

Solubility of non-aromatic hexafluorophosphate-based salts and ionic liquids in water determined by electrical conductivity



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ABSTRACT

The knowledge of the salts solubility in water is of major interest for process design and optimization and for environmental monitoring. The determination of the water solubility of non-aromatic salts or ionic liquids requires the use of specific and expensive analytical equipment. In this work the use of electrical conductivity for the quantification of the solubility of sparingly soluble salts in water is proposed. Novel data for the water solubility of 1-methyl-1-propylpyrrolidinium hexafluorophosphate, 1-methyl-1-propylpiperidinium hexafluorophosphate, tetrabutylammonium hexafluorophosphate, and tetrabutylphosphonium hexafluorophosphate, in the temperature range from 288.15 to 318.15 K, are reported. Using the gathered results, along with literature data, a correlation between the aqueous solubility of [PF₆]-based salts with their molar volume is proposed. The COSMO-RS predictive model was also used to estimate the solid–liquid equilibrium of the investigated systems. Since all the compounds are solid at room temperature, they were further characterized by differential scanning calorimetry, and the temperatures of solid–solid and solid–liquid phase transitions, as well as the respective enthalpies of phase transition, are presented.

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1. Introduction

Ionic liquids (ILs) belong to the molten salts group and are formed by large organic cations and organic or inorganic anions. The organic cations are usually asymmetric and have a high vibrational freedom. The charge delocalization of the IL ions reduces the stability of the crystalline phases, and thus, their melting temperatures. The inherent ionic nature of ILs provides them unique properties, such as a negligible vapor pressure and low flammability, high chemical and thermal stabilities, a large electrochemical window and a high electrical conductivity [1]. In addition, the huge number of possible combinations between cations and anions and/or their multifaceted chemical structures allow the tuning of their properties and they are commonly described as “designer solvents” [2].

The knowledge of the solubility of ILs and other sparingly soluble salts in water is of high relevance for both environmental and process related routines, particularly when large scale applications are foreseen. In fact, although ILs cannot contribute to air pollution because of their negligible vapor pressures, even those considered

“hydrophobic” present a non-negligible solubility in water [3–7], and thus lead to environmental concerns [8]. On the other hand, the knowledge of the water content in ILs is also important because it significantly affects their physical properties such as viscosities, densities and surface tensions [9–13]. Water may also act as a co-solvent, for example, increasing the mutual solubilities between alcohols and ILs, or as an anti-solvent, reducing the solubility of gases in ILs [14–16]. However, not only the amount of water solubility data available for ILs is limited [3–7,17–25] but most of these results only regard aromatic-based compounds.

The previous methods applied to quantify the solubility of ILs in water include UV–vis spectroscopy [3–5,7,25], thermogravimetric analysis (TGA) [25], Karl–Fisher titration [25], electrospray ionization mass spectrometry (ESI-MS) [6,17], gravimetric studies making use of conventional balances [21] and ion selective electrodes (ISE) [24]. UV–vis spectroscopy is an easy and accurate technique and already proved to be an appropriate method to quantify the solubility of a vast number of ILs in water [3–5,7,25]; yet, the major problem associated to this technique is that is limited to colored substances or compounds that present π – π transitions (like aromatic rings and double bonds). For non-aromatic salts, thermogravimetry and mass spectrometry approaches could be used. Nevertheless, both techniques require the use of specific and expensive equipment and are not adequate for routine

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measurements. In addition, the ESI-MS is not a straight quantification technique, and thus, its use is more complex since it always requires the calibration with an internal standard [6]. Karl–Fisher titration is commonly and more accurately used to determine the water content, and hence it is not suitable for determining the solubility of sparingly soluble compounds in a water-rich phase since it will provide a high associated uncertainty. The gravimetric method also presents large errors when applied to low IL content samples, while the ISE method requires specific electrodes to different anions or cations limiting therefore its versatility. In this context, we propose here electrical conductivity measurements of aqueous solutions as an alternative, easy and fast method applicable to salts sparingly soluble in water.

In this work, the solubility in water of sparingly soluble and non-aromatic hexafluorophosphate-based salts and ILs (comprising piperidinium-, pyrrolidinium-, ammonium- and phosphonium-based cations) was determined in the temperature range from 288.15 to 318.15 K. With the novel gathered experimental data, along with additional literature results, a correlation for the aqueous solubility of $[\text{PF}_6]^-$ -based salts with their molar volume is further proposed allowing a fast estimation of solubilities of these compounds in water.

