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Solubility of Adamantane in Phosphonium-Based Ionic Liquids†

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The solubility of adamantane was measured in eight phosphonium-based ionic liquids (ILs) having cations with different alkyl chain lengths, namely, tributyl(methyl)phosphonium, triisobutyl(methyl)phosphonium, tetraoctylphosphonium, and tetradecyltrihexylphosphonium, combined with several anions, namely, bromide, chloride, dicyanamide, methanesulfonate, methylsulfate, bistriflamide, and tosylate. The experimental measurements were carried over the temperature range from (380 to 463) K and at pressures close to 0.1 MPa. The solubility of adamantane was shown to be essentially dependent on the alkyl chain length of the IL cation and, to a lesser extent, on the nature of the IL anion. In general, higher solubilities of adamantane were observed with ILs presenting more hydrophobic character.

Introduction

Adamantane ($C_{10}H_{16}$), the simplest of the diamondoids, is a highly symmetrical tricyclic molecule that consists of fused chair-form cyclohexane rings. It exhibits four bridgehead positions that are easily substituted using Friedel−Crafts alkylation. Substitution at the bridgehead carbons allows for the formation of starlike polymers having a tetrahedral array of rigid arms serving as molecular reinforcement.[1] Indeed, adamantane has been shown to be highly valuable when inserted in the backbones of many polymers, such as polysulfones, polyesters, polyamides, and polyimides.[2−5] The insertion of such a thermally and oxidatively stable, bulky, rigid, and hydrophobic compound into polymers modifies and improves their physical properties, providing enhanced thermal stability, superior glass-transition temperatures, increased chain stiffness, decreased crystallinity, improved solubility, and lower dielectric constant values.[5] Nevertheless, a wide part of such reactions occur in nonbenign media through the use of toxic and volatile organic solvents, and the search for neoteric solvents as media for chemical synthesis is receiving increased attention from academia and industry. In this field, ionic liquids (ILs) and supercritical CO_2 are the main candidates.

ILs are generally composed of a large asymmetric organic cation and either an organic or inorganic anion.[6] The asymmetry of the cation is believed to be responsible for the low melting temperatures (< 100 °C for the generally accepted definition of ILs), while the nature of the anion is considered to be mainly responsible for most of their physical properties.[6] Moreover, their insignificant vapor pressures (undoubtedly the most attractive physical property) reduce environmental pollution and working exposure hazards.[7] In addition, a key feature of these compounds is that their physical and chemical properties can be tailored by the sensible selection of the cation and/or anion. Thus, the first goal of this work was to obtain experimental information on the solid−liquid phase diagrams of adamantane and ILs with the aim of selecting the proper medium for chemical synthesis that could engage adamantane insertion.

On the other hand, the presence of diamondoids in petroleum was first recognized in 1933, when adamantane was isolated from Czechoslovakian crude oil.[8] Among other properties, adamantane presents high thermal stability, which permits it to remain in oils and gas condensates over geological time at elevated subsurface temperatures and pressures.[9] Diamondoids can be found in reservoir fluids, particularly in gas condensates and natural gas, and may constitute a flow assurance problem because changes in pressure and temperature during the extraction and transport of the hydrocarbons may promote their precipitation, leading to deposition problems and plugging of pipelines and process equipment.[9,10] It is possible to prevent precipitation of diamondoids by removing them from the gas, even if only partially. Therefore, in the quest for new and cleaner solvents for the removal of diamondoids from natural gas or gas condensates, the solubility of adamantane in ILs was here studied. Indeed, several solid−liquid phase diagrams regarding adamantane and gases,[10] supercritical fluids,[11] pressurized hot water,[12] and hydrocarbons[13] have been reported in the literature.

Most of the experimental studies concerning ILs have addressed the determination of the thermophysical properties of pure ILs and liquid−liquid phase equilibria of systems containing ILs, while solubility data for solid solutes and solid−liquid phase diagrams are particularly scarce in the literature. Some of the works regard solubility data for inorganic salts,[14] taurine,[15] dibasic carboxylic acids,[16] drugs,[17] flavonoids,[18] and cinnamic esters[19] in ILs. A further particular work reports the solid−liquid phase diagram for 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide ([C_2mim][Tf_2N]) +benzene binary system, where the equimolar inclusion compound [C_2mim][Tf_2N]·C_6H_6 with a congruent melting temperature was identified.[20] On the other hand, Domańska et al.[21−23] have already presented novel solid−liquid phase diagrams involving phosphonium-based ILs and alcohols or hydrocarbons. To the best of our knowledge, this is the first

