J. Chem. Thermodynamics 41 (2009) 645–650

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Measurements of activity coefficients at infinite dilution of aliphatic and aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, MTBE, and water in ionic liquid [BMIM][SCN] using GLC ☆

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ARTICLE INFO

Article history:
Received 17 October 2008
Received in revised form 22 November 2008
Accepted 19 December 2008
Available online 30 December 2008

Keywords:
Ionic liquid
1-Butyl-3-methylimidazolium thiocyanate
Gas–liquid chromatography
Activity coefficient
Thermodynamics

ABSTRACT

The activity coefficients at infinite dilution, γ_{13}^{∞} for 32 solutes: alkanes, alken-1-es, alkyn-1-es, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, *tert*-butyl methyl ether, and water in the ionic liquid 1-butyl-3-methylimidazolium thiocyanate [BMIM][SCN] were determined by gas-liquid chromatography at the temperatures from 298.15 K to 368.15 K. The values of the partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. The selectivities for the hexane/benzene, cyclohexane/benzene, hexane/thiophene, and other separation problems were calculated from the γ_{13}^{∞} and compared to the other ionic liquids, *N*-methyl-2-pyrrolidinone, and sulfolane, taken from the recent literature. This work demonstrates that with chosen ionic liquid it is possible to separate different organic compounds with the highest selectivity, ever published.

1. Introduction

Ionic liquids (ILs), due to their unique properties such as wide liquid range, stability at high temperatures, no flammability, and negligible vapour pressure are the subject of an increasing number of investigations. These features ensure that ILs are good candidates for the separation processes and can successfully replace the conventional volatile, flammable, and toxic organic solvents. For ILs to be used effectively as solvents, it is essential to know how they interact with different solutes. Particularly, by varying the cation, anion, and/or substituent groups, the properties of ILs can be readily tuned to fit into specific requirements. The important measure of this property is given by the activity coefficient at infinite dilution, γ_{13}^{∞}, which describes the non-ideality for chosen species in a mixture {where 1 refers to the solute and 3 to the solvent (here IL)}. The primary appeal of ILs is based on their unique physical properties, including the ability to solvate a wide range of materials. The activity coefficient at infinite dilution, γ_{13}^{∞}, is especially important because it describes the extreme case in which only solute–solvent interactions contribute to non-ideality. Additionally, the values of γ_{13}^{∞} may have practical implications in chemical and industrial processes. Currently, a large number of experimental γ_{13}^{∞} data are available in the literature for imidazolium ionic liquids [1–10].

Since the ILs have a negligible vapour pressure, the gas-liquid chromatography (GLC) is a suitable method for measuring the activity coefficients at infinite dilution γ_{13}^{∞}. From experimental values of γ_{13}^{∞} the selectivity at infinite dilution $S_{ij}^{\infty} = \gamma_{i3}^{\infty}/\gamma_{j3}^{\infty}$ and the capacity at infinite dilution $k_j^{\infty} = 1/\gamma_{j3}^{\infty}$ can be calculated for different separation problems as first information about two important components of the industrial mixture [11]. Experimental γ_{13}^{∞} values provide useful information about interaction between these two components (solvent (IL) and solute). However, the knowledge about γ_{13}^{∞} can only provides an idea of the system behaviour, not about the economics of a process which depend on many factors.

In most cases, a special technique based on the gas chromatographic determination of the solute retention time in a packed column filled with the IL as a stationary phase has been used [3,5,6,8–10]. An alternative method is the "dilutor technique" [1,2]. Values of γ_{13}^{∞} (where 1 refers to the solute = organic solvent, or water and 3 to the solvent = liquid phase ionic liquid) provide a useful tool for solvent selection in extractive distillation or solvent extraction processes. It is sufficient to know the separation factor of the components to be separated at infinite dilution in order to determine the applicability of a compound (a new IL) as a selective solvent.

In many publications, the activity coefficients at infinite dilution, γ_{13}^{∞} have been determined for alkanes, alk-1-enes, alk-1-ynes, cycloalkanes, aromatic hydrocarbons, carbon tetrachloride, and methanol in the IL at different temperatures. For example for

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☆ Presented at the 20th International Conference on Chemical Thermodynamics, Warsaw, Poland, 3–8 August 2008.

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0021-9614/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2008.12.018

1-ethyl-3-methylimidazolium thiocyanate, [EMIM][SCN] for every hydrocarbon (alkane, cycloalkane, alk-1-ene, and alk-1-yne) the activity coefficient increases with an increase of the carbon chain/ring length [4]. Usually, the value of activity coefficient decreases when the interaction between the solvent and the IL increases. It can be seen from comparison of the activity coefficients, γ_{13}^{∞} for different aromatic hydrocarbons, or alcohols in ILs [3,6,9]. The value of the activity coefficient in water is the lowest in comparison with alcohols, or benzene [4]. The influence of the alkyl chain in the cation of IL for the bis {(trifluoromethyl)sulfonyl}imide anion, $[Tf_2N]^-$ shows that for hexane, hex-1-ene, benzene, and cyclohexane the increase of the alkyl chain at the cation decreases the activity coefficient for every kind of hydrocarbon in the IL. It is found that the selectivities and capacities of different solutes are dependent on the opposite direction on the alkyl chain length of the cation of the IL. From the wide analysis of these two parameters, it was deduced that the best IL for the economic realization of the separation of aromatics and aliphatics is 1-butyl-3-methylimidazolium bis {(trifluoromethyl)sulfonyl}imide, $[BMIM][Tf_2N]$ [9]. The partial molar excess enthalpies at infinite dilution values $\Delta H_1^{E\infty}$, were found to increase within the increasing carbon number of solute in each of the series: alkane, alk-1-ene, alk-1-yne, and cycloalkane [1,3,5,6,8,9].

