

Solubility of Water in Tetradecyltrihexylphosphonium-Based Ionic Liquids

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The solubility of water in tetradecyltrihexylphosphonium-based ionic liquids (ILs) with the bromide, bis(trifluoromethylsulfonyl)imide, bis(2,4,4-trimethylpentyl)phosphinate, chloride, decanoate, and dicyanamide anions was measured at temperatures between (288.15 and 318.15) K and atmospheric pressure. The effect of the nature of the IL anion, as well as the influence of temperature, are analyzed and discussed. From the experimental results, it was found that the anion-induced hydrophobicity increases from bis(2,4,4-trimethylpentyl)phosphinate < decanoate < chloride < bromide < dicyanamide < bis(trifluoromethylsulfonyl)imide. COSMO-RS, a predictive method based on unimolecular quantum chemistry calculations, was used to predict the solubility of the water–IL binary systems. COSMO-RS was found to provide fine qualitative and quantitative predictions of the experimental data for extremely hydrophobic ILs. Less accurate predictions were observed with the increase of the anion hydrophilic character.

Introduction

In recent years, there has been a surge in the study of room temperature ionic liquids (ILs) as possible “greener solvents” for the replacement of the usual organic volatile and nonbenign compounds for liquid–liquid extractions and separation processes. ILs have aroused a high interest among the scientific and industrial communities due to their physical and chemical properties, such as no significant vapor pressures, high ionic conductivity, general nonflammability at room temperature, and high temperature stability. Moreover, ILs are a class of organic molten electrolytes whose physical and chemical properties can be tailored by careful selection of cation, anion, or alkyl substitution groups.^{1,2} This feature is of considerable interest when carrying out liquid–liquid extractions or product separations, as the relative solubilities of the IL and the extraction phase can also be adjusted to a specific goal.

The use of ILs as extraction media has been proposed by several authors.^{3–7} In particular, Huddleston et al.³ performed the extraction of organic acids, while Cull et al.⁴ studied antibiotics extraction by ionic liquids. The extraction of several amino acids by ILs was also verified by Smirnova et al.⁵ and Wang et al.⁶ Although most of the studies have been devoted to imidazolium- and pyridinium-based ILs, recently Marták and Schollosser⁷ presented the potential of phosphonium-based ILs to extract lactic acid (LA) from aqueous systems. Interestingly, this extraction occurs by a coordinating mechanism via hydrogen bonding between the IL and LA (LAH···IL) and forming final complexes of the kind [LAH]_p[IL][H₂O]₂ (3 ≥ p ≥ 1) where the dissolved water plays an important role.⁷ The extraction of organic products and/or metabolites from aqueous media requires ILs with low solubility of water since the higher the water solubility in ILs the lower their extractive potential will be. This is due to the intrinsic competition equilibrium between water and the organic compound under study for the IL, which

is directly related to the IL hydrophobic nature. Therefore, the knowledge of the mutual solubilities between water and ILs is of major significance prior to their consideration for extractive applications and concerning their practical point of view. Phosphonium-based ILs come up as a new option of extremely hydrophobic ILs, especially when large alkyl chain lengths are present, and thus their use can be advantageous for the extraction of nonpolar compounds.

Contributions dealing with experimental solubilities between several family based ILs and water have already been reported in the literature.^{8–23} However, to the best of our knowledge, besides the data provided by the manufacturer, only one report at room temperature was found for the liquid–liquid equilibria of three phosphonium-based ILs with water.⁷

Besides, the solubility of water in the ionic liquid phase is also important as it significantly affects the IL's pure physical properties such as polarity, viscosities, densities, and surface tensions.^{24–27} Considerable efforts have been made to understand the singular effect of water in the IL phase behavior.^{28,29} For example, water can act as a cosolvent, increasing the liquid–liquid miscibility between alcohols and ILs, or as an antisolvent, reducing the solubility of gases in ILs.^{28,29} Moreover, the knowledge of ILs and water mutual solubilities is also of significant meaning in the assessment of their environmental hazard. It is known that the IL ecotoxicity can be directly linked to their lipophilicity.^{30–32} Hydrophobic ILs tend to accumulate in biological membranes, and thus their toxicity impact will increase with their hydrophobic character. Thus, the prior knowledge of the ILs and water mutual solubilities can provide a way of predicting the environmental risk of ILs.

