J. Chem. Thermodynamics 42 (2010) 1361–1366

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Measurements of activity coefficients at infinite dilution of organic solutes and water in 1-propyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide ionic liquid using g.l.c.

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ARTICLE INFO

Article history:
Received 7 May 2010
Accepted 29 May 2010
Available online 4 June 2010

Keywords:
Piperidinium ionic liquid
Activity coefficients at infinite dilution
Gas–liquid chromatography
Liquid–liquid extraction

ABSTRACT

Activity coefficients at infinite dilution (γ_{13}^{∞}) of 38 different solutes (including alkanes, cyclohydrocarbons, alkenes, alkynes, benzene, alkylbenzenes, alcohols, water, thiophene, THF, MTBE, ethers, acetone, and *n*-ketones) in the ionic liquid 1-propyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide have been determined by using the g.l.c. method and have been reported over the temperature range from (308.15 to 358.15) K. The partial molar excess enthalpies of mixing at infinite dilution have been determined based on temperature dependence of γ_{13}^{∞} and discussed in terms of the intermolecular interactions. Selectivity and capacity at infinite dilution has been also calculated for chosen separation processes in systems (*n*-hexane + benzene) and (cyclohexane + benzene) to evaluate if the studied ionic liquid is capable to be a good entrainer for these processes, *e.g.* in the liquid–liquid extraction. The results obtained are much better than many other ionic liquids with bis{(trifluoromethyl)sulfonyl}imide-based anion. However, the results are worse than for the thiocyanate-based ionic liquids.

1. Introduction

Ionic liquids (ILs) are organic salts which have become to be one of the most studied classes of solvents and are considered as valid potential substitutes for many volatile organic solvents. The ILs melt at a relatively low temperature, have low vapour pressure, high chemical stability, large liquidus temperature range, and reveal specific interactions with many organic compounds. This is due to asymmetry and charge dispersion of their organic and inorganic ions. The major advantage of the ILs in electrochemistry is a much wider electrochemical window in comparison to the traditional electrolytes. The ILs exhibit excellent solvent qualities for many organic compounds and they provide attractive extractive possibilities. All of these properties make the ILs very promising new substances, particularly in chemical engineering [1–3]. Their physico-chemical properties can be finely adjusted by a careful selection of cation and anion.

In our laboratory, the measurements of the activity coefficients at infinite dilution (γ_{13}^{∞}) of the polar and non-polar solutes as well as of water in the ILs have been measured for many types of ILs as imidazolium-based [4], pyridinium-based [5,6], sulphonium-based [7], phosphonium-based [8], and pyrrolidinium-based [9]. Recently, the influence of both cation and anion structure on the selectivity and capacity in potential liquid–liquid extraction processes have been investigated [10]. Excellent results of selectivities in different separation problems were obtained earlier by us for 1-alkyl-3-methylimidazolium thiocyanates [4,11]. For the 1-butyl-3-methylimidazolium thiocyanate, [BMIM][SCN] the value of selectivity in the separation problem of the *n*-hexane/benzene was 88.0 at $T = 308.15$ K [11].

The gas–liquid chromatography (g.l.c.) as an experimental technique can be easily used because of non-volatility of the ILs.

The present work is a continuation of our studies on applications of the ILs in the liquid mixtures separations [4–9] with the new cation, namely piperidinium-based ionic liquid.

Firstly, the (solid + liquid) and (liquid + liquid) phase equilibria in binary systems of piperidinium-based ionic liquids (PIPILs) with alcohols, water, aliphatic hydrocarbons, cyclohydrocarbons, and aromatic hydrocarbons were measured [12]. The measurements were made for 1-butyl-1-methylpiperidinium thiocyanate [BMPIP][SCN] and for the 1-ethyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide [EMPIP][NTf$_2$] [12]. The studied ILs were chosen to detect the influence of cation, or anion on the phase equilibria properties. Our results indicate significant differences in the solubility of these two PIPILs in alcohols. The solubility of [BMPIP][SCN] in aliphatic and aromatic hydrocarbons suggest high selectivity for different separation problems. The solubility of 1-propyl-1-methylpiperydinium bis{(trifluoromethyl)sulfonyl}imide [PMPIP][NTf$_2$] was also measured in water [13]. However, the PIPILs are mainly used as an electrochemical media [14–18].

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0021-9614/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2010.05.017

The 1-ethyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide, [EMPIP][NTf$_2$] shows a highly endothermic solid–solid phase transition prior to fusion [19]. The density and isothermal compressibility of different ILs, including the piperidinium-based ILs, were measured and discussed for different anions [20,21]. The viscosity for 1-propyl-1-methyl-piperidinium-based cation is higher than for imidazolium-, pyrrolidinium- and ammonium-based cations [22].

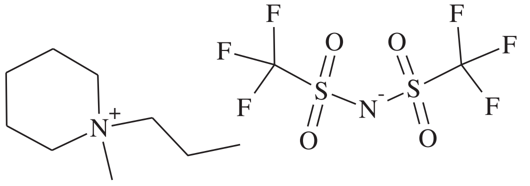
The γ_{13}^{∞} for PIPILs to our best knowledge have not been measured. For this study, activity coefficients at infinite dilution, γ_{13}^{∞} for 38 solutes: alkanes, cyclohydrocarbons, alkenes, alkynes, benzene, alkylbenzenes, alcohols, water, thiophene, tetrahyrdofuran (THF), methyl *tert*-butyl ether (MTBE), linear ethers, acetone, and linear ketones in the ionic liquid 1-propyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide [PMPIP][NTf$_2$], were determined by gas–liquid chromatography at temperatures from (308.15 to 358.15) K. This work will also give information about the influence of the cation on the selectivity and capacity of ionic liquids based on bis(trifluoromethylsulfonyl)imide anion.