† Part of the "2009 Iberian Conference on Ionic Liquids".
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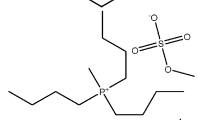
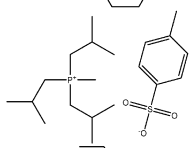
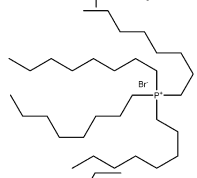
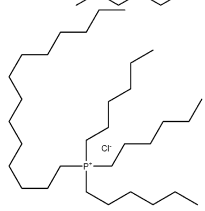
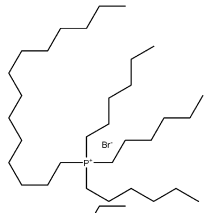
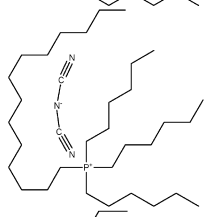
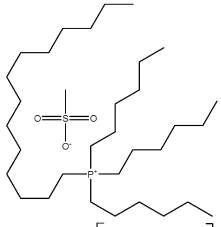
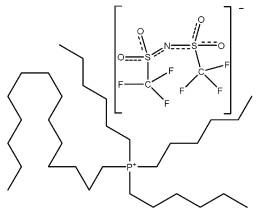
10.1021/je9006772 © 2010 American Chemical Society
Published on Web 12/14/2009

Table 1. List of the Organic Compounds Used (Solute and Solvents) and Their Respective Molecular Structures and Abbreviations

Compound	Molecular Structure	Abbreviation
Adamantane		adam
Tributyl(methyl)phosphonium methylsulfate		$[P_{4441}][CH_3SO_4]$
Triisobutyl(methyl)phosphonium tosylate		$[P_{i(444)1}][Tos]$
Tetraoctylphosphonium bromide		$[P_{8888}][Br]$
Tetradecyltrihexylphosphonium chloride		$[P_{66614}][Cl]$
Tetradecyltrihexylphosphonium bromide		$[P_{66614}][Br]$
Tetradecyltrihexylphosphonium dicyanamide		$[P_{66614}][N(CN)_2]$
Tetradecyltrihexylphosphonium methanesulfonate		$[P_{66614}][CH_3SO_3]$
Tetradecyltrihexylphosphonium bistriflamide		$[P_{66614}][Tf_2N]$

report presenting solubility saturation data for the diamondoid adamantane in ILs.

This manuscript presents experimental solubility data for adamantane in eight phosphonium-based ILs over the temperature range from (380 to 463) K and at pressures close to 0.1 MPa. From the dependence of the solubility on temperature, the molar thermodynamic functions (Gibbs energy, enthalpy, and entropy) of solution of adamantane in these ILs (where ideal solution can be considered) at 425 K were determined and are discussed.

Table 2. Mole-Fraction Solubilities of Adamantane (x_{adam}) and Respective Activity Coefficients (γ) in Phosphonium-Based ILs at Different Temperatures

IL	x_{adam}	T/K	γ
$[P_{4441}][CH_3SO_4]$	0.024	385.56	13.62
	0.025	384.24	12.87
	0.025	384.52	12.90
	0.025	384.98	12.95
	0.050	409.80	8.21
	0.109	440.78	4.87
	0.125	443.88	4.35
	0.148	454.96	3.99
$[P_{i(444)1}][Tos]$	0.033	380.40	9.36
	0.056	388.24	6.01
	0.101	416.10	4.31
	0.133	427.71	3.59
	0.158	440.30	3.35
$[P_{8888}][Br]$	0.238	388.05	1.40
	0.300	400.52	1.26
	0.357	414.61	1.20
	0.381	421.38	1.19
	0.464	440.40	1.14
$[P_{66614}][Cl]$	0.370	426.02	1.28
	0.420	435.13	1.21
	0.532	462.80	1.17
$[P_{66614}][Br]$	0.298	410.30	1.38
	0.405	429.74	1.20
	0.454	441.88	1.18
$[P_{66614}][N(CN)_2]$	0.300	408.04	1.35
	0.394	431.95	1.26
	0.474	451.42	1.21
$[P_{66614}][CH_3SO_3]$	0.297	403.02	1.30
	0.387	419.70	1.15
	0.465	439.17	1.13
$[P_{66614}][Tf_2N]$	0.358	419.44	1.25
	0.458	439.65	1.15
	0.520	452.87	1.12