The main goal of this work is to investigate the relationship between the ionic structures of hydrophobic ILs and their ability to solubilize water to fully characterize the ILs and their liquid–liquid phase behavior. For that purpose, the tetradecyltrihexylphosphonium cation was studied in combination with six anions, chloride, bromide, bis(2,4,4-trimethylpentyl)phos-

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Table 1. Mole Fraction Solubility of Water (x_w) in Phosphonium-Based ILs at 298.15 K and the Respective Relative Deviations between the Experimental Data from This Work and Those Reported in the Literature

IL	x_w^a	x_w^b	x_w^7	relative deviation ^b	relative deviation ⁷
				%	%
$[(C_6H_{13})_3P(C_{14}H_{29})][N(SO_2CF_3)_2]$	0.087	0.230	---	-62.2	---
$[(C_6H_{13})_3P(C_{14}H_{29})][N(CN)_2]$	0.510	0.494	0.511	3.15	-0.269
$[(C_6H_{13})_3P(C_{14}H_{29})][Br]$	0.678	0.596	---	13.8	---
$[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$	0.817	0.824	0.829	-0.946	-1.51
$[(C_6H_{13})_3P(C_{14}H_{29})][CH_3(CH_2)_8CO_2]$	0.864	0.907	---	-4.66	---
$[(C_6H_{13})_3P(C_{14}H_{29})][PO_2(C_2H_5)(CH_3)CH_2C(CH_3)_3]$	0.891	0.918	0.878	-2.91	1.42

^a This work. ^b Manufacturer's data.

phinate, bis(trifluoromethylsulfonyl)imide, decanoate, and dicyanamide, to conclude about the anion influence on those solubilities.

The COSMO-RS, Conductor-Like Screening Model for Real Solvents, is a method for the prediction of phase equilibria and bulk properties of fluids based on unimolecular quantum calculations.³³⁻³⁷ The application of COSMO-RS to the liquid-liquid equilibria description of ILs and alcohols, hydrocarbons, ethers, ketones, and water systems has already been successfully carried out.³⁸⁻⁴⁴ The COSMO-RS proved to be an a priori model capable of predicting the phase equilibria behavior between water and imidazolium-, pyridinium-, piperidinium-, and pyrrolidinium-based ILs.^{8,9,44} In this work, COSMO-RS was used to study the equilibria of phosphonium-based ILs and water, and its applicability to these systems was evaluated.

Experimental Section

Materials. The experimental solubility of water was measured for six phosphonium-based ILs, namely, tetradecyltrihexylphosphonium chloride, $[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$, tetradecyltrihexylphosphonium bromide, $[(C_6H_{13})_3P(C_{14}H_{29})][Br]$, tetradecyltrihexylphosphonium bis(trifluoromethylsulfonyl)imide, $[(C_6H_{13})_3P(C_{14}H_{29})][N(SO_2CF_3)_2]$, tetradecyltrihexylphosphonium bis(2,4,4-trimethylpentyl)phosphinate $[(C_6H_{13})_3P(C_{14}H_{29})][PO_2(C_2H_5)(CH_3)CH_2C(CH_3)_3]$, tetradecyltrihexylphosphonium decanoate, $[(C_6H_{13})_3P(C_{14}H_{29})][CH_3(CH_2)_8CO_2]$, and tetradecyltrihexylphosphonium dicyanamide, $[(C_6H_{13})_3P(C_{14}H_{29})][N(CN)_2]$. All the ILs were acquired at Fluka, from Cytec Industries Inc., with a stated mole fraction purity $\geq 95\%$ for tetradecyltrihexylphosphonium decanoate and tetradecyltrihexylphosphonium bis(2,4,4-trimethylpentyl)phosphinate, $\geq 96\%$ for tetradecyltrihexylphosphonium bromide and tetradecyltrihexylphosphonium chloride, and $\geq 97\%$ for tetradecyltrihexylphosphonium bis(trifluoromethylsulfonyl)imide and tetradecyltrihexylphosphonium dicyanamide, as verified by ³¹P NMR spectra. The chloride mass fraction content is $< 10^{-3}$ for all samples. Vacuum at a moderate temperature and for at least 48 h was applied to all the IL samples prior to their use to reduce volatile compounds (which can result from the synthesis) that may be present. The water content in all samples after the drying procedure is less than $5 \cdot 10^{-4}$ in mass fraction. No further purification of the compounds was carried out. The water used was double distilled, passed by a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus.

