

Miscibility behavior of trihexyl(tetradecyl)phosphonium tetrafluoroborate with cyclic hydrocarbons



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ABSTRACT

Liquid–liquid miscibility temperatures as a function of composition have been determined experimentally for the binary systems formed by trihexyl(tetradecyl)phosphonium tetrafluoroborate with cyclohexane, cycloheptane, methylcyclohexane, 1,2-dimethylcyclohexane and 1,3-dimethylcyclohexane. All the measured systems present solubility curves characterized by the asymmetry with respect to the equimolar composition and represent the phase diagrams with the upper critical solution temperatures. The effect of the deuterium substitution in cyclohexane and methylcyclohexane has also been studied revealing small upward shift of the UCSTs which means slightly worse miscibility of ILs studied with selected deuterated cycloalkanes.

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1. Introduction

Over the last decade, ionic liquids became one of the most popular objects of interest in the physical and organic chemistry as well as in the chemical technology. It is because of their unique properties – among others their versatile ability of solubility in different compounds. There are many data on miscibility of imidazolium based ionic liquids but there are few attempts only regarding the miscibility of phosphonium based ionic liquids. Sarcasan et al. [1] reported miscibility data on trihexyl(tetradecyl)phosphonium chloride ($[P_{6,6,6,14}]Cl$) and bromide ($[P_{6,6,6,14}]Br$) with alkanes while Domańska et al. [2,3] presented extensive data on the phase behavior of tetrabutylphosphonium methanesulfonate and *p*-toluenesulfonate + alcohols and aromatic hydrocarbons systems. Anderson et al. [4] reported the miscibility data on trihexyl(tetradecyl) phosphonium chloride with nonane and water. The solubility in water was also studied by Freire et al. [5]. Rebelo's group [6] described the miscibility behavior of selected tetralkylphosphonium ionic liquids with alkanes, alcohols and their fluorinated counterparts. They tested the ionic liquids with the following anions: acetate, bis(trifluoromethyl)sulfonyl imide, trifluoromethanesulfonate and dicyanamide. More recently, interesting work presented phase behavior of phosphonium based ionic liquids having triflate $[OTf_2]^-$ and bistriflamide $[NTf_2]^-$ anions

with PEG of different average molecular mass were published by Calado et al. [7].

There are several reasons why one might consider phosphonium ionic liquids. At first, they are very stable, what is very important feature, in particular for processes operated at temperatures greater than 373 K. It should be however mentioned that high viscosity might be a disadvantageous factor in technological applications. They can be also attractive from another point of view. The steric bulk of the large alkyl side chain around the phosphonium cation interferes strongly with electrostatic interactions between anion and cation – which is generally localized on the phosphorous – allowing for greater impact of the properties of the anion itself, as compared to salts with more strongly interacting smaller cations (ammonium, imidazolium).

In the recent paper [8] we presented the phase diagrams characterizing the miscibility of $[P_{6,6,6,14}]Cl$ with the range of aliphatic hydrocarbons. As expected the phase diagrams obtained show upper critical solution temperature (UCST) with high asymmetry in respect to the equimolar composition. The solubility decreases with the increasing chain length of the alkanes. In the present study, we replaced chloride anion for tetrafluoroborate anion in the phosphonium ionic liquid. This replacement had a huge impact on its phase behavior. It appeared that contrary to $[P_{6,6,6,14}]Cl$, this new ionic liquid is completely immiscible with aliphatic hydrocarbons. On the other hand, it shows interesting phase behavior for the mixtures of $[P_{6,6,6,14}]BF_4$ with cyclic hydrocarbons. In this paper we present the miscibility study of $[P_{6,6,6,14}]BF_4$ with cyclohexane, methylcyclohexane, dimethylcyclohexanes and cycloheptane along with the

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study of the isotope effect on miscibility of deuterated cyclohexane and methylcyclohexane.

2. Materials and methods

The list of the cyclic hydrocarbons used in this study is as follows: cyclohexane, cyclohexane- d_{12} , methylcyclohexane, methylcyclohexane- d_{14} , cycloheptane, 1,2-dimethylcyclohexane and 1,3-dimethylcyclohexane. Their suppliers and the related stated purities have been presented in Table 1. They were additionally dried over molecular sieves 5 Å. Deuterated cyclohexane- d_{12} and methylcyclohexane- d_{14} were stored over molecular sieves previously treated with D_2O and carefully dried. Trihexyl(tetradecyl)phosphonium tetrafluoroborate was additionally degassed and dried under vacuum in the presence of P_2O_5 for 72 h to reduce the content of water and volatile compounds. All samples were analyzed by Karl Fischer titration using KF Trace Titroline and the determined water contents are collected in Table 1.

The samples for the miscibility measurements were prepared gravimetrically directly inside the cell using an analytical high precision balance. The samples for miscibility measurements were placed in 1 ml volume, a very tight cell, equipped with Rotaflow (screw cock) needle valve. It was immersed in thermostated bath, heated until a one-phase system was reached and then cooled very slowly with a rate < 0.1 K/min. The phase transition (cloud points) at ambient pressure was determined by the visual detection of the appearance of the solution turbidity while lowering temperature of the system. Temperature was measured using an RTD probe (100 Ω of Omega Engineering calibrated against ITS 90) coupled with Keithley 199 DMM with a precision of ± 5 mK. The overall uncertainty of the transition temperature measurements resulting from the visual observation of the turbidity is obviously higher than the instrumental error and is estimated to be $\pm 5 \times 10^{-2}$ K.