The solubility of the $[\text{PF}_6]^-$ -based salts in water was also predicted using the Conductor-Like Screening Model for Real Solvents, COSMO-RS. COSMO-RS is based on unimolecular quantum calculations and is commonly used for the prediction of phase equilibrium and bulk properties of fluids [26–29]. COSMO-RS already proved to be an *a priori* model capable of predicting the phase equilibrium behavior of systems involving ILs [30]. In the past few years, we have shown its ability to predict either the liquid–liquid equilibrium of binary mixtures composed of ILs and water [31], alcohols [32] or hydrocarbons [33], or more complex ternary mixtures comprising ILs, water and alcohols or ILs and aliphatic and aromatic hydrocarbons [34,35]. Most of our previous studies [3,4,7] regard liquid–liquid equilibrium between ILs and water making use of room temperature ILs, and the COSMO-RS model is now evaluated on its ability to describe the solubility of solid salts in water at diverse temperatures.

All the hexafluorophosphate-based salts were also characterized by differential scanning calorimetry (DSC) to determine their phase transition temperatures and respective enthalpies of phase transition.

2. Experimental

2.1. Chemicals

The study of the solubility in water was carried out for the salts or ILs described in Table 1. The cyclic hexafluorophosphate-based salts are considered ILs since their melting temperatures are nearly 373 K, as it will be shown later in the DSC results. On the other hand, the $[\text{P}_{4444}][\text{PF}_6]$ and $[\text{N}_{4444}][\text{PF}_6]$ present melting temperatures higher than 373 K. Yet, to avoid any ambiguity, all these compounds will be thereafter referred as hexafluorophosphate-based salts. All salts were dried and purified under high vacuum

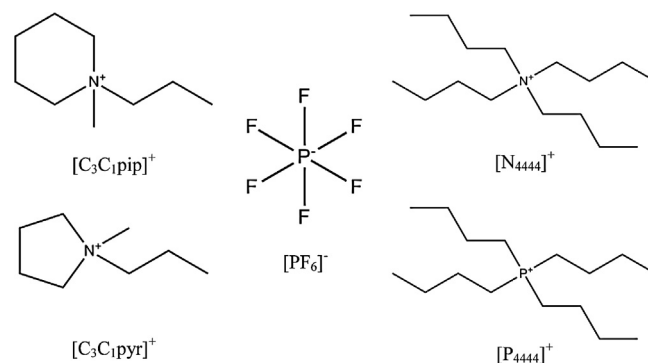


Fig. 1. Chemical structures of the ions composing the salts studied in this work.

(10^{-5} Pa) for at least 48 h before the equilibration with water. After this drying step, the purity of each sample was additionally confirmed by ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra. The water used in the equilibration studies was double distilled, passed by a reverse osmosis system and further treated with a MilliQ plus 185 water purification apparatus. It has a resistivity of $18.2\ \text{M}\Omega\ \text{cm}$ and Total Organic Carbon content lower than $5\ \mu\text{g}\ \text{dm}^{-3}$. The supplier, purification method used and mass fraction purity of each ionic liquid are presented in Table 1.

The chemical structures of the ions that compose the investigated hexafluorophosphate-based salts are depicted in Fig. 1.

2.2. DSC measurements

The phase transition temperatures and enthalpies of all $[\text{PF}_6]^-$ -based salts were determined by differential scanning calorimetry using a Q200 DSC from TA Instruments. Samples of about 5 mg were tightly sealed in hermetic aluminum pans. The temperature range for the different salts was between 183.15 and 423.15 K for $[\text{C}_3\text{C}_1\text{pip}][\text{PF}_6]$, 183.15 and 423.15 K for $[\text{C}_3\text{C}_1\text{pyr}][\text{PF}_6]$, 183.15 and 548.15 K for $[\text{N}_{4444}][\text{PF}_6]$ and 183.15 and 523.15 K for $[\text{P}_{4444}][\text{PF}_6]$. The analytical procedure included a cooling ramp down to 183.15 K and a heating ramp up to the maximum temperature (salt dependent) at a rate of $0.167\ \text{K}\ \text{s}^{-1}$. In the case of $[\text{C}_3\text{C}_1\text{pip}][\text{PF}_6]$ the results presented were obtained with a heating rate of $0.0167\ \text{K}\ \text{s}^{-1}$. The underlying reason for this is the appearance of an extra solid–solid phase transition at this slow heating rate. All salts were submitted to three cycles of cooling and heating. A constant nitrogen flow of $0.833\ \text{cm}^3\ \text{s}^{-1}$ was supplied to the DSC cell in order to avoid condensation of water at the lower temperatures. At least 2 independent runs were performed for each salt.

2.3. Solubility measurements

The solubility measurements of the $[\text{PF}_6]^-$ -based salts in water were performed from 288.15 to 318.15 K and at atmospheric pressure. The salt and water phases were initially vigorously agitated in closed glass vials and then allowed to reach saturation equilibrium and complete phase separation, during a period of at least 48 h. This period proved to be the minimum time required to guarantee

Table 1

Salts or ILs used and respective acronym, supplier, purification method, mass fraction purity and method used to confirm the purity.