Experimental Procedure. The measurements of the solubility of water in ILs were carried out at temperatures from (288.15 to 318.15) K and at atmospheric pressure. The IL and the water phases were initially vigorously agitated and allowed to reach the saturation equilibrium by the separation of both phases for at least 72 h. This time was found to be the minimum time required to allow a complete separation of the two phases, and

no further variations in water mole fraction solubilities occurred for the ILs under study.

The temperature was maintained by keeping the samples in equilibrium inside an aluminum block specially designed for this purpose, which is positioned in an isolated air bath capable of maintaining the temperature within ± 0.01 K (achieved with a PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature sensor). For temperatures below room temperature, a Julabo circulator, model F25-HD, was attached to the overall oven system allowing the passage of a thermostated fluid flux around the aluminum block.

The solubility of water in the IL-rich phase was determined using a Metrohm 831 Karl Fischer (KF) coulometer. The IL-rich phase was sampled at each temperature from the equilibrium vials, using glass syringes maintained dry and at the same temperature of the measurements, and directly injected in the KF coulometric titrator. All the mole fraction quantifications were performed gravimetrically within a precision of $\pm 10^{-4}$ g. For each sample and at a specific temperature, at least five individual measurements were performed, allowing the determination of an average solubility value as well as the associated expanded uncertainty of the experimental measurements.^{45,46}

Results and Discussion

Experimental Results. The water solubility in the phosphonium-based ILs was measured in the temperature range between (298.15 and 318.15) K and at atmospheric pressure for six ILs with the cation tetradecyltrihexylphosphonium in common and combined with the anions chloride, bromide, bis(trifluoromethylsulfonyl)imide, bis(2,4,4-trimethylpentyl)phosphinate, decanoate, and dicyanamide.

The water solubility data obtained were compared with the data reported by the Cytec manufacturer and literature data whenever possible.⁷ The relative deviations between the solubility of water measured in this work and that from the literature are presented in Table 1. Positive and negative relative deviations from this work to both the data provided by the manufacturer and the literature data⁷ were observed, attesting the absence of systematic errors. Unfortunately, only a few data at room temperature are available, and no experimental details are provided.⁷ Nevertheless, it should be noticed that the IL hydrophobicity here reported follows essentially the same trend observed in the two other literature sources as presented in Table 1, with only one exception verified for tetradecyltrihexylphosphonium bis(2,4,4-trimethylpentyl)phosphinate and tetradecyltrihexylphosphonium decanoate. The water solubility in both ILs is very close, and the deviations could arise from the equilibration time required to saturate the IL-rich phase.

The experimental solubility data measured and the respective expanded uncertainty with an approximately 95 % level of confidence are presented in Table 2.^{45,46} It can be observed that for all the studied ILs the solubility of water increases with the

Table 2. Mole Fraction Solubility of Water (x_w) in Phosphonium-Based ILs as a Function of Temperature

IL	T/K						
	288.15	293.15	298.15	303.15	308.15	313.15	318.15
	$x_w \pm \sigma^a$						
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]N(SO ₂ CF ₃) ₂	0.077 ± 0.002	0.081 ± 0.001	0.087 ± 0.001	0.092 ± 0.001	0.097 ± 0.002	0.104 ± 0.001	0.108 ± 0.001
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]N(CN) ₂	0.502 ± 0.002	0.505 ± 0.001	0.510 ± 0.002	0.515 ± 0.002	0.520 ± 0.002	0.526 ± 0.002	0.533 ± 0.003
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]Br	0.673 ± 0.001	0.675 ± 0.002	0.678 ± 0.002	0.682 ± 0.001	0.686 ± 0.002	0.690 ± 0.002	0.696 ± 0.002
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]Cl	0.811 ± 0.001	0.814 ± 0.003	0.817 ± 0.003	0.819 ± 0.004	0.822 ± 0.004	0.826 ± 0.002	0.830 ± 0.003
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]CH ₃ (CH ₂) ₈ CO ₂	0.855 ± 0.004	0.860 ± 0.004	0.864 ± 0.005	0.870 ± 0.005	0.875 ± 0.005	0.882 ± 0.004	0.888 ± 0.003
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]PO ₂ (C ₂ H ₅ (CH ₃)CH ₂ C(CH ₃) ₃)	0.885 ± 0.002	0.888 ± 0.006	0.891 ± 0.006	0.895 ± 0.004	0.900 ± 0.003	0.903 ± 0.005	0.908 ± 0.005

