



(Solid + liquid) and (liquid + liquid) phase equilibria measurements and correlation of the binary systems {tri-*iso*-butyl(methyl)phosphonium tosylate + alcohol, or +hydrocarbon}

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ABSTRACT

Phase diagrams for the binary systems {tri-*iso*-butyl(methyl)phosphonium tosylate ionic liquid (*i*-B₃MPTOS + 1-alcohol, or *n*-alkane, or *n*-alkylbenzene)} have been measured at atmospheric pressure by a dynamic method. (Solid + liquid) phase equilibria were measured for systems of alcohols (1-decanol and 1-dodecanol) and the ionic liquid and (liquid + liquid) phase equilibria for binaries containing hydrocarbons (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene). The reduction of experimental data has been carried out by correlation using the Non-Random Two Liquid (NRTL) equation. The measured diagrams have been compared with analogous diagrams reported previously for systems with ionic liquids containing the symmetric quaternary phosphonium cation. The influence of the asymmetry of the cation on the phase behaviour of phosphonium ionic liquids has been discussed.

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1. Introduction

On one hand ionic liquids (ILs) form a highly polar (ionic) environment and on the other hand ILs are composed of hydrophobic (non-polar or slightly polar) organic groups. They are miscible (totally or partially) with many commonly used classes of organic compounds (hydrocarbons, alcohols, ketones, ethers, etc.). The study of the solubility of ILs in many different solvents is of great importance in the investigation of the interactions of these two classes of chemicals in view of their applications in new technologies. During the last few years the number of measurements of the thermophysical and thermodynamic properties of ILs and applications in different fields of pure and applied chemistry has increased remarkably [1–8].

The application of ILs in chemical engineering is especially an important issue as far as thermal separation processes are taken into consideration. In particular, effective and profitable design of industrial liquid–liquid extraction or either extractive or azeotropic distillation of close-boiling mixtures (e.g. those containing both aromatic and aliphatic hydrocarbons [9]) requires a lot of input data concerning with thermodynamic properties (activity coefficients, excess volumes and enthalpies of mixing) as well as transport properties (densities, viscosities, diffusivities, speeds of sound of

pure components and their mixtures). Those data are determined by means of experiments, or can be calculated (predicted), e.g. using a group contribution method or an appropriate equation of states which derivation is based on statistical thermodynamics [10]. However, the latter way is not sufficient in terms of accuracy and therefore experiments are more preferable to obtain reliable information.

Our laboratory deals with measurements and investigation on phase equilibria in binary and ternary systems containing ionic liquids and organic solvents, especially those which are highly polar and capable of most types of intermolecular interactions: dispersive, π – π , *n*– π , hydrogen bonding, dipolar, ionic/charge–charge, van der Waals forces. The chemical structure of an IL has a remarkable influence on its phase behaviour and this is taken into our considerations and discussions.

Until recently, the most popular imidazolium and tetraalkylammonium ionic liquids with cations functionalized by alkyl, or hydroxyl, or alkoxyalkyl, or aromatic substituents and bromide [Br][−], nitrate [NO₃][−], tetrafluoroborate [BF₄][−], hexafluorophosphate [PF₆][−], bis(trifluoromethylsulfonyl)imide [NTf₂][−], dicyanoimide [N(CN)₂][−], alkylsulfonate [RSO₃][−], trifluoroacetate [CF₃COO][−], thiocyanate [SCN][−], anions have attracted our attention [11–17].

Nowadays, we have decided to begin an extensive research on phase equilibria in systems containing phosphonium-based ionic liquids (PILs) [18,19]. To our best knowledge, until today there were not many papers involving this issue, except for the

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work of Ventura et al., which reports a high-pressure phase equilibrium study of the {PIL+water+CO₂} system [20] and that of Pison et al., on the solubility of fluorinated alkanes in trihexyltetradecylphosphonium bis{(trifluoromethyl)sulfonyl}imide [21]. However, many papers involving other properties such as density, viscosity, surface tension [22,23] and activity coefficients at infinite dilution have been published [24–26]. In quoted papers PILs were expected to be good media for liquid–liquid extraction of alkanes from aliphatic–aromatic mixtures. Unfortunately *n*-hexane/benzene selectivities were observed to be very low [24–26].

PILs seem to be interesting from the point of view of potential applications since they are completely soluble in alcohols and well soluble in aromatic hydrocarbons. Moreover, PILs can be also considered as potential equivalents for ammonium ILs, since some of the properties of these salts are similar as can be concluded from their physical properties [23].

Otherwise, PILs show lower viscosities and higher conductivities what makes them attractive for many new applications [27]. Furthermore, other investigations involving those salts have been and still are carried out—they have been used as reactive extractants [28], chemical reaction solvents, lubricants [29], or plasticizers in ion-selective electrodes [30]. Moreover, Rodríguez and co-workers reported recently the possibility of usage of the PILs as liquid-in-glass thermometers [31].