Experimental Section

Materials. Tributyl(methyl)phosphonium methylsulfate ($[P_{4441}][CH_3SO_4]$), triisobutyl(methyl)phosphonium tosylate ($[P_{i(444)1}][Tos]$), tetraoctylphosphonium bromide ($[P_{8888}][Br]$; CAS 23906-97-0), tetradecyltrihexylphosphonium chloride ($[P_{66614}][Cl]$; CAS 258864-54-9), tetradecyltrihexylphosphonium bromide ($[P_{66614}][Br]$; CAS 654057-97-3), tetradecyltrihexylphosphonium dicyanamide ($[P_{66614}][N(CN)_2]$; CAS 701921-71-3), tetradecyltrihexylphosphonium methanesulfonate ($[P_{66614}][CH_3SO_3]$; CAS 547718-83-2), and tetradecyltrihexylphosphonium bistriflamide ($[P_{66614}][Tf_2N]$; CAS 460092-03-9) with mass-fraction purities of > 95 % were kindly provided by Cytec Industries. All of the IL samples (ca. 10 mL) were dried under constant stirring at moderate temperatures (maximum of 333 K) and under vacuum for a minimum of 24 h. This step was extremely important in order to reduce volatile impurities as well as water, since all of these ILs are extremely hygroscopic.[24] The water content in each sample after the drying procedure was found to be less than $5 \cdot 10^{-4}$ in mass fraction, as determined by Karl Fischer titration (Metrohm 831 Karl Fischer coulometer). No further purification of the ILs was performed. The adamantane (CAS 281-23-2) was acquired from Fluka with a mass-fraction purity of 99 %. The molecular structures of both adamantane and the ILs are presented in Table 1.

Experimental Solubility Measurements. A synthetic method based on the optical observation of the disappearance of the last crystal of adamantane upon heating was used to measure the solubility of the solid in various ILs. Binary mixtures

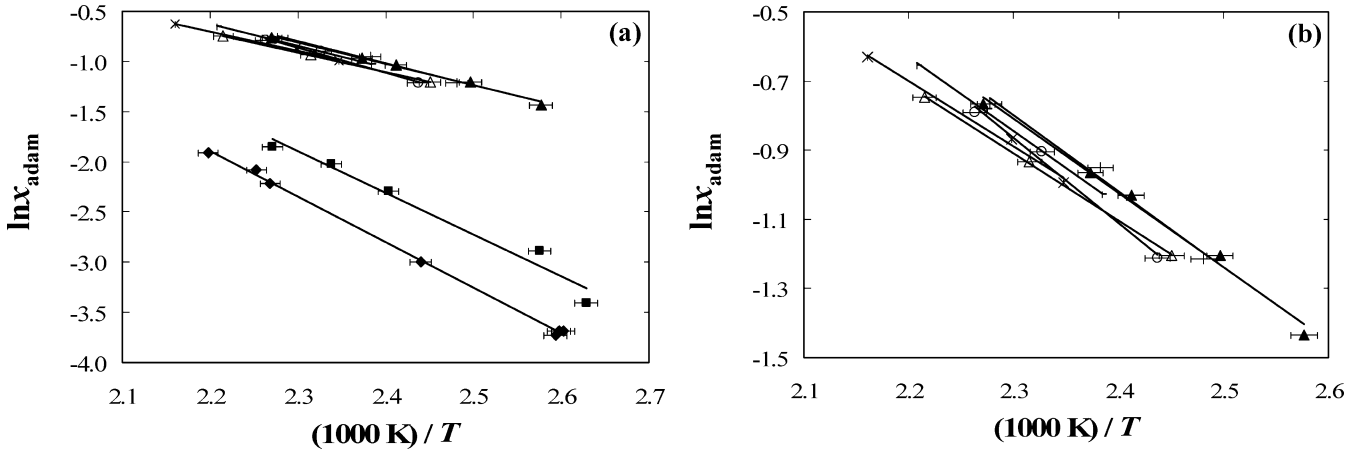


Figure 1. Mole-fraction solubilities of adamantane (x_{adam}) as functions of temperature (a) in all of the studied phosphonium-based ILs and (b) in the $[P_{66614}]$-based ILs: ♦, $[P_{4441}][CH_3SO_4]$; ■, $[P_{i(444)1}][Tos]$; ▲, $[P_{8888}][Br]$; ×, $[P_{66614}][Cl]$; ○, $[P_{66614}][Br]$; Δ, $[P_{66614}][N(CN)_2]$; +, $[P_{66614}][CH_3SO_3]$; (−), $[P_{66614}][Tf_2N]$. The solid lines represent fits of the experimental data using eq 4.

composed of adamantane and IL were gravimetrically prepared (within an uncertainty of $\pm\ 2\cdot10^{-5}$ g) in glass ampules containing a magnetic stirrer. The ampules were sealed and then immersed into a thermostatic oil bath equipped with a calibrated Pt100 temperature sensor with an uncertainty of ± 0.01 K. For each mixture, the temperature corresponding to the disappearance of the last crystal of the solid phase under slow heating (ca. 6 $K\cdot h^{-1}$) was registered as the saturation temperature of adamantane in that binary system and/or composition. Only one reading was performed for each binary system composition because of the difficulty of recrystallizing adamantane in ILs upon cooling. Nevertheless, the temperature uncertainty of the experimental procedure was estimated to be about ± 0.7 K on the basis of temperature readings performed for three different ampules containing the same binary composition.

Results and Discussion

Experimental Solubility Measurements. Table 2 reports the measured solubilities of adamantane in the ILs along with the experimental activity coefficients, and Figure 1 illustrates the mole-fraction solubilities of adamantane in the different ILs studied as functions of temperature. A clear distinction between the solubilities of adamantane in phosphonium-based ILs with short alkyl chains ($[P_{4441}][CH_3SO_4]$ and $[P_{i(444)1}][Tos]$) and those in the ones with longer alkyl chains can be observed, with smaller solubilities in the former as a result of the higher polarity of these ILs. While the experimental activity coefficients of adamantane in these mixtures are in general positive but smaller than 1.3, for these two systems they reach values of about 10 for the less-concentrated mixtures. Thus, the main interactions ruling the solubility of adamantane in the studied ILs are dispersive van der Waals interactions. An increase in the length of the alkyl substituents on the IL cation, which increases the IL hydrophobicity, enhances the dispersive-type interactions between adamantane and the IL cation and thus its solubility. From a comparison of the two structural isomers $[P_{8888}][Br]$ and $[P_{66614}][Br]$, it can be observed that $[P_{8888}][Br]$ presents a higher solubility for adamantane than its molecular structural analogue. It seems that $[P_{8888}][Br]$ presents a much more effective package at the molecular level, enhancing the solvation ability of this IL toward adamantane. The solubility data show that the solubility of adamantane is primarily dependent on the IL cation alkyl chain length and depends to only a minor extent on the nature of the IL anion. Hydrophobic anions such as $[Tf_2N]^-$ or sulfonate-based ions are better solvents for solubilizing adamantane than are, for example, the halide anions. According to the results obtained, the ranking of the ILs' ability to solubilize adamantane follows the order $[P_{8888}][Br] \approx [P_{66614}][CH_3SO_3] \approx [P_{66614}][Tf_2N] > [P_{66614}][Br] \approx [P_{66614}][Cl] \approx [P_{66614}][N(CN)_2] \gg [P_{i(444)1}][Tos] \gg [P_{4441}][CH_3SO_4]$.

Thermodynamic Functions of Solution. When adamantane solubilizes in the IL solvent, the process is followed by a change in the thermodynamic functions of the system, in particular the molar Gibbs energy $[\Delta_{sol}G_m(T)]$, molar enthalpy $[\Delta_{sol}H_m(T)$, and molar entropy $[\Delta_{sol}S_m(T)]$ of solution.[25] These thermodynamic functions can be estimated by means of the van't Hoff equation and derived from the temperature dependence of the experimental solubility data for those systems with small deviations from ideal behavior, according to the following equations:[25]

$$\Delta_{sol}G_m(T) = -RT(\ln x_{adam})_p \tag{1}$$

$$\frac{\Delta_{sol}H_m(T)}{RT^2} = \left(\frac{\partial \ln x_{adam}}{\partial T}\right)_p \tag{2}$$

$$\Delta_{sol}S_m(T) = \frac{\Delta_{sol}H_m^\circ(T) - \Delta_{sol}G_m^\circ(T)}{T} \tag{3}$$

where x_{adam} is the mole fraction solubility of adamantane, R is the gas constant, and T is the temperature at a constant pressure p. These thermodynamic parameters regard the transference of the solute molecules to a "hypothetical" ideal-dilute solution where solute−solute interactions can be neglected.

In order to evaluate these thermodynamic functions for the studied systems, the temperature behavior of the measured data was fitted using the following equation [which assumes that $\Delta_{sol}H_m(T)$ over the studied temperature range is temperature-independent]:

$$\ln x_{adam} = A + \frac{B}{T/K} \tag{4}$$

where T is the temperature and A and B are the regression constants, which are related to $\Delta_{sol}S_m(T)$, $\Delta_{sol}H_m(T)$, and R.

The correlations obtained from eq 4 are graphically represented as the solid lines in Figure 1. Values of the fitting parameters A and B as well as their standard deviations[26] are reported in Table 3. The proposed correlations show a relative maximum deviation of 5 % from the experimental mole fraction data, which was observed for the IL $[P_{i(444)1}][Tos]$, while for the rest of the ILs, the relative maximum deviation in the mole-fraction solubility, is 3 %.

Table 3. Values of the Fitting Parameters Obtained from Equation 4 for the Mole-Fraction Solubility of Adamantane in Phosphonium-Based ILs and the Corresponding Standard Deviations (σ)

IL	$A \pm \sigma$	10^{-3} $(B \pm \sigma)$/K
$[P_{4441}][CH_3SO_4]$	8.1 ± 0.2	−4.55 ± 0.09
$[P_{i(444)1}][Tos]$	7.6 ± 0.1	−4.1 ± 0.4
$[P_{8888}][Br]$	4.1 ± 0.3	−2.1 ± 0.1
$[P_{66614}][Cl]$	3.5 ± 0.4	−1.9 ± 0.2
$[P_{66614}][Br]$	4.8 ± 0.6	−2.5 ± 0.3
$[P_{66614}][N(CN)_2]$	3.6 ± 0.1	−1.95 ± 0.04
$[P_{66614}][CH_3SO_3]$	4.2 ± 0.6	−2.2 ± 0.3
$[P_{66614}][Tf_2N]$	4.1 ± 0.2	−2.14 ± 0.09

Table 4. Molar Thermodynamic Functions of Solution for Adamantane in Phosphonium-Based ILs at 425 K and the Corresponding Standard Deviations (σ)

IL	$\Delta_{sol}G_m(T) \pm \sigma$ / kJ·mol^{-1}	$\Delta_{sol}H_m(T) \pm \sigma$ / kJ·mol^{-1}	$\Delta_{sol}S_m(T) \pm \sigma$ / J·K^{-1}·mol^{-1}
$[P_{8888}][Br]$	3.27 ± 0.02	17.8 ± 1.0	34.2 ± 2.4
$[P_{66614}][Cl]$	3.50 ± 0.02	15.8 ± 1.5	29.0 ± 3.6
$[P_{66614}][Br]$	3.51 ± 0.02	20.5 ± 2.2	39.9 ± 5.2
$[P_{66614}][N(CN)_2]$	3.58 ± 0.02	16.2 ± 0.3	29.7 ± 0.8
$[P_{66614}][CH_3SO_3]$	3.24 ± 0.02	18.2 ± 2.2	35.2 ± 5.3
$[P_{66614}][Tf_2N]$	3.39 ± 0.02	17.8 ± 0.7	33.8 ± 1.7

The values of the molar thermodynamic functions of solution for adamantane in the systems whose behavior was close to ideal were estimated at 425 K (approximately the midpoint of the temperature interval studied, which was chosen in order to reduce the propagation of errors and therefore to separate the chemical effects from those derived exclusively from statistical treatments) using eqs 1 to 3, and the results are reported in Table 4.

All of the values calculated for the molar Gibbs energy of solution are positive, meaning that the adamantane solution process is not spontaneous. This may be explained in terms of the concentration scale used (mole fraction), where the reference state is the ideal solution having unity as the concentration of adamantane, that is, the solid pure solute. Moreover, the molar enthalpy of solution is positive in all of the studied cases, showing that the solution process is endothermic. The molar enthalpies of solution of adamantane in the studied ILs are almost independent of the IL anion. The ILs $[P_{8888}][Br]$, $[P_{66614}][CH_3SO_3]$, and $[P_{66614}][Tf_2N]$ present lower molar enthalpies of solution and thus a higher capability to solubilize adamantane. These low molar enthalpies of solution indicate that the enthalpic energetic balance involved in the dissolution of adamantane in these ILs is more favorable. Finally, the molar entropy change is positive in all cases, indicating that the entropy of solubilizing adamantane is unfavorable in all the ILs examined.

Conclusions

Original experimental solubility data for adamantane in eight phosphonium-based ILs over the temperature range from (380 to 463) K at a pressure close to 0.1 MPa have been reported. The results fundamentally indicate that the solubility of adamantane in ILs primarily depends on the alkyl chain length in the IL cation and to a lesser extent on the nature of the IL anion. In general, the solubility of adamantane increases with increasing hydrophobic character of the IL.

Acknowledgment

The authors acknowledge Cytec Industries for providing all of the phosphonium-based ILs used in this work.

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Received for review August 11, 2009. Accepted December 3, 2009. The authors thank Fundação para a Ciência e a Tecnologia for PhD Grant SFRH/BD/28258/2006.

JE9006772