^a Expanded uncertainty with an approximately 95 % level of confidence.

Table 3. Parameters for the Correlation of the Mole Fraction Solubility of Water as a Function of Temperature Using Equation 1

IL	(A ± σ ^a)	(B ± σ ^a)/K
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]N(SO ₂ CF ₃) ₂	1.10 ± 0.06	-1058 ± 17
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]N(CN) ₂	-0.06 ± 0.03	-181 ± 10
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]Br	-0.04 ± 0.02	-102 ± 8
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]Cl	0.03 ± 0.01	-70 ± 3
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]CH ₃ (CH ₂) ₈ CO ₂	0.25 ± 0.01	-117 ± 5
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)]PO ₂ (C ₂ H ₅ (CH ₃)CH ₂ C(CH ₃) ₃)	0.16 ± 0.01	-81 ± 3

^a Expanded uncertainty with an approximately 95 % level of confidence.

temperature. This particular family of phosphonium-based ILs is known as “hydrophobic”, but from the water solubility results, it can be seen that some of them are substantially “hygroscopic”. The mole fraction solubility of water in the studied family ranges from 0.087 to 0.891 at 298.15 K, reflecting the large influence of the anion in controlling the liquid–liquid miscibility of ILs with water.^{8,9} While it is expected that the water-rich phase can be considered almost as a pure phase with the dissolved IL close to infinite dilution,⁷ the IL-rich phase cannot be considered as a near pure IL phase. In fact, in some cases, the IL-rich phase is even richer in water than in IL.

The experimental results obtained in this work show that the hydrophobicity decrease due to the anion identity follows the sequence bis(trifluoromethylsulfonyl)imide > dicyanamide > bromide > chloride > decanoate > bis(2,4,4-trimethylpentyl)phosphinate, that is verified at all the temperatures studied. The highest hydrophilic character of the anions bis(2,4,4-trimethylpentyl)phosphinate and decanoate are due to the presence of two oxygen-rich functional groups with the capability of hydrogen bonding with water. Particularly, for tetracyclotrihexylphosphonium bis(2,4,4-trimethylpentyl)phosphinate fully saturated with water, at 298.15 K, there are 8 moles of water per mole of IL which agrees with the 4 to 8 moles of water per mole of IL as reported by Marták and Schlosser.⁷

Assuming that in the temperature range studied the molar enthalpy of solution of water in each IL can be considered temperature independent, eq 1 can be thus used to correlate the experimental solubility data

$$\ln x_w = A + \frac{B}{T/K} \quad (1)$$

where x_w is the mole fraction solubility of the water in IL; T is the temperature; and A and B are correlation parameters. The correlation constants obtained from the fitting for the water solubility are presented in Table 3. The good description of the experimental data by this correlation is shown in Figure 1. A maximum relative deviation from the experimental mole fraction data of 0.8 % was observed.

From the dependence of the solubility of water with temperature, it can be stated that phosphonium-based ILs will present a higher molar enthalpy of solution for water when compared with the usual imidazolium-based IL family.^{8,9} The solubility of water in all the studied ILs is well above what could be