IL	Acronym	Supplier	Purification method	Mass fraction purity (%)	Purity confirmation
Cation	Anion				
1-Butyl-3-methylimidazolium		$[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$	Iolitec	99	
1-Methyl-1-propylpyrrolidinium		$[\text{C}_3\text{C}_1\text{pyr}][\text{PF}_6]$	Iolitec	99	
1-Methyl-1-propylpiperidinium	Hexafluorophosphate	$[\text{C}_3\text{C}_1\text{pip}][\text{PF}_6]$	Iolitec	99	^1H , ^{13}C , ^{31}P and ^{19}F NMR
Tetrabutylammonium		$[\text{N}_{4444}][\text{PF}_6]$	Apollo Scientific	98	
Tetrabutylphosphonium		$[\text{P}_{4444}][\text{PF}_6]$	Fluka	99	

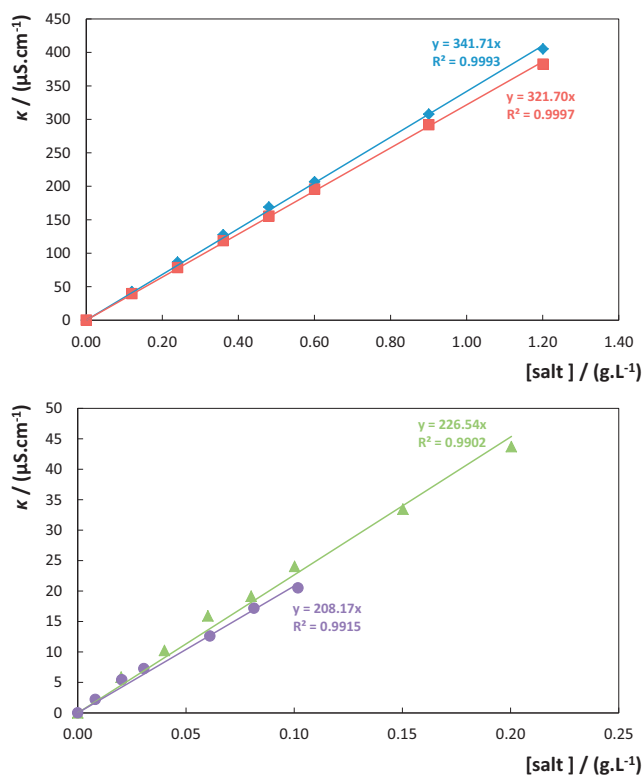


Fig. 2. Calibration curves for (♦) $[C_3C_1\text{pyr}][PF_6]$, (■) $[C_3C_1\text{pip}][PF_6]$, (▲) $[N_{4444}][PF_6]$ and (●) $[P_{4444}][PF_6]$.

that no further variations in water mole fractions occurred. The temperature was maintained by keeping the vials containing the phases in equilibrium inside of an aluminum block, that is further kept inside of an air bath, and specially designed for this purpose [3,4,6,7,36]. A Julabo circulator, model F25-HD, is also coupled to the system allowing the passage of a thermostatic fluid around the aluminum block. The system is capable of maintaining the temperature within ± 0.01 K by means of a PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature probe inserted into the aluminum block.

The solubility of each salt in the aqueous-rich phase was determined by conductivity with a Mettler Toledo S47 SevenMulti™ dual meter pH/conductivity, coupled with an InLab®741 Conductivity Probe as electrode. The calibration of the conductivity meter was previously carried out with two solutions of KCl with concentrations of 0.1 M and 0.01 M. After equilibration, the water-rich phase was sampled from the equilibrium glass vials using glass syringes maintained dry and at the same temperature of the measurements. The samples were weighted and further diluted in ultra-pure water in a ratio ranging between 1:10 and 1:20. Previous optimization tests regarding the appropriate dilution were carried aiming at obtaining significant conductivity values and within the equipment capability. Former calibration curves were performed for each salt and in an adequate concentration range. Each stock solution was prepared gravimetrically within $\pm 10^{-5}$ g and at least 2 calibration curves were determined for each salt to guarantee the accuracy of the data and to confirm that no gravimetric errors occurred during the stock solutions preparation. The obtained calibration curves are presented in Fig. 2. The solubility data is the result of an average of at least five independent measurements, i.e., five equilibrated samples.

In order to validate the equipment and methodology adopted, the solubility of $[C_4C_1\text{im}][PF_6]$ in water obtained in this work was compared with the literature data [4] quantified by UV–vis

spectroscopy. The experimental procedure regarding the equilibration period and sampling is similar to the previous optimized methodology [4].