3. Results and discussion

The experimental values of the liquid–liquid phase separation temperatures as a function of composition (mole fractions, x_{IL}) for the binary mixtures of $[P_{6,6,6,14}]BF_4$ with cyclohexane, methylcyclohexane, dimethylcyclohexanes, cycloheptane were used to construct the appropriate phase diagrams shown in Fig. 1. The detailed experimental numerical cloud points for the above-mentioned systems in the form of $T-x$ data are given in Table 2. Because of the wide temperature range, the data were fitted to the extended scaling equation [9–11] (including Wagner expansion term $\beta + \Delta$):

$$|x - x_c| = A_1 t^\beta + A_2 t^{\beta+\Delta} \quad (1)$$

where $t = 1 - T/T_c$; x and T are mole fractions of ionic liquid and temperature, x_c and T_c the corresponding critical values; β is the universal critical exponent and Δ is the correction exponent in Wagner expansion; A_1 , A_2 are the critical amplitudes. Assuming the asymptotic Ising behavior and using the fixed value of $\beta = 0.325$ and $\Delta = 0.5$ a nonlinear list squares procedure was used to fit our experimental data to Eq. (1). The results of the analysis are given in Table 3. The data presented in Fig. 1 reveal the same general picture. The miscibility curves represent the phase diagrams with the upper critical solution temperature (UCST) with marked asymmetry and visibly shifted to the low mole fractions range. These characteristics are typical for ionic liquid–molecular solvents systems.

More detailed analyze shows that the phase behavior in the system consisting of phosphonium ionic liquid and cyclic alkanes is very sensitive to the parameters characterizing the solvent. The UCST is shifted to the higher values (the miscibility is worsening) when the number of carbon atoms in the cycloalkanes increases

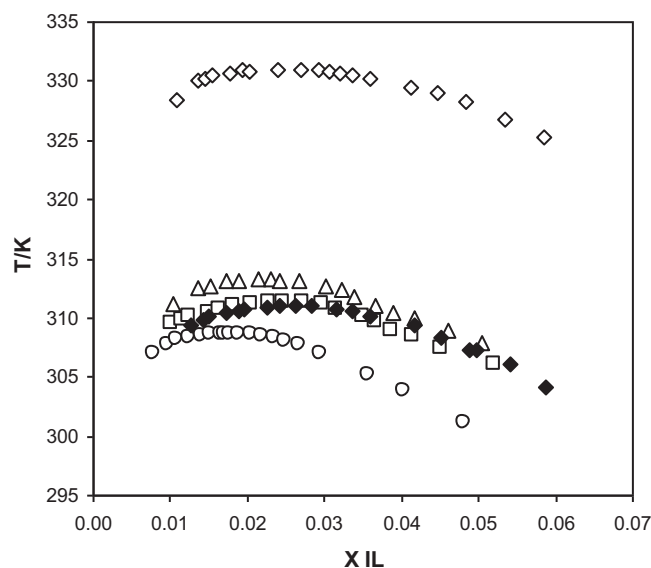


Fig. 1. Liquid–liquid equilibrium curves at 0.1 MPa for $[P_{6,6,6,14}][BF_4]$ /hydrocarbon systems; cyclohexane (\circ), cycloheptane (\square), methylcyclohexane (\triangle), 1,2-dimethylcyclohexane (\blacklozenge) and 1,3-dimethylcyclohexane (\diamond). x_{IL} represents mole fraction of ionic liquid in the solution.

as is observed for the case cyclohexane \rightarrow methylcyclohexane and cyclohexane \rightarrow cycloheptane. In both cases the number of carbon atoms increases to seven. This shift is much stronger for methylcyclohexane than for cycloheptane (Fig. 2). Hence the addition of the methyl group has much stronger effect on miscibility than just simple enlargement of the ring. It is probably related with a smaller spatial rearrangement of the molecule in the latter case.

The addition of the next methyl group into the ring shifts the UCST even more to the higher values – the miscibility worsens. However in this case the relative position of the two methyl groups makes difference in the miscibility. 1,3-Dimethylcyclohexane is significantly worse miscible with ionic liquid than 1,2-dimethylcyclohexane (Fig. 3).

One would anticipate that the conformation of the 1,2-isomer would favor its better accommodation in the hydrophobic region

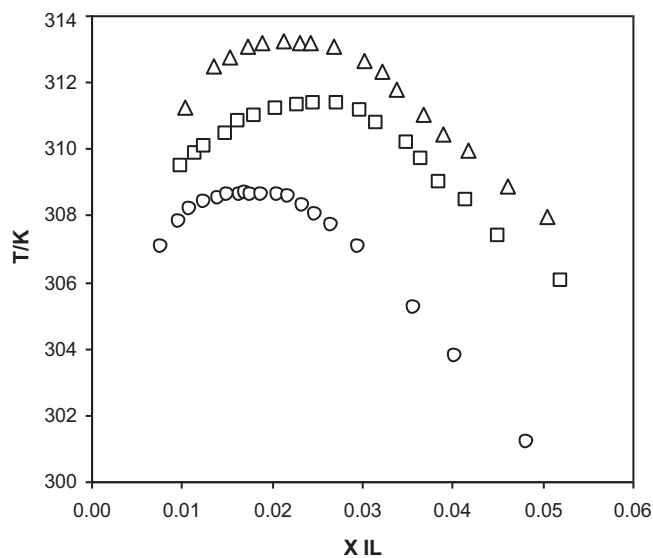


Fig. 2. Liquid–liquid equilibrium curves at 0.1 MPa for $[P_{6,6,6,14}][BF_4]$ /hydrocarbon systems; cyclohexane (\circ), cycloheptane (\square), methylcyclohexane (\triangle). x_{IL} represents mole fraction of ionic liquid in the solution.

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