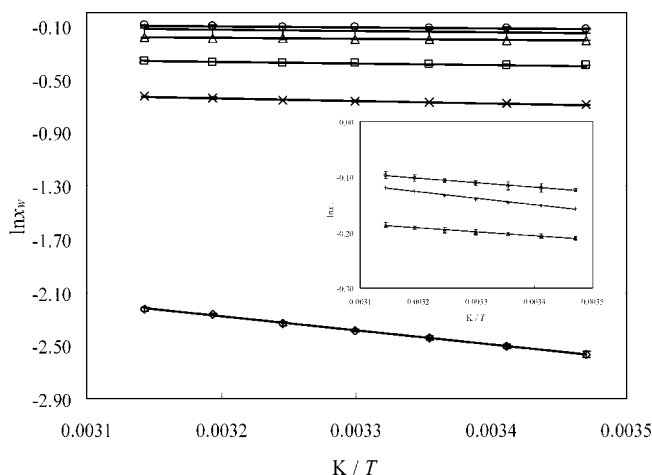


Figure 1. Mole fraction solubility of water (x_w) as a function of temperature for the following ILs: \diamond , [(C₆H₁₃)₃P(C₁₄H₂₉)]N(SO₂CF₃)₂; \times , [(C₆H₁₃)₃P(C₁₄H₂₉)]N(CN)₂; \square , [(C₆H₁₃)₃P(C₁₄H₂₉)]Br; Δ , [(C₆H₁₃)₃P(C₁₄H₂₉)]Cl; $+$, [(C₆H₁₃)₃P(C₁₄H₂₉)]CH₃(CH₂)₈CO₂; \circ , [(C₆H₁₃)₃P(C₁₄H₂₉)]PO₂(C₂H₅(CH₃)CH₂C(CH₃)₃). The solid lines represent the correlation of the experimental data using eq 1.

considered infinite dilution, and the associated molar thermodynamic functions of solution cannot be directly determined without the activity coefficient of water. Nevertheless, some general remarks can be made based on the slope obtained from eq 1 (that reflects the direct water solubility dependence of temperature). From our previous results,⁹ the slope obtained from eq 1 for 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is very close to the slope obtained for tetracyclotrihexylphosphonium bis(trifluoromethylsulfonyl)imide that once again indicates that it is the anion which major determines the water solubility. Also, the slope observed for 1-butyl-3-methylimidazolium tricyanomethane is quite similar to the slope obtained for tetracyclotrihexylphosphonium dicyanamide due to the chemical structure analogies of both anions.⁸ Moreover, the results obtained in this work show that the tetracyclotrihexylphosphonium-based ILs are more hydrophobic than the 1-butyl-3-methylimidazolium- and 1-butyl-3-methylpyrrolidinium-based ILs, when comparing the solubility of water where the anion bis(trifluoromethylsulfonyl)imide is in common.^{8,9}

COSMO-RS Prediction Results. Given the large number of available ionic liquids, a predictive method that could scan their

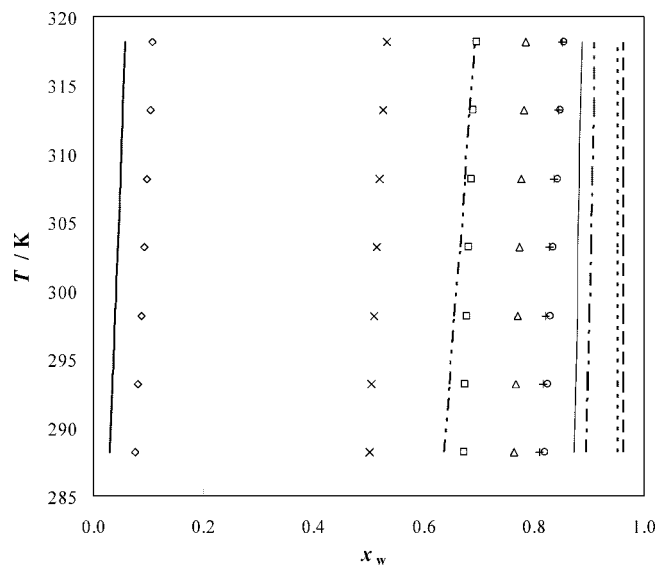


Figure 2. Temperature–mole fraction solubility of water (x_w) phase behavior for the following ILs: \diamond , wavy line, $[(C_6H_{13})_3P(C_{14}H_{29})][N(SO_2CF_3)_2]$; \times , - - - -, $[(C_6H_{13})_3P(C_{14}H_{29})][N(CN)_2]$; \square , - - -, $[(C_6H_{13})_3P(C_{14}H_{29})][Br]$; Δ , - - -, $[(C_6H_{13})_3P(C_{14}H_{29})][Cl]$; $+$, - - -, $[(C_6H_{13})_3P(C_{14}H_{29})][CH_3(CH_2)_8CO_2]$; \circ , - - -, $[(C_6H_{13})_3P(C_{14}H_{29})][PO_2-(C_2H_5(CH_3)CH_2C(CH_3)_3)]$. The lines represent the COSMO-RS predictions.