2.4. COSMO-RS calculations

The standard procedure for COSMO-RS calculations consists of two major steps. First, the continuum solvation COSMO calculations of electronic density and molecular geometry were performed with the TURBOMOLE 6.1 program package on the density functional theory level, utilizing the BP functional B88-P86 with a triple- ζ valence polarized basis set (TZVP) and the resolution of identity standard (RI) approximation [37]. Second, the solubility calculation of the several salts in water was performed with the COSMOthermX.2.1 program using the parameter file BP-TZVP_C21.0111 (COSMOlogic GmbH & Co KG, Leverkusen, Germany) [38]. In all calculations the IL or salt are always treated by means of their isolated ions. The solubility was then computed from the mean chemical potentials of the ions and the free energy of fusion, ΔG_{fus} . In the COSMOthermX program, the ΔG_{fus} can be entered directly or, alternatively, the enthalpy, ΔH_{fus} , or entropy of fusion, ΔS_{fus} , as well as the respective melting temperature, T_m , can be entered. In this work, the ΔH_{fus} and T_m values of the studied hexafluorophosphate-based salts were taken from the respective DSC measurements and used in the COSMO-RS calculations.

3. Results and discussion

3.1. Phase transitions and melting temperatures

The phase transitions of the $[PF_6]$ -based salts, all solid at room temperature, were determined by DSC measurements. Besides the solid–liquid phase transitions, all these compounds also present solid–solid phase transitions. $[P_{4444}][PF_6]$ shows only one solid–solid phase transition, while the other three compounds present two solid–solid phase transitions in the temperature range evaluated. The phase transition temperatures and respective enthalpy changes are reported in Table 2. Since at least 2 independent runs were carried out for each salt, all the results are provided as an average with an associated uncertainty. The melting temperatures of the quaternary ammonium- and phosphonium-based salts are 524.3 K and 498.6 K, respectively. These salts are far from the definition of ILs since their melting temperatures are well above 373 K. On the other hand, the melting temperatures of piperidinium- and pyrrolidinium-based salts are 368.2 K and 383.6 K. Thus, the piperidinium- and pyrrolidinium-based salts can be considered within the definition of ILs, although the melting temperature of the pyrrolidinium-based salt that is slightly above 373 K.

3.2. Validation of the solubility measurements

In order to validate the equipment and methodology here proposed, the solubility of $[C_4\text{mim}][PF_6]$ in water was also measured by electrical conductivity and the respective results were compared with previous literature data determined by a different technique (UV–vis spectroscopy) [4]. The average relative deviation between the results obtained by electrical conductivity and UV–vis spectroscopy at 2 different temperatures is 2.99%. Given the very low solubility of $[C_4\text{mim}][PF_6]$ in water (mole fraction in the range of 10^{-3}), the results here obtained are in acceptable agreement with those previously reported [4]. In fact, the deviations only occur at the third significant figure that is within the associated uncertainty of the UV–vis quantification [4]. Moreover, higher deviations are currently observed amongst different authors [4,24]. Thus, the technique here proposed reveals to be an alternative and simple

Table 2
Melting and solid phase transitions of the [PF₆]-based salts studied in this work obtained at 0.1 MPa.

Salt	1st Transition		2nd Transition		Melting temperature	
	$T \pm 2u(T)^a$ (K)	$\Delta H \pm 2u(\Delta H)^a$ (kJ mol ⁻¹)	$T \pm 2u(T)^a$ (K)	$\Delta H \pm 2u(\Delta H)^a$ (kJ mol ⁻¹)	$T \pm 2u(T)^a$ (K)	$\Delta H \pm 2u(\Delta H)^a$ (kJ mol ⁻¹)
[N ₄₄₄₄][PF ₆]	303.95 ± 0.04	2.10 ± 0.08	360.70 ± 0.30	2.06 ± 1.16	524.3 ± 0.4	16.41 ± 0.26
[P ₄₄₄₄][PF ₆]	265.37 ± 0.04	1.81 ± 0.04	–	–	498.6 ± 0.1	14.67 ± 0.04
[C ₃ C ₁ pip][PF ₆]	310.60 ± 0.32	7.89 ± 0.18	350.96 ± 0.02	2.78 ± 0.02	368.2 ± 0.1	5.15 ± 0.04
[C ₃ C ₁ pyr][PF ₆]	348.58 ± 0.64	2.76 ± 0.08	360.88 ± 0.84	2.30 ± 0.08	383.6 ± 0.7	3.66 ± 0.14

^a Expanded uncertainty at the 0.95 confidence level, $2u(T)$ and $2u(\Delta H)$, evaluated from the standard deviation and applying a coverage factor $k = 2$.

method to quantify the solubility of sparingly soluble salts in aqueous solutions.

It should be remarked that under more severe conditions of pH and temperature, the [PF₆]⁻ anion is not stable and hydrolyses when in contact with aqueous media [39]. In this work this inherent degradation of the fluorinated anion was taken into consideration. At the temperatures and pH ranges here used we can guarantee that no degradation of the anion occurs.