2. Experimental

2.1. Materials

The ionic liquid, 1-propyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide had a purity of >0.99 mass fraction and was delivered by IoLiTec (Ionic Liquids Technologies GmbH, Denzlingen, Germany, CAS, 608140-12-1). The ionic liquid was further purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at the temperature 340 K for approximately 12 h. This procedure removed any volatile chemicals from the ionic liquid. The analysis made by HPLC did not show any organic impurities. The solutes, purchased from Aldrich and Fluka, had purities >0.99 mass fraction and were used without further purification because the g.l.c. technique separated any impurities on the column. Chromosorb W HP 80/100 mesh was used as the solid support and was supplied by SUPELCO. This material was also purified by the same method used for the ionic liquid. The mass of the IL and Chromosorb was checked before conditioning and after loading. The same masses obtained before and after loading confirm that the IL and Chromosorb were clean, without water and volatile chemicals.

The chemical structure of the investigated ionic liquid is presented in the scheme below:



2.2. Apparatus and experimental procedures

The experiments were performed using a Perkin Elmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The data were collected and processed using TotalChrom Workstation software. The column preparation and the packing method used in this work have been described previously [4–8]. Glass columns of length 1 m and 4 mm internal diameter were used. Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of Chromosorb into a solution of the ionic liquid in methanol followed by evaporation of the solvent using a rotary evaporator. The masses of the stationary phase and of the solid support were weighed with a precision ±0.0001 g. The solvent column packing varied from 0.448 to 0.549 mass fraction of the ionic liquid, large enough to prevent any residual adsorption of solute onto the column packing, as was observed in recently published work [23]. For each temperature, the measurements were repeated by using two different columns with different mass percent packing. Care was taken to ensure that the methanol had completely evaporated from the IL coated solid before making up the column. Before experiments each column was conditioned by passing carrier gas at high flow rate (about $2\ \text{cm}^3 \cdot \text{s}^{-1}$) and at the high temperature (about 350 K) over a period of about 8 h.

The outlet pressure P_o was kept at atmospheric pressure. The pressure drop ($P_\text{i} - P_\text{o}$) varied between (40 and 80) kPa depending on the flow rate of the carrier gas. The pressure drop was measured by a pressure transducer implemented in the g.c. with an uncertainty of ±0.1 kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of ±0.1 hPa.

The carrier gas was helium and the flow rate of the carrier gas was determined using a calibrated soap bubble flow meter, which was placed at the outlet after the detector. The flow rate was set for a series of runs and was allowed to stabilize for at least 15 min before any γ_{13}^{∞} determinations were made. The flow rates were corrected for water vapour pressure and ranged from $(1.1\ \text{to}\ 2.5)\ \text{cm}^3 \cdot \text{s}^{-1}$. Solute injections ranged from $(0.01\ \text{to}\ 0.3) \cdot 10^{-3}\ \text{cm}^3$ and were considered to be at infinite dilution on the column. Injection was provided manually with the syringe $1 \cdot 10^{-3}\ \text{cm}^3$.

Experiments were carried out at different temperatures (in steps of 10 K) in the range from (308.15 to 358.15) K. The temperature of the column was maintained constant to within ±0.02 K. The temperature of the column was controlled in the ovens of g.c. with an additional electronic thermometer P 550 (Dostmann electronic GmbH). At a given temperature, each experiment was repeated 2 to 4 times to check the reproducibility. Retention times were generally reproducible within (0.001 to 0.01) min. At each temperature, values of the dead time t_G identical to the retention time of a non-retainable component were measured. While our g.c. was equipped with a TCD detector, air was used as a non-retainable component. The estimated overall error in γ_{13}^{∞} was less than 3%, taking into account the possible errors in determining the column loading, the retention times and solute vapour pressure. The g.l.c. technique was tested for the system hexane in hexadecane at $T = 308.15$ K and the results compared very favourably with the literature values [24].

3. Theoretical basis

The equation developed by Everett [25] and Cruickshank *et al.* [26] was used in this work to calculate the γ_{13}^{∞} of solutes in the ionic liquid.

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3 RT}{V_\text{N} P_1^*}\right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_\text{o} J_2^3 (2B_{12} - V_1^{\infty})}{RT}. \tag{1}$$

In this work, subscript 1 refers to a solute, 2 refers to the carrier gas, and 3 refers to the solvent, [PMPIP][NTf$_2$]. The n_3 is the number of moles of solvent on the column packing, R is the gas constant, T the column temperature, V_N denotes the net retention volume of the solute, P_1^* the saturated vapour pressure of the solute at temperature T, B_{11} the second virial coefficient of pure solute, V_1^* the molar volume of the solute, P_o the outlet pressure, $P_\text{o} J_2^3$ the mean column pressure, B_{12} (where 2 refers to helium), the mixed second virial coefficient of the solute and the carrier gas and V_1^{∞} the partial molar volume of the solute at infinite dilution in the solvent. The values of B_{11} and B_{12} were calculated using the McGlashan and Potter equation [27]: