities (ρ) for the ILs studied in this work as a function of temperature at
 2 $P = 101.33$ kPa.

T/K	$\rho/(\text{kg. m}^{-3})$			
	[BMPyr]	[PrMPyr]	[MPrPip]	[EMIM]
293.15	1310.11	1342.64	1324.65	1446.27
298.15	1306.1	1338.66	1320.82	1441.73
303.15	1302.33	1334.67	1316.97	1437.16
308.15	1298.46	1330.66	1313.11	1432.56
313.15	1294.56	1326.68	1309.32	1428.07
318.15	1290.74	1322.67	1305.53	1423.53
323.15	1286.91	1318.74	1301.75	1419.06
328.15	1283.08	1314.86	1298	1414.56
333.15	1279.33	1310.99	1294.24	1410.13
338.15	1275.52	1307.12	1290.51	1405.7
343.15	1271.79	1303.24	1286.81	1401.32
348.15	1268.02	1299.39	1283.12	1396.92
353.15	1264.27	1295.6	1279.44	1392.57
358.15	1260.55	1291.79	1275.77	1388.17
363.15	1256.85	1288.03	1272.12	1383.85
368.15	1253.16	1284.22	1268.46	1379.54
373.15	1249.47	1280.49	1264.88	1375.24

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1 **Table 3:** Activity coefficients at infinite dilution of 50 organic compounds and water in N-
 2 propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide.^a a Standard uncertainties are
 3 $u_r(\gamma_{1,L}^\infty) = 5\%$, $u(T) = 0.1$ K.
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	$\gamma_{1,L}^\infty$ at T/K					
	373.15	363.15	353.15	343.15	333.15	323.15
Hexane	19.3	20.4	22.2	23.8	25.4	27.6
3-Methylpentane	17.0	17.8	19.4	20.6	22.1	24.1
Heptane	27.3	29.5	32.9	35.6	38.2	41.9
2,2,4-Trimethylpentane	29.4	31.1	34.1	36.3	39.7	42.6
Octane	39.7	42.5	47.9	52.1	56.9	62.6
Nonane	57.6	62.0	68.2	76.1	83.7	93.2
Decane	83.3	89.8	100.7	111.1	122.1	138.4
Undecane	118	127	144	158	177	197
Dodecane	165	177	200	222	244	275
Tridecane	233	256	291	315	349	408
Tetradecane	323	352	398	425	490	570
Methylcyclopentane	11.1	11.8	12.6	13.5	14.3	15.5
Cyclohexane	10.5	11.2	11.9	12.8	13.6	14.7
Methylcyclohexane	15.2	16.3	17.2	18.2	19.6	21.1
Cycloheptane	14.0	14.9	16.0	16.9	18.1	19.5
Benzene	1.23	1.2	1.18	1.14	1.12	1.09
Toluene	1.76	1.71	1.67	1.62	1.59	1.55
Ethylbenzene	2.62	2.57	2.53	2.47	2.43	2.4
m-Xylene	2.51	2.44	2.39	2.31	2.27	2.22
p-Xylene	2.47	2.4	2.35	2.27	2.21	2.16
o-Xylene	2.19	2.13	2.08	2.01	1.96	
1-Hexene	10.1	10.5	11.0	11.4	11.9	12.6
1-Heptene	15.1	15.8	16.5	17.1	17.9	18.9
1-Octene	21.5	23.0	24.3	25.1	26.7	28.2
1-Hexyne	3.9	3.87	3.84	3.8	3.78	3.73
1-Heptyne	5.59	5.58	5.56	5.55	5.54	5.52
Acetone	0.66	0.65	0.63	0.61	0.59	0.58
2-Butanone	0.88	0.86	0.84	0.8	0.79	0.77
2-Pentanone	1.2	1.17	1.15	1.11	1.08	1.06
3-Pentanone	1.22	1.18	1.16	1.12	1.09	1.05
1,4 Dioxane	0.85	0.81	0.79	0.76	0.73	0.7
Methanol	1.11	1.18	1.26	1.33	1.44	1.56
Ethanol	1.4	1.48	1.6	1.71	1.86	2.04
1-Propanol	1.72	1.8	1.97	2.11	2.31	2.55
2-Propanol	1.62	1.71	1.84	1.96	2.14	2.35
2-Methyl-1-propanol	2.1	2.2	2.43	2.63	2.92	3.26
1-Butanol	2.21	2.3	2.55	2.73	3.03	3.35
Diethyl ether	3.53	3.54	3.56	3.57	3.59	3.6
Diisopropyl ether	8.68	8.88	9.1	9.38	9.5	9.69

Chloroform	1.13	1.08	1.05	1	0.96	0.92
Dichloromethane	0.91	0.9	0.87	0.84	0.82	0.8
Tetrachloromethane	3.43	3.4	3.38	3.34	3.31	3.27
Acetonitrile	0.54	0.54	0.53	0.52	0.51	0.51
Nitromethane	0.54	0.53	0.53	0.52	0.51	0.51
1-Nitropropane	0.85	0.83	0.83	0.8		
Triethylamine	10.3	10.6	10.9	11.2	11.6	11.9
Pyridine	0.7	0.68	0.67	0.65	0.64	
Thiophene	0.98	0.95	0.93	0.9	0.86	0.84
Tetrahydrofuran	1.06	1.04	1.02	0.99	0.96	0.94
Ethylacetate	1.46	1.43	1.39	1.36	1.34	1.3
Water	1.97	2.04	2.28	2.47	2.73	3.11

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1 **Table 4.** Activity coefficients at infinite dilution of 50 organic compounds and water in 1-
 2 butyl-1-methylpyrrolidiniumbis(fluorosulfonyl)imide. ^a a Standard uncertainties are
 3 $u_r(\gamma_{1,2}^\infty) = 5\%$, $u(T) = 0.1$ K.
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	$\gamma_{1,L}^\infty$ at T/K					
	373.15	363.15	353.15	343.15	333.15	323.15
Hexane	17.5	18.3	19.4	21.1	22.8	23.4
3-Methylpentane	15.3	17.0	16.6	18.6	20.6	19.6
heptane	24.7	26.1	27.9	30.3	33.0	33.8
2,2,4-Trimethylpentane	27.8	28.5	30.5	32.5	35.6	34.9
Octane	38.4	37.6	40.4	44.7	47.4	49.1
Nonane	51.1	52.8	56.6	61.3	67.0	71.1
Decane	68.8	74.2	80.1	87.5	94.8	103
Undecane	94.0	105	112	124	134	149
Dodecane	129	142	165	171	185	209
Tridecane	177	196	216	237	262	
Tetradecane	238	267	295	322	363	
methylcyclopentane	10.5	10.8	11.3	12.1	12.6	13.3
Cyclohexane	9.63	10.0	10.5	11.2	11.9	12.2
Methylcyclohexane	13.5	14.1	14.9	15.8	16.6	17.1
Cycloheptane	12.3	12.9	13.5	14.3	15.1	15.7
Benzene	1.18	1.16	1.13	1.09	1.05	1.02
Toluene	1.66	1.64	1.59	1.53	1.48	1.42
Ethylbenzene	2.42	2.41	2.35	2.28	2.21	2.2
m-Xylene	2.35	2.32	2.25	2.17	2.09	
p-Xylene	2.32	2.29	2.2	2.12	2.04	
o-Xylene	2.04	2.01	1.96	1.88	1.81	
1-Hexene	9.5	9.43	9.91	10.4	10.7	11.6
1-Heptene	13.6	13.9	14.4	15.1	15.6	16.5
1-Octene	18.9	19.6	20.5	21.4	22.2	23.8
1-Hexyne	3.71	3.67	3.63	3.55	3.48	3.49
1-Heptyne	5.14	5.15	5.11	5.04	4.94	4.99
Acetone	0.66	0.65	0.63	0.61	0.59	0.59
2-Butanone	0.85	0.84	0.81	0.78	0.75	0.74
2-Pentanone	1.13	1.11	1.08	1.05	1.01	1
3-Pentanone	1.14	1.13	1.09	1.05	1.01	0.99
1,4 Dioxane	0.84	0.83	0.8	0.76	0.73	0.71
Methanol	1.14	1.22	1.3	1.39	1.49	1.64
Ethanol	1.41	1.52	1.63	1.75	1.88	2.09
1-Propanol	1.7	1.83	1.96	2.1	2.27	2.55
2-Propanol	1.62	1.73	1.84	1.97	2.13	2.37
2-Methyl-1-propanol	2.04	2.2	2.36	2.55	2.8	3.18
1-Butanol	2.13	2.29	2.46	2.66	2.89	3.25
Diethyl ether	3.51	3.44	3.43	3.37	3.41	3.45
Diisopropyl ether	8.27	8.28	8.5	8.58	8.76	8.95

Chloroform	1.1	1.07	1.02	0.97	0.92	0.89
Dichloromethane	0.92	0.9	0.87	0.84	0.81	0.8
Tetrachloromethane	3.23	3.19	3.15	3.11	3.03	3.05
Acetonitrile	0.56	0.56	0.56	0.55	0.54	0.54
Nitromethane	0.57	0.57	0.57	0.56	0.55	
1-Nitropropane	0.85	0.84	0.83	0.8		
Triethylamine	9.75	9.83	10.0	10.2	10.4	10.7
Pyridine	0.68	0.67	0.65	0.63		
Thiophene	0.96	0.93	0.9	0.87	0.83	0.82
Tetrahydrofuran	1.02	1	0.98	0.95	0.91	0.9
Ethylacetate	1.42	1.39	1.36	1.32	1.28	1.28
Water	2.01	2.33	2.55	2.83	3.12	3.59

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1 **Table 5.** Activity coefficients at infinite dilution of 50 organic compounds and water in 1-
 2 methyl-1-propylpiperidinium bis(fluorosulfonyl)imide. ^a a Standard uncertainties are
 3 $u_r(\gamma_{1,2}^\infty) = 5\%$, $u(T) = 0.1$ K.
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	$\gamma_{1,L}^\infty$ at T/K					
	373.15	363.15	353.15	343.15	333.15	323.15
Hexane	19.1	20.2	24.3	26.1	28.7	32.0
3-Methylpentane	15.9	18.4	21.8	24.2	25.9	29.8
Heptane	26.8	28.8	34.3	38.0	41.1	46.5
2,2,4-Trimethylpentane	29.6	32.2	36.5	41.4	44.8	50.7
Octane	40.1	43.3	48.8	52.8	58.3	65.3
Nonane	54.4	59.0	66.6	73.9	81.0	91.5
Decane	77.1	84.6	96.7	105	115	130
Undecane	107	117	134	146	163	186
Dodecane	148	162	186	203	225	260
Tridecane	203	224	250	284	317	371
Tetradecane	276	309	353	391	429	502
Methylcyclopentane	11.1	11.8	14.0	14.8	16.0	17.8
Cyclohexane	10.4	11.1	13.0	13.7	15.0	16.6
Methylcyclohexane	14.9	16.6	18.2	19.5	21.2	23.2
Cycloheptane	13.5	14.4	16.3	17.3	18.4	20.2
Benzene	1.2	1.18	1.17	1.14	1.13	1.11
Toluene	1.69	1.64	1.64	1.59	1.54	1.54
Ethylbenzene	2.47	2.42	2.4	2.36	2.31	2.29
m-Xylene	2.34	2.28	2.23	2.19	2.13	2.1
p-Xylene	2.3	2.23	2.21	2.15	2.08	2.05
o-Xylene	2.04	1.99	1.98	1.91	1.85	
1-Hexene	9.74	10.1	11.3	12.1	12.8	14.1
1-Heptene	14.8	15.3	17.0	17.8	18.6	20.0
1-Octene	20.4	21.6	23.9	25.1	26.3	28.5
1-Hexyne	3.85	3.88	3.9	3.93	3.96	3.99
1-Heptyne	5.4	5.43	5.5	5.56	5.62	5.7
Acetone	0.7	0.68	0.68	0.66	0.64	0.62
2-Butanone	0.91	0.89	0.88	0.85	0.83	0.82
2-Pentanone	1.25	1.22	1.19	1.15	1.12	1.09
3-Pentanone	1.24	1.21	1.2	1.16	1.12	1.1
1,4 Dioxane	0.88	0.85	0.84	0.81	0.78	0.76
Methanol	1.18	1.24	1.35	1.44	1.56	1.74
Ethanol	1.47	1.56	1.71	1.83	1.99	2.24
1-Propanol	1.77	1.88	2.07	2.23	2.44	2.76
2-Propanol	1.69	1.78	1.96	2.09	2.28	2.58
2-Methyl-1-propanol	2.15	2.3	2.54	2.75	3.04	3.51
1-Butanol	2.25	2.4	2.64	2.85	3.13	3.59
Diethyl ether	3.54	3.65	3.73	3.85	3.94	4.03
Diisopropyl ether	9	9.32	9.78	10.4	10.8	11.2
Chloroform	1.11	1.07	1.05	1	0.95	0.94

Dichloromethane	0.93	0.91	0.9	0.88	0.85	0.84
Tetrachloromethane	3.34	3.29	3.4	3.34	3.31	3.34
Acetonitrile	0.59	0.58	0.58	0.58	0.57	0.57
Nitromethane	0.59	0.59	0.58	0.58	0.57	0.56
1-Nitropropane	0.9	0.88	0.89	0.86		
Triethylamine	10.0	10.4	10.9	11.5	12.1	12.6
Pyridine	0.7	0.69	0.68	0.66	0.64	
Thiophene	0.96	0.93	0.92	0.88	0.86	0.83
Tetrahydrofuran	1.09	1.06	1.04	1.02	1	0.98
Ethylacetate	1.53	1.5	1.48	1.46	1.43	1.41
Water	2.22	2.34	2.63	2.87	3.17	3.71

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1 **Table 6.** Activity coefficients at infinite dilution of 50 organic compounds and water in 1-
 2 ethyl-1-methylimidazolium bis(fluorosulfonyl)imide. ^a a Standard uncertainties are
 3 $u_r(\gamma_{1,2}^\infty) = 5\%$, $u(T) = 0.1$ K.
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	$\gamma_{1,2}^\infty$ at T/K					
	373.15	363.15	353.15	343.15	333.15	323.15
Hexane	22.0	26.7	32.4	36.9	42.0	45.1
3-Methylpentane	18.5	23.8	28.2	31.9	36.2	37.9
Heptane	40.3	45.8	49.8	57.7	63.6	71.0
2,2,4-Trimethylpentane	40.5	47.8	50.9	60.7	65.7	72.6
Octane	59.9	70.0	75.6	88.1	98.6	110
Nonane	90.7	104	114	136	151	168
Decane	133	154	171	200	226	257
Undecane	197	225	249	288	340	387
Dodecane	283	322	361	427	493	561
Tridecane	407	471	501	606	723	783
Tetradecane	570	577	729	777	982	1135
Methylcyclopentane	14.4	17.1	18.2	20.3	21.7	23.8
Cyclohexane	14.2	16.4	16.8	19.1	20.7	22.6
Methylcyclohexane	20.4	23.0	24.6	28.0	30.7	33.0
Cycloheptane	19.3	21.2	22.7	25.7	28.0	30.4
Benzene	1.56	1.56	1.55	1.55	1.55	1.53
Toluene	2.35	2.35	2.33	2.32	2.32	2.32
Ethylbenzene	3.67	3.69	3.67	3.80	3.80	3.80
m-Xylene	3.61	3.61	3.57	3.67	3.64	3.62
p-Xylene	3.54	3.52	3.51	3.5	3.49	3.49
o-Xylene	3.04	3.02	3.03	3.02	3.01	2.99
1-Hexene	13.0	13.8	15.7	17.4	18.5	20.2
1-Heptene	21.2	22.9	24.7	27.3	29.2	31.0
1-Octene	32.0	34.3	36.8	41.5	44.8	48.2
1-Hexyne	5.15	5.21	5.31	5.42	5.51	5.55
1-Heptyne	7.54	7.73	7.86	8.33	8.45	8.56
Acetone	0.63	0.62	0.6	0.61	0.59	0.57
2-Butanone	0.9	0.89	0.87	0.86	0.83	0.81
2-Pentanone	1.32	1.3	1.27	1.24	1.21	1.19
3-Pentanone	1.38	1.35	1.32	1.29	1.26	1.23
1,4 Dioxane	0.8	0.77	0.74	0.74	0.71	0.69
Methanol	1.07	1.14	1.2	1.35	1.46	1.58
Ethanol	1.4	1.5	1.61	1.82	1.99	2.18
1-Propanol	1.79	1.93	2.07	2.35	2.58	2.86
2-Propanol	1.68	1.81	1.92	2.18	2.38	2.64
2-Methyl-1-propanol	2.27	2.45	2.66	3.05	3.4	3.85
1-Butanol	2.38	2.58	2.77	3.17	3.51	3.95
Diethyl ether				4.21	4.21	4.2
Diisopropyl ether	10.0	10.4	10.7	11.2	11.5	11.7

Chloroform	1.42	1.38	1.34	1.32	1.32	1.27
Dichloromethane	1.14	1.12	1.09	1.07	1.05	1.03
Tetrachloromethane	4.43	4.53	4.52	4.78	4.79	4.81
Acetonitrile	0.53	0.53	0.52	0.54	0.53	0.52
Nitromethane	0.53	0.52	0.52	0.53		
1-Nitropropane	0.92	0.92	0.90	0.90		
Triethylamine	12.2	12.8	13.5	14.1	15.0	15.3
Pyridine	0.73	0.72	0.70	0.71		
Thiophene	1.24	1.23	1.20	1.22	1.20	1.18
Tetrahydrofuran	1.13	1.12	1.12	1.11	1.09	1.06
Ethylacetate	1.46	1.45	1.40	1.42	1.39	1.35
Water	1.69	1.83	1.99	2.26	2.48	2.77

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Table 7. Selectivities S_{12}^{∞} and capacities k_2 at infinite dilution for thiophene (1)/water (2), benzene (1)/water (2), acetone (1)/water (2), 1-butanol (1)/water (2), acetonitrile (1)/water (2), pyridine (1)/water (2) separation problems for the selected ILs at T= 323.15 K.

Ionic Liquids	S_{12}^{∞}						k_2						ref
	Thiophene /water	Benzene /water	Acetone /water	1-butanol /water	Acetonitrile /water	Pyridine /water	Thiophene	Benzene	Acetone	1-butanol	Acetonitrile	Pyridine	
[MPrPip][FSI]	4.47	3.34	5.98	1.03	6.51		1.20	0.90	1.61	0.28	1.75	-	This work
[PrMPip][Tf ₂ N]	6.78	7.25	23.50	1.49	18.58	13.60	1.12	1.20	1.95	0.39	-	-	[54]
[BMPyr][FSI]	4.38	3.52	6.08	1.10	6.65	3.59	1.22	0.98	1.69	0.31	1.85	1.00	This work
[BMPyr][FAP]	0.22	0.13		0.18			0.79	0.46	3.79	0.26	3.06	2.34	[55]
[BMPyr][TCB]	2.82	2.29	4.24	1.12			1.51	1.23	2.09	0.38	2.13	1.64	[56]
[BmPyr][TCM]	1.26	0.89	1.44	0.69	1.64		1.37	0.96	3.89	0.27	3.27	2.23	[57]
[BMPyr][CF ₃ SO ₃]	0.77	0.56		0.56			0.93	0.68	2.27	0.60	-	-	[57]
[COC ₂ mPyr][Tf ₂ N]	3.13	2.70	5.88	1.08	5.99	4.61	1.11	0.96	1.56	0.75	1.78	-	[58]
[COC ₂ mPyr][FAP]	9.99	10.35	26.69	1.85	22.42	15.28	1.46	1.51	-	0.67	1.78	-	[59]
[PrMPyr][FSI]	3.70	2.85	5.36	0.93	6.10		1.19	0.92	1.72	0.30	1.96	-	This work
[EMIM][FSI]	2.35	1.81	4.86	0.70	5.33	1.71	0.85	0.65	1.75	0.25	1.92	0.62	This work
[EMIM][FAP]	12.01	12.89	29.39	2.03	23.73	18.17	1.55	1.66	3.89	0.25	3.08	2.25	[60]
[EMIM] [SCN]		0.08		0.13				0.29	-	0.49	-	-	[61]
[BMIM][SCN]		0.17	0.31	0.29	0.40	0.36		0.51	-	0.65	-	-	[62]
[BMIM][DCA]	4.28	3.76	6.88	1.38			1.21	1.06	0.95	0.90	1.23	1.12	[63]
[P1.4.4.4][TOS]	0.67	0.43		1.74			1.22	0.78	12.29	0.65	-	14.41	[64]
[HMIM][TCB]	2.89	2.52	0.54	1.42	0.48	4.81	1.55	1.35	0.29	0.76	0.26	2.57	[65]
[N-C ₃ OHPY][FAP]	2.40	2.34	19.82	1.30			1.10	1.07	9.09	0.60	-	-	[66]
[C ₂ OHmim][FAP]	1.89	1.86	21.60	1.35		30.26	0.90	0.88	2.36	0.49	-	-	[67]
[bmPY][Tf ₂ N]	4.95	4.37	7.59	1.57			1.54	1.36	-	3.14	-	-	[68]

Table 8. Root mean square errors (RMSE) and average absolute relative deviations (AARD) between COSMO-RS predicted and experimental γ^∞ calculated for different chemical families and [FSI] ILs.

	RMSE	AARD
[EMIM][FSI]		
All solutes	0.197	32.89
Alkanes	0.25	23.37
Cycloalkanes	0.05	9.09
Aromatics	0.227	44.20
Ketones	0.10	25.34
Alcohols	0.216	37.62
Dichloromethanes	0.19	46.97
[BMPyr][FSI]		
All solutes	0.08	35.31
Alkanes	0.153	30.80
Cycloalkanes	0.126	22.64
Aromatics	0.198	55.08
Ketones	0.201	35.31
Alcohols	0.12	28.07
Dichloromethanes	0.198	36.57
[PrMPyr][FSI]		
All solutes	0.19	42.67
Alkanes	0.18	39.48
Cycloalkanes	0.08	15.14
Aromatics	0.29	92.32
Ketones	0.117	29.25
Alcohols	0.19	49.85
Dichloromethanes	0.19	42.30
[MPrPip][FSI]		
All solutes	0.21	18.52
Alkanes	0.18	48.57
Cycloalkanes	0.20	46.02
Aromatics	0.23	86.33
Ketones	0.22	51.05
Alcohols	0.14	64.83
Dichloromethanes	0.20	201.09

Table 9. Solubility parameter δ_2 calculated at 298.15 K.

Ionic liquid	$\delta_2(\text{MPa}^{1/2})$		$\Delta H_{vap}/\text{kJ}\cdot\text{mol}^{-1}$			
	From slop	From intercept	Exp.	average	Ref. [88]	
[MPrPip] [FSI]	25.04	24.88	157.4	155.4	156.4	
[BMPyr][FSI]	25.27	24.80	158.5	152.7	155.6	
[PrMPyr][FSI]	25.88	25.23	157.0	149.2	153.1	143.9
[EMIM][FSI]	26.43	25.78	143.8	136.9	140.4	134.6

Table 10. LSER characterization of [FSI] based ILs studied in this work. The pertinent statistical information, namely the number of experimental data points (N), the standard deviation (SD), the squared correlation coefficient (R^2) and the Fisher F-statistic (F), are given right below the respective correlation equation.

	c	r	s	a	b	l	SD	F	R^2
T (K)	[MPrPip][FSI]								
323.15	-0.769	0.320	2.50	2.19	0.31	0.585	0.088	552	98.4
333.15	-0.738	0.309	2.38	2.10	0.259	0.543	0.086	590	98.6
343.15	-0.728	0.331	2.27	1.98	0.252	0.504	0.081	686	98.7
353.15	-0.714	0.331	2.18	1.86	0.238	0.468	0.077	648	98.7
363.15	-0.672	0.331	2.08	1.75	0.201	0.433	0.072	663	98.7
373.15	-0.663	0.333	2.00	1.64	0.185	0.403	0.070	650	98.7
T (K)	[BMPyr][FSI]								
323.15	-0.614	0.205	2.40	2.10	0.272	0.578	0.089	397	98.2
333.15	-0.63	0.255	2.31	2.01	0.255	0.538	0.083	575	98.6
343.15	-0.629	0.264	2.22	1.90	0.238	0.500	0.079	631	98.7
353.15	-0.621	0.268	2.13	1.80	0.211	0.464	0.076	625	98.6
363.15	-0.638	0.270	2.07	1.72	0.197	0.436	0.073	633	98.7
373.15	-0.662	0.274	2.02	1.67	0.178	0.412	0.071	628	98.6
T (K)	[EMIM][FSI]								
323.15	-0.669	0.222	2.56	2.21	0.427	0.519	0.088	508	98.5
333.15	-0.668	0.254	2.48	2.09	0.432	0.486	0.076	699	98.9
343.15	-0.659	0.224	2.41	2.00	0.371	0.453	0.074	822	99.0
353.15	-0.624	0.235	2.31	1.89	0.344	0.417	0.073	752	98.9
363.15	-0.612	0.234	2.22	1.78	0.321	0.386	0.073	701	98.8
373.15	-0.549	0.237	2.11	1.65	0.281	0.348	0.073	636	98.7
T (K)	[PrMPyr][FSI]								
323.15	-0.604	0.276	2.46	2.14	0.302	0.555	0.085	551	98.6
333.15	-0.596	0.268	2.36	2.06	0.253	0.516	0.083	590	98.6
343.15	-0.602	0.282	2.27	1.94	0.239	0.481	0.079	655	98.7
353.15	-0.599	0.291	2.19	1.83	0.221	0.446	0.075	660	98.7
363.15	-0.604	0.286	2.11	1.75	0.201	0.418	0.072	662	98.7
373.15	-0.603	0.295	2.04	1.64	0.186	0.388	0.070	659	98.7

Table 11. LSER coefficients of the four ILs studied in this work as function of temperature.

	x_0	x_1
[MPrPip][FSI]		
c	0.0021	-1.4521
r	0.0002	0.2459
s	-0.01	5.7066
a	-0.0112	5.8193
b	-0.0023	1.0495
l	-0.0036	1.7586
[BMPyr][FSI]		
c	-0.0007	-0.3777
r	0.0006	0.0697
s	-0.0077	4.8873
a	-0.0089	4.9702
b	-0.0019	0.8926
l	-0.0033	1.6238
[EMIM][FSI]		
c	0.0023	-1.4289
r	0.0003	0.1076
s	-0.0089	5.4618
a	-0.011	5.7564
b	-0.0031	1.4469
l	-0.0034	1.6195
[PrMPyr][FSI]		
c	0	0.602
r	0.0005	0.1258
s	-0.0084	5.1528
a	-0.0101	5.4146
b	-0.0022	0.9837
l	-0.0033	1.6252

Table 12. LSER descriptors of ionic liquids determined at 323.15 K. ρ : Multiple correlation coefficient; SE :standard error in the estimation; and n :number of solutes.

Ionic liquids	System constants						Statistics			Ref.
	e	s	a	b	l	c	ρ	SE	n	
[MPrPip] [FSI]	0.320	2.50	2.19	0.31	0.585	-0.769				This work
[PMPip][Tf ₂ N]	0.172	2.093	2.185	0.318	0.569	-0.467	0.989	0.103	80	[83]
[BMPip][Tf ₂ N]	0.094	2.442	2.106	0.005	0.611					[81]
[BMPip][SCN]	0.587	2.629	4.683	0.062	0.536	0.984				[81]
[C5MPip] [Tf ₂ N]	0	5.15	4.76	0.372	1.48	-1.13	0.989	0.146	36	[80]
[C6MPip] [Tf ₂ N]	0	4.77	4.58	0.407	1.51	-1.03	0.989	0.138	36	[80]
[PrMPyr][FSI]	0.276	2.46	2.14	0.302	0.555	-0.604				This work
[BMPyr][FSI]	0.205	2.40	2.10	0.272	0.578	-0.614				This work
[BMPyr] [CF ₃ SO ₃]	0.233	2.322	3.499	0.254	0.558	-0.699	0.995	0.094	69	[82]
[BMPyr][FAP]	0	2.121	0.910	0.435	0.56	-0.291	0.987	0.103	91	[82]
[EMIM][FSI]	0.222	2.56	2.21	0.427	0.519	-0.669				This work
[EMIM][Tf ₂ N]	0.148	2.277	2.172	1.041	0.629	-0.439	0.998	0.079	53	[77]
[EMIM][DEPO ₄]	0.26	1.97	6.90	0	0.54	-0.09	0.992	0.097	37	[11]
[EMIM][TFA]	0.608	1.63	4.21	1.81	0.584	-0.918	0.998	0.05	32	[78]
[EMIM] tosylate	0.54	2.40	4.81	0.17	0.48	-0.84	0.99	0.080	29	[14]
[EtOHMIM][PF ₆]	0	3.03	2.89	1.13	0.47	-1.14	0.989	0.090	38	[11]
[EtOHMIM][BF ₄]	0	3.03	3.64	0.763	0.50	-1.35	0.970	0.095	37	[11]
[DMIM][DMPO ₄]	0.86	2.59	7.27	0	0.35	-0.61	0.986	0.101	45	[11]
[BMIM][BF ₄]	0.56	2.82	3.27	0.48	0.50	-0.77	0.992	0.065	43	[12]
[BMIM][CF ₃ SO ₃]	0.399	2.03	3.49	0.681	0.647	-0.784	0.995	0.06	32	[79]
[BMIM] octyl sulfate	0	1.47	4.05	0	0.68	-0.237	0.990	0.082	29	[14]
n-Acryloyloxypropyl-N-methylimidazolium bromide	0	2.88	5.50	0	0.48	-1.03	0.99	0.080	30	[75]
n-Methacryloyloxyhexyl-N-methylimidazolium bromide	0	2.46	5.36	0	0.57	-0.87	0.99	0.088	28	[75]
1-Propenyl-3-methyl-imidazolium bromide	0	2.16	5.19	0	0.53	-1.86	0.990	0.089	28	[74]
1-Propenyl-3-octyl-imidazolium bromide	0	1.72	4.96	0	0.57	-1.60	0.989	0.088	28	[74]
1-Propenyl-3-decyl-imidazolium bromide	0	1.73	4.89	0	0.66	-1.58	0.990	0.089	28	[74]
1-Propenyl-3-dodecyl-imidazolium bromide	0	1.44	4.87	0	0.72	-1.51	0.991	0.088	28	[74]
n-Butylammonium thiocyanate	0.14	1.65	2.76	1.32	0.45	-0.75	0.995	0.058	23	[80]
1,2-Dimethyl-3-ethylimidazolium bis(trifluorosulfonyl)-amide	0.214	2.347	2.075	0.896	0.655	-0.565	0.996	0.071	38	[77]

Figure 1. Representation of the logarithm of activity coefficient at infinite dilution for selected solutes as function of $1/T$. o: butanone, \square : thiophene, \diamond : benzene, \times : water and Δ : 1-propanol.

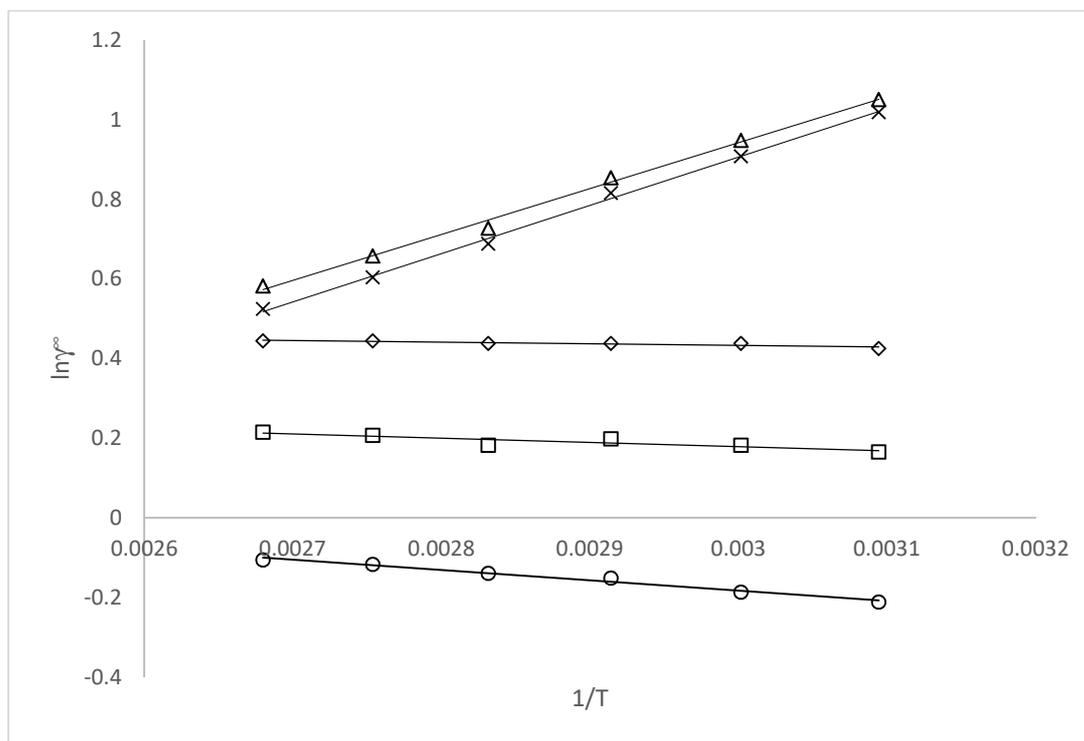


Figure 2. COSMO-RS predicted vs experimental infinite dilution activity coefficient γ^{∞} of molecular solutes in the IL : \square : [EMIM][FSI]; \diamond [BMPyr][FSI]; \times : [PrMPyr][FSI]; o: [MPrPip][FSI].

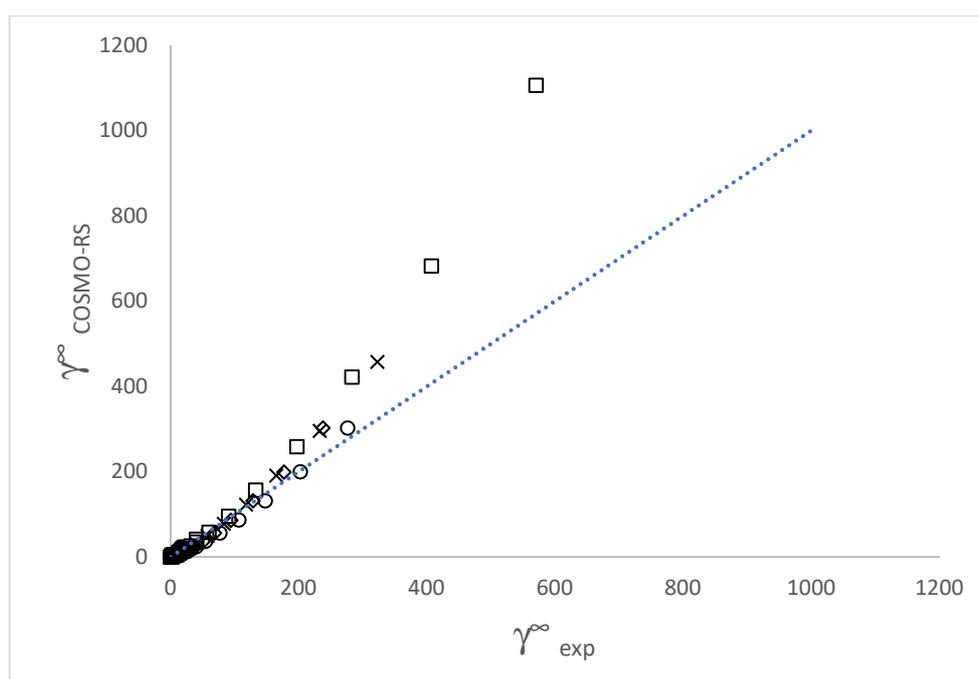


Figure 3. Comparison between the observed $\log K$ data and calculated $\log K$ values based on Eqn. X for organic solutes dissolved in \circ : [PrMPip][FSI], \triangle : [BMPyr][FSI], \square : [EMIM][FSI] and \diamond : [MPrPyr][FSI] at 323.15 K.

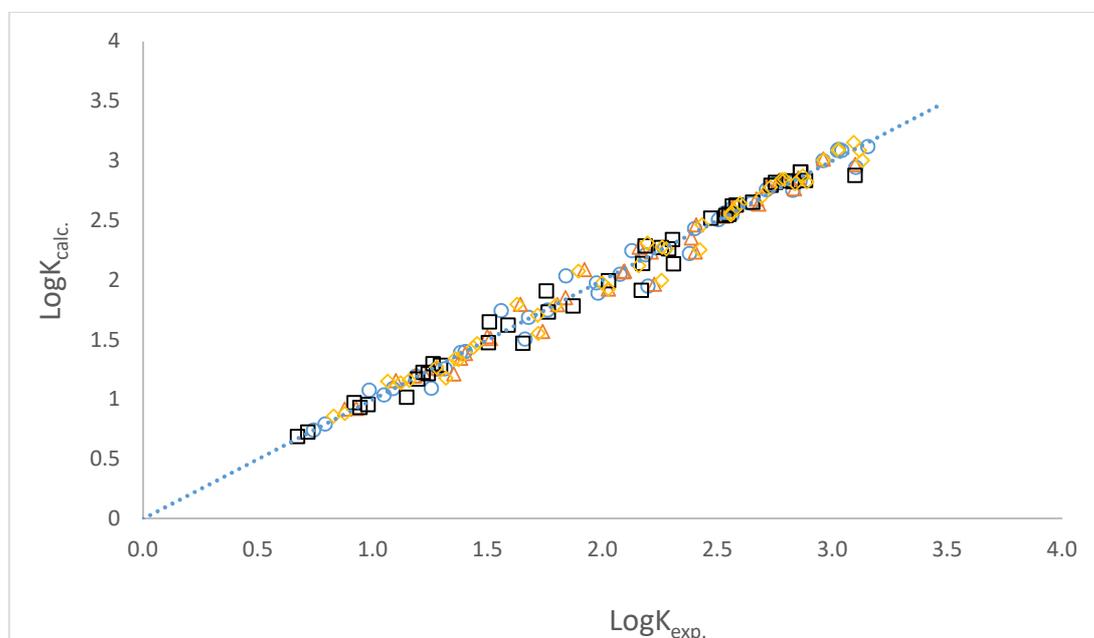
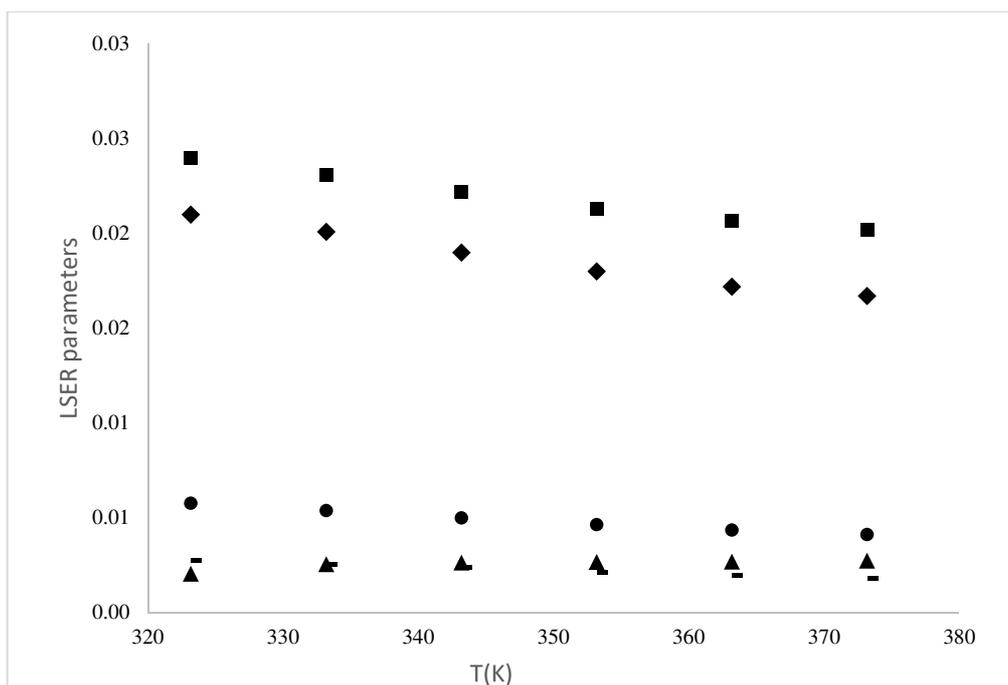


Figure 4. LSER parameters of [BMPyr][NTf₂] as a function of temperature. l : (\bullet), r : (\blacktriangle), s : (\blacksquare), a : (\blacklozenge), b : ($-$).



Graphical abstract