3.3. Solubility of hexafluorophosphate-based salts in water

The solubility of the [PF₆]-based salts combined with the cations [C₃C₁pip]⁺, [C₃C₁pyr]⁺, [N₄₄₄₄]⁺ and [P₄₄₄₄]⁺ in water were determined in the temperature range from 288.15 to 318.15 K. In this temperature range all the salts are solid and the results correspond to solid–liquid equilibrium data. The experimental solubilities of each salt, expressed in mole fraction, are presented in Table 3 and depicted in Fig. 3.

For all systems there is an increase in the salt solubility in water with an increase in temperature. Regarding the cation influence, the solubility of the hexafluorophosphate-based salts decreases in the following order: pyrrolidinium > piperidinium >> ammonium > phosphonium. The two last [PF₆]-based salts show a very low solubility in water and in the order of 10⁻⁵ (mole fraction), while the salts comprising the piperidinium and pyrrolidinium cations present a solubility in water in the order of 10⁻³ (mole fraction).

Comparing with literature data concerning the solubility of other salts in water with the same anion [7], and at a fixed temperature of 288.15 K, the solubility of the [PF₆]-based salts decreases in the rank: pyrrolidinium > imidazolium > piperidinium ≈ pyridinium >> ammonium > phosphonium. On the other hand, at the temperature of 318.15 K this sequence changes and follows the order: pyrrolidinium > pyridinium >

piperidinium > imidazolium >> ammonium > phosphonium. This change behavior is due to the fact that the [C₃C₁im][PF₆] or [C₃-3-C₁py][PF₆] and water correspond to liquid–liquid equilibrium systems while [C₃C₁pyr][PF₆] or [C₃C₁pip][PF₆] and water are solid–liquid systems, and that the solubilities of the former display a higher temperature dependency.

3.4. COSMO-RS prediction results

Aiming at predicting the solubility of the studied [PF₆]-based salts in water, the COSMO-RS model [26–29,40] was here evaluated. The results obtained are depicted in Fig. 3. The solubility was predicted by taking into account the enthalpy of fusion and the additional enthalpies of phase transition of the respective salts. The predicted solubility values are given in Supporting Information. The predicted solubility values from COSMO-RS are closer to experimental data when the total enthalpy of fusion and enthalpies of phase transition are used. Moreover, the pattern regarding the solubility dependence with temperature is also well described, as depicted in Fig. 3.

One advantage of COSMO-RS is that it provides the charge distribution of the specific polarity on the molecular surface that can be described by a σ -profile histogram. Fig. 4 presents the sigma profiles of the studied cations and the common anion. The sigma profiles of all the cations are similar in nature. Peaks are only observed between $-1 \text{ e nm}^{-2} < \sigma < 1 \text{ e nm}^{-2}$ which correspond to a nonpolar character. The higher peak intensity indicates a higher nonpolar character that translates the more hydrophobic nature of the studied salts. Accordingly, the cation core hydrophobic character observed experimentally and according to [C₃C₁pyr]⁺ < [C₃C₁pip]⁺ < [P₄₄₄₄]⁺ was also perceived with the COSMO-RS predictions. Only one exception was detected with [N₄₄₄₄]⁺, probably due to the very low solubility of the studied salt in water. Nevertheless, the prediction of the correct trend on the influence of salt cations and anions in the phase behavior using

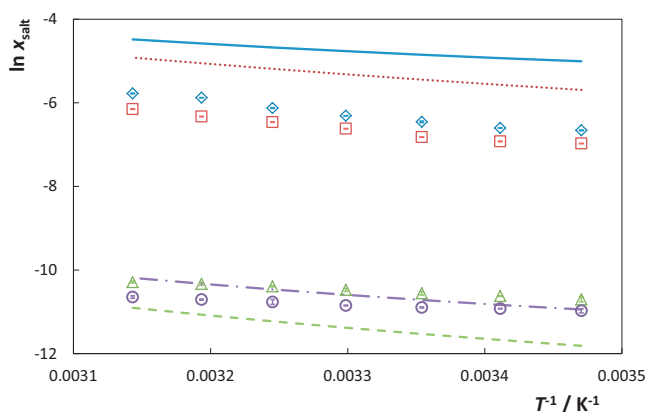


Fig. 3. Mole fraction solubility of the [PF₆]-based salts in water as function of temperature: (○, ◻) [C₃C₁pyr][PF₆], (□, ⋯) [C₃C₁pip][PF₆], (Δ, ◊) [N₄₄₄₄][PF₆] and (◐, ◑) [P₄₄₄₄][PF₆], and respective error bars. The symbols and the lines represent, respectively, the experimental data and the COSMO-RS predicted results.

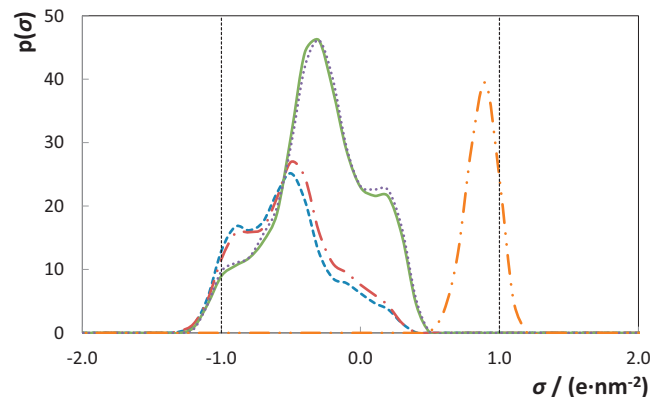


Fig. 4. Sigma profiles of the cations and anion composing the studied salts: [C₃C₁pyr]⁺, (—); [C₃C₁pip]⁺, (---); [N₄₄₄₄]⁺, (⋯); [P₄₄₄₄]⁺, (- · - ·); and [PF₆]⁻, (- - - -).

Table 3
Experimental mole fraction solubilities (x_{salt}) and respective uncertainty ($2u(x_{\text{salt}})$) of the $[\text{PF}_6]$ -based salts in water, as function of temperature and at 0.1 MPa.

T (K)	$[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ $10^3 (x_{\text{salt}} \pm 2u(x_{\text{salt}}))^a$	$[\text{C}_3\text{C}_1\text{pyr}][\text{PF}_6]$ $10^3 (x_{\text{salt}} \pm 2u(x_{\text{salt}}))^a$	$[\text{C}_3\text{C}_1\text{pip}][\text{PF}_6]$ $10^3 (x_{\text{salt}} \pm 2u(x_{\text{salt}}))^a$	$[\text{N}_{4444}][\text{PF}_6]$ $10^5 (x_{\text{salt}} \pm 2u(x_{\text{salt}}))^a$	$[\text{P}_{4444}][\text{PF}_6]$ $10^5 (x_{\text{salt}} \pm 2u(x_{\text{salt}}))^a$
288.15	1.08 ± 0.02	1.28 ± 0.02	0.936 ± 0.004	2.24 ± 0.26	1.71 ± 0.16
293.15	1.15 ± 0.02	1.36 ± 0.02	0.985 ± 0.012	2.43 ± 0.04	1.80 ± 0.02
298.15	1.22 ± 0.02	1.57 ± 0.06	1.090 ± 0.008	2.60 ± 0.22	1.85 ± 0.06
303.15	1.41 ± 0.04	1.82 ± 0.02	1.337 ± 0.006	2.82 ± 0.20	1.94 ± 0.04
308.15	1.61 ± 0.02	2.19 ± 0.04	1.562 ± 0.016	3.07 ± 0.10	2.11 ± 0.24
313.15	1.77 ± 0.02	2.81 ± 0.02	1.787 ± 0.016	3.26 ± 0.24	2.24 ± 0.08
318.15	2.02 ± 0.02	3.10 ± 0.04	2.133 ± 0.024	3.40 ± 0.16	2.38 ± 0.14

^a Expanded uncertainty at the 0.95 confidence level, $2u(x_{\text{salt}})$, evaluated from the standard deviation and applying a coverage factor $k = 2$.

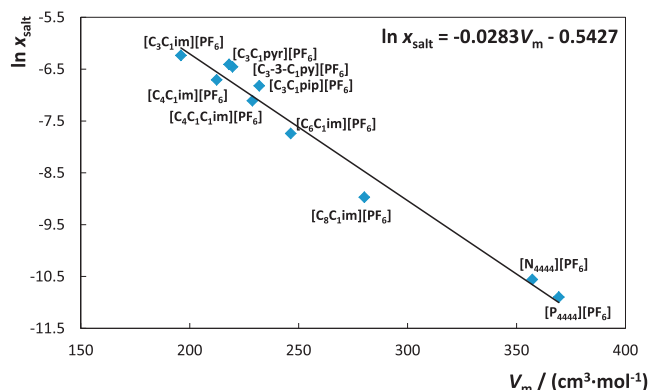


Fig. 5. Solubility of $[\text{PF}_6]$ -based salts in water (expressed as mole fraction of solute) as a function of the salt molar volume. All data are at 298.15 K.

the COSMO-RS model is of main importance when the goal is a screening of salts solubility before experimental measurements. In spite of the quantitative deviations of the COSMO-RS predictions, this method shows to be a useful tool in predicting the solid–liquid phase behavior of salts and water, allowing thus a beforehand choice of the cation and anion composing the salt for specific purposes.

3.5. Correlation for the solubility of the hexafluorophosphate-based salts in water

Any dissolution process depends upon the free energy change of both the solute and solvent. According to the theory of hydrophobic solvation [41,42], the aqueous solubility of organic compounds is related with the work required to create a cavity on the solvent to accommodate the solute. The solubility of hydrophobic solutes in water is thus often correlated with their molecular volumes. In this context, we have further investigated the effect of the solutes molar volume on the solubility of the $[\text{PF}_6]$ -based salts in water. The molar volumes of each salt at 298.15 K were estimated using the COSMO-RS model, and the aqueous solubility experimental data used were those obtained in this work together with other results taken from the literature [4,7]. The dependency of the salt solubility in water with the salt molar volume (both properties at 298.15 K) is depicted in Fig. 5. In fact, a very good correlation is observed and covers a wide range of magnitudes regarding the solubility mole fraction data. This type of correlation was already shown before [5,6]; yet, it is here shown that a large range of solubility of ILs or IL analogs in water can be estimated only making use of their molar volumes.

4. Conclusions

In this work the solubility in water of different $[\text{PF}_6]$ -based salts (combined with the cations $[\text{C}_3\text{C}_1\text{pip}]^+$, $[\text{C}_3\text{C}_1\text{pyr}]^+$, $[\text{N}_{4444}]^+$ and $[\text{P}_{4444}]^+$), and their dependence with temperature, was investigated. All the studied salts are solid at room temperature and they

were also characterized by DSC. The salts with the piperidinium and pyrrolidinium cations present melting temperatures around 373 K whereas the salts with the ammonium and phosphonium cations have higher melting temperatures and well above 373 K. Moreover, different solid–solid phase transitions were observed for all the salts.

In order to quantify the solubility of the different hexafluorophosphate-based salts in water, the electrical conductivity was used as a quantification technique. The solubility of the various salts in water follows the cation order: pyrrolidinium > piperidinium \gg ammonium > phosphonium. The ammonium and phosphonium-based salts are by far less soluble in water. The COSMO-RS predictive model was also used to estimate the solid–liquid equilibrium of the systems here studied. The predictive results are in close agreement with the experimental data supporting the applicability of this model to predict the solubility of salts in water, and thus allowing an appropriate screening of compounds, before carrying extensive experimental work.

Finally, an improved correlation between the solubility of $[\text{PF}_6]$ -based salts in water and their molar volume was achieved. This correlation can be used beforehand to estimate the solubility of other hexafluorophosphate-based salts in water by the previous knowledge of their molar volumes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fluid.2013.07.061>.

References

- [1] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2008.
- [2] N.V. Plechkova, K.R. Seddon, *Chemical Society Reviews* 37 (2008) 123–150.
- [3] M.G. Freire, P.J. Carvalho, R.L. Gardas, I.M. Marrucho, L.M.N.B.F. Santos, J.A.P. Coutinho, *Journal of Physical Chemistry B* 112 (2008) 1604–1610.
- [4] M.G. Freire, C.M.S.S. Neves, P.J. Carvalho, R.L. Gardas, A.M. Fernandes, I.M. Marrucho, L.M.N.B.F. Santos, J.A.P. Coutinho, *Journal of Physical Chemistry B* 111 (2007) 13082–13089.
- [5] M.G. Freire, C.M.S.S. Neves, K. Shimizu, C.E.S. Bernardes, I.M. Marrucho, J.A.P. Coutinho, J.N.C. Lopes, L.P.N. Rebelo, *Journal of Physical Chemistry B* 114 (2010) 15925–15934.
- [6] M.G. Freire, C.M.S.S. Neves, S.P.M. Ventura, M.J. Pratas, I.M. Marrucho, J. Oliveira, J.A.P. Coutinho, A.M. Fernandes, *Fluid Phase Equilibria* 294 (2010) 234–240.

- [7] C.M.S.S. Neves, M.L.S. Batista, A.F.M. Cláudio, L.M.N.B.F. Santos, I.M. Marrucho, M.G. Freire, J.A.P. Coutinho, *Journal of Chemical and Engineering Data* 55 (2010) 5065–5073.
- [8] S.M. Ventura, A.M. Gonçalves, T. Sintra, J. Pereira, F. Gonçalves, J.P. Coutinho, *Ecotoxicology* 22 (2013) 1–12.
- [9] H.F.D. Almeida, J.A. Lopes-da-Silva, M.G. Freire, J.A.P. Coutinho, *Journal of Chemical Thermodynamics* 57 (2013) 372–379.
- [10] P.J. Carvalho, T. Regueira, L.M.N.B.F. Santos, J. Fernandez, J.A.P. Coutinho, *Journal of Chemical and Engineering Data* 55 (2009) 645–652.
- [11] M.G. Freire, P.J. Carvalho, A.M. Fernandes, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, *Journal of Colloid and Interface Science* 314 (2007) 621–630.
- [12] C.M.S.S. Neves, P.J. Carvalho, M.G. Freire, J.A.P. Coutinho, *Journal of Chemical Thermodynamics* 43 (2011) 948–957.
- [13] K.R. Seddon, A. Stark, M.J. Torres, *Pure and Applied Chemistry* 72 (2000) 2275–2287.
- [14] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, *Green Chemistry* 3 (2001) 156–164.
- [15] V. Najdanovic-Visak, L.P.N. Rebelo, M. Nunes da Ponte, *Green Chemistry* 7 (2005) 443–450.
- [16] S.P.M. Ventura, J. Pauly, J.L. Daridon, J.A. Lopes da Silva, I.M. Marrucho, A.M.A. Dias, J.A.P. Coutinho, *Journal of Chemical Thermodynamics* 40 (2008) 1187–1192.
- [17] Z.B. Alfassi, R.E. Huie, B.L. Milman, P. Neta, *Analytical and Bioanalytical Chemistry* 377 (2003) 159–164.
- [18] J.L. Anthony, E.J. Maginn, J.F. Brennecke, *Journal of Physical Chemistry B* 105 (2001) 10942–10949.
- [19] A. Chapeaux, L.D. Simoni, M.A. Stadtherr, J.F. Brennecke, *Journal of Chemical and Engineering Data* 52 (2007) 2462–2467.
- [20] J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, *Journal of Physical Chemistry B* 108 (2004) 5113–5119.
- [21] F.M. Maia, O. Rodríguez, E.A. Macedo, *Industrial and Engineering Chemistry Research* 51 (2012) 8061–8068.
- [22] J. McFarlane, W.B. Ridenour, H. Luo, R.D. Hunt, D.W. DePaoli, R.X. Ren, *Separation Science and Technology* 40 (2005) 1245–1265.
- [23] L.P.N. Rebelo, V. Najdanovic-Visak, Z.P. Visak, M. Nunes da Ponte, J. Szydłowski, C.A. Cerdeirina, J. Troncoso, L. Romani, J.M.S.S. Esperanca, H.J.R. Guedes, H.C. de Sousa, *Green Chemistry* 6 (2004) 369–381.
- [24] N. Shvedene, S. Borovskaya, V. Sviridov, E. Ismailova, I. Pletnev, *Analytical and Bioanalytical Chemistry* 381 (2005) 427–430.
- [25] D.S.H. Wong, J.P. Chen, J.M. Chang, C.H. Chou, *Fluid Phase Equilibria* 194–197 (2002) 1089–1095.
- [26] A. Klamt, *Journal of Physical Chemistry* 99 (1995) 2224–2235.
- [27] A. Klamt, *COSMO-RS from quantum chemistry to fluid phase thermodynamics and drug design*, Elsevier, Amsterdam, Boston, 2005.
- [28] A. Klamt, F. Eckert, *Fluid Phase Equilibria* 172 (2000) 43–72.
- [29] A. Klamt, G. Schuurmann, *Journal of the Chemical Society, Perkin Transactions* 2 (0) (1993) 799–805.
- [30] M. Diedenhofen, A. Klamt, *Fluid Phase Equilibria* 294 (2010) 31–38.
- [31] M.G. Freire, S.P.M. Ventura, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, *Fluid Phase Equilibria* 268 (2008) 74–84.
- [32] M.G. Freire, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, *Fluid Phase Equilibria* 255 (2007) 167–178.
- [33] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, *Industrial and Engineering Chemistry Research* 50 (2011) 5279–5294.
- [34] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, *Industrial and Engineering Chemistry Research* 51 (2012) 3483–3507.
- [35] C.M.S.S. Neves, J.F.O. Granjo, M.G. Freire, A. Robertson, N.M.C. Oliveira, J.A.P. Coutinho, *Green Chemistry* 13 (2011) 1517–1526.
- [36] M.G. Freire, P.J. Carvalho, R.L. Gardas, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, *Journal of Chemical and Engineering Data* 53 (2008) 2378–2382.
- [37] University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, TURBOMOLE V6.1 2009, 1989–2007, 25 GmbH, since 2007, available from <http://www.turbomole.com>
- [38] F. Eckert, A. Klamt, *COSMOtherm Version C2.1 Release 01.08*, COSMOlogic GmbH & Co. KG, Leverkusen, Germany, 2006.
- [39] M.G. Freire, C.M.S.S. Neves, I.M. Marrucho, J.A.P. Coutinho, A.M. Fernandes, *Journal of Physical Chemistry A* 114 (2009) 3744–3749.
- [40] F. Eckert, A. Klamt, *AIChE Journal* 48 (2002) 369–385.
- [41] A. Pohorille, L.R. Pratt, *Journal of the American Ceramic Society* 112 (1990) 5066–5074.
- [42] L.R. Pratt, A. Pohorille, *Proceedings of the National Academy of Sciences* 89 (1992) 2995–2999.