phase equilibria prior to making extensive experimental measurements would be valuable. In this aspect, COSMO-RS appears as an interesting approach to predict liquid–liquid and vapor–liquid phase equilibria of systems involving ILs and different solvents, as shown before.^{38,44}

The COSMO-RS is a method for predicting the thermodynamic properties of mixtures on the basis of unimolecular quantum chemical calculations for individual molecules. Further details concerning the COSMO-RS theory can be found elsewhere.^{38,44}

A pseudobinary approach was used to determine the liquid–liquid phase behavior of the studied ILs plus water within the COSMOtherm program.^{47,48} The cation and anion were introduced as separated species with the same mole fraction. The chemical potentials were calculated for the ternary system (anion + cation + water)—where the chemical potential of the IL is the sum of the chemical potentials of both the cation and anion—converting thus the mole fraction solubilities to a binary system. All the COSMO-RS calculations were done at the BP/TZVP level (Turbomole^{49,50} DFT/COSMO calculation with the BP functional and TZVP⁵¹ basis set using the optimized geometries at the same level of theory) and at the parameter file BP_TZVP_C21_0105 with the derived ion lowest energy conformers. The relationship between the experimental data obtained in this work and the predictive results by COSMO-RS is presented in Figure 2.

The results obtained with COSMO-RS show reasonable qualitative and quantitative agreement with the experimental data, although some deviations were found. COSMO-RS does not predict well the hydrophobic tendency of the anions. The major difference observed is for the anions chloride and bromide where the COSMO-RS predictions imply that these are the most hydrophilic anions, while experimental data indicate that the most hydrophilic anions are decanoate and bis(2,4,4-trimethylpentyl)phosphinate anions. This could arise from the assumption that the chloride and bromide anions present a higher charge density due to their smaller size and allow therefore stronger Coulombic interactions. Nevertheless, the oxygen lone pair of

electrons in the anions decanoate and bis(2,4,4-trimethylpentyl)phosphinate seem to dominate the solubility of water through hydrogen bonding as verified experimentally. Note that COSMO-RS predicts well the experimental phase behavior of both chloride and bromide anions.

The results obtained show that the larger the difference in polarities between the mixture components, the better the qualitative and quantitative predictions using COSMO-RS. Systems with extremely hydrophobic anions are described more accurately by this model than those based on more hydrophilic anions. This is in agreement with our previous findings⁴⁴ where the COSMO-RS provided a better phase behavior description of the system water and bis(trifluoromethylsulfonyl)imide-based ILs than water and tetrafluoroborate- or hexafluorophosphate-based ILs.

Conclusions

The relatively high solubilities of water in the IL-rich phase may have important implications in the design of separation processes that employ ILs. Original experimental solubility data of water in six tetradecyltrihexylphosphonium-based ILs, at temperatures ranging between (288.15 and 318.15) K and at atmospheric pressure, are presented. The solubility of water in these compounds is strongly dependent on the anion ranging from 0.087 up to 0.891 at 298.15 K for the studied ILs. Although these ILs are considered hydrophobic, some of them are extremely hygroscopic. From the obtained solubility results, it is possible to define the hydrophobic nature of the studied ILs where the anion hydrophobic tendency follows the order: bis(trifluoromethylsulfonyl)imide > dicyanamide > bromide > chloride > decanoate > bis(2,4,4-trimethylpentyl)phosphinate.

The COSMO-RS predictive ability was evaluated through the comparison with the experimental results. COSMO-RS seems to describe well the phase diagrams of extremely hydrophobic ILs and water. Some limitations were found with the increase of the IL hydrophilic character. COSMO-RS seems to be a reliable method for the thermodynamic evaluation of ionic liquids before extensive experimental measurements.

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