We have just reported solubilities of tetra-*n*-butylphosphonium methanesulfonate (B₄PCH₃SO₃) [18], and tosylate (B₄PTOS) [19] in alcohols and *n*-alkylbenzenes. A noticeable influence of the anion exchange on the phase behaviour was observed. In the case of solubilities in alcohols simple eutectic (solid + liquid) equilibria phase diagrams (SLE) and complete miscibility in the liquid phase in the whole range of mole fractions was observed for both ILs. The solubility of the IL in an alcohol decreases as the number of carbon atoms in alcohol increases, as was observed in many systems. The solubility is lower in the case of the methanesulfonate anion in comparison with the tosylate anion. On the other hand, miscibility gaps with upper critical solution temperature (UCST) have been detected in the systems of B₄PCH₃SO₃ with ethylbenzene and propylbenzene [18] and that of B₄PTOS in propylbenzene [19]. The UCST increases with the chain length of alkyl substituent at the benzene ring.

The influence of the asymmetry of the cation on the phase behaviour of phosphonium ionic liquids is an important information allowing making predictions of phase behaviour of unknown systems, at least in qualitatively manner. Phase diagrams for the binary systems {tri-*iso*-butyl(methyl)phosphonium tosylate ionic liquid (*i*-B₃MPTOS)+1-alcohol, or *n*-alkane, or benzene, or *n*-alkylbenzene} are reported in this work.

2. Experimental

2.1. Materials

The investigated ionic liquid, tri-*iso*-butyl(methyl)phosphonium tosylate (*i*-B₃MPTOS) have been purchased from Ionic Liquids Technologies (iolitec GmbH & Co. KG, Denzlingen, Germany). Basic physicochemical information about the IL is given in Table 1. The compound's sample is a viscous and yellowish liquid. The purity of the sample is >0.95 mass fraction. The purification procedure performed in our laboratory involved subjecting the sample to a high vacuum at 323 K for around 24 h to remove any volatile chemicals (e.g. unreacted phosphines and synthesis reaction solvents) and water. The electrolyte content of the IL was not checked by us.

Solvents used in phase equilibria measurements were purchased from Sigma–Aldrich Chemie GmbH (Steinheim, Germany). All of them (except 1-dodecanol, which was used without any purification procedures) were distilled fractionally until to mass

percent purity (checked by using gas chromatography) of 99.8% and then stored over freshly activated molecular sieves of type 4A (Union Carbide).

The water content of *i*-B₃MPTOS and the solvents was determined by the Karl-Fisher titration (method TitroLine KF). Samples of an IL and the solvents were dissolved in dry methanol and titrated with steps of 2.5 μL. The analysis showed that the water mass fraction in the pure IL, in solvents and in the mixtures with the ionic liquid, were <230 × 10⁻⁶.

2.2. Differential scanning microcalorimetry (DSC)

The glass transition temperature and heat capacity C_{p(g)} at glass transition temperature for *i*-B₃MPTOS ionic liquid were measured by a Perkin-Elmer Pyris 1 differential scanning calorimetry apparatus. Measurements were carried out at a scan rate of 10 K min⁻¹, with a power sensitivity of 16 mJ s⁻¹ and a recorder sensitivity of 5 mV. Each time the instrument was used, it was calibrated with a 99.9999 mol% purity indium sample. The calorimetric accuracy was ±1%, and the calorimetric precision was ±0.5%.

2.3. Apparatus and experimental method

SLE and (liquid + liquid) phase equilibria (LLE) measurements were carried out using a visual method, according to procedures described in detail previously [32]. Mixtures (*i*-B₃MPTOS + solvent) were prepared by weighing the pure components within an accuracy of 1 × 10⁻⁴ g. The sample was heated very slowly (at less than 2 K h⁻¹) with continuous stirring inside a Pyrex glass cell placed in thermostat. The temperature of the disappearance of the solid phase or one of the two liquid phases, detected visually, were measured with a calibrated Gallenkamp Autotherm II thermometer totally immersed in the water bath. The uncertainty of temperature and compositions (mole fractions) measurements was ±0.05 K and ±0.0005, respectively. The reproducibility of the measured saturated phase boundary temperatures was about 0.1 K.

The solubility and mutual miscibility of the IL with the solvents was studied in the range of concentrations from 0 to 1 mole fraction of the IL. In the case of aliphatic hydrocarbons only the ionic liquid rich mole fraction binodal curves have been measured.

3. Results and discussion

According to the DSC measurements, the value of glass transition temperature of *i*-B₃MPTOS was (225.5 ± 0.1) K and heat capacity change at the glass transition temperature was (123.9 ± 3) J mol⁻¹ K⁻¹ (see Fig. 1S in the Supplementary Material).

The results of the SLE and LLE measurements are listed in Tables 2–4 and are presented graphically in Figs. 1–4.

Complete miscibility in the liquid phase was observed for the systems of linear aliphatic alcohols *n*-(C₁–C₁₂)OH (from methanol to *n*-decanol) with *i*-B₃MPTOS in the full range of mole fraction at T = 298.15 K. However, in the case of 1-decanol and 1-dodecanol the (solid + liquid) phase equilibria diagrams, i.e. solubilities of the solvents in the IL, have been determined below the fusion temperature of the solvent (Fig. 1). Complete miscibility was observed at higher temperatures.

In the case of aliphatic hydrocarbons only right sides of the LLE binodal curves (IL-rich phase compositions) have been measured (Fig. 2). Unfortunately, it was impossible to detect visually the cloud point of the solvent rich phase for the investigated systems. The left-hand limits of the equilibrium curves in this system and many others [9,11–18] are very close to zero mole fraction of the IL, that is x₁ = 10⁻⁴ to 10⁻⁵. These data were calculated previously for some ILs by COSMO-RS [11] within x₁ = 10⁻⁴ to 10⁻⁵

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