The selectivity S_{ij}^{∞} values for the separation of the {hexane (i) + benzene (j)} for example at $T = 298.15$ K using different IL compounds and some very polar solvents used in industry have values up to 95.4 for the [EMIM][SCN] [4]. The results demonstrate also a significant influence of the cation on the S_{ij}^{∞} values. For a given anion $[Tf_2N]^-$, the values of S_{ij}^{∞} are much higher for the shorter alkyl chain at the imidazole ring. The results at $T = 298.15$ K for $[MMIM]^+$, or $[EMIM]^+$, or $[BMIM]^+$ and $[HMIM]^+$ are 30.8, or 24.5, or 16.7 or 12.4, respectively [1,9]. It was shown earlier in many investigations that the selectivities of ILs in separating organic liquids are often higher than those for commonly used solvents, such as NMP, or (NMP + water). Comparing different results for many ILs, the selectivity S_{ij}^{∞} and capacity values for the separation of the {hexane (i) + benzene (j)} mixture have to be calculated; also the density, viscosity, toxicity, and cost for the investigated IL have to be discussed. The results presented show that the activity coefficients and intermolecular interactions of different solutes with the IL are very much dependent on the chemical structure of the IL.

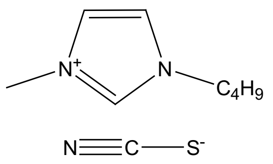
Some ILs were found few years ago as good entrainers for the aliphatic/aromatic separation: 1-methyl-3-methylimidazolium methylsulphate, $[MMIM][CH_3SO_4]$, or 1-ethyl-3-methyl ethylsulphate, $[EMIM][C_2H_5SO_4]$, and 4-methyl-*N*-butylpyridinium salt, $[MBPy][BF_4]$ have been chosen as the best ILs for the experiment [12]. It was shown that the $[MBPy][BF_4]$ IL is the best for highest capacity and selectivity [12]. In conclusion, the examination has to be always done for selectivity together with capacity in a variety of solutes in ILs to provide a picture of interactions and costs.

This paper presents values of γ_{13}^{∞} for 32 solutes (alkanes, alken-1-es, alkyn-1-es, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, *tert*-butyl methyl ether, and water) in the ionic liquid [BMIM][SCN] over the temperature range from $T = 298.15$ K to $T = 368.15$ K. This particular ionic liquid was chosen after analysis of the influence of anion of IL on the selectivity and after very good results, obtained with [EMIM][SCN] [4].

2. Experimental

2.1. Materials

The ionic liquid 1-butyl-3-methylimidazolium thiocyanate, [BMIM][SCN] had a purity of >0.98 mass fraction and was supplied by Fluka. Structure of investigated ionic liquid is presented below.



The ionic liquid was further purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at temperature about 343 K for approximately 5 h. This procedure removed any volatile chemicals and water from the ionic liquid. The solutes (alkanes, alken-1-es, alkyn-1-es, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, *tert*-butyl methyl ether), purchased from Aldrich and Fluka, were used without further purification because the GLC technique separated any impurities on the column.

2.2. Apparatus and experimental method

The experiments were performed using a PerkinElmer 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, has been described previously [3–9]. Glass columns of length 1 m and internal diameter 4 mm were used. Chromosorb W HP 80/100 mesh was used as the solid support and was supplied by SUPELCO. Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of Chromosorb in a solution of the ionic liquid in methanol followed by evaporation of the solvent using a rotating 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 0.452 to 0.493 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 works [13,14]. It was not possible to make a column with packing above 0.50 mass fraction, because part of the IL did not cover the solid support. For each temperature, the measurements were repeated by using two different columns with different mass fraction packing. Care was taken to ensure that the methanol had completely evaporated from the IL coated solid before making up the column. Each column was conditioned before the experiment by blowing carrier gas at high flow rate (about $2.5\ cm^3 \cdot s^{-1}$) at the high temperature (about 363 K) through about 8 h.

The outlet pressure P_o was kept at atmospheric pressure. The pressure drop $(P_i - P_o)$ was varied between (28 and 42) kPa depending on the flow rate of the carrier gas. The pressure drop was measured by gas chromatograph 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. 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 (0.6 to 1.1) $cm^3\ s^{-1}$. Solute injections ranged from $(0.01\ to\ 0.1)10^{-3}\ cm^{-3}$ in the liquid phase and were considered to be at infinite dilution on the column. Experiments were carried out at different temperatures (in steps of 10 K) between $T = 298.15$ K and $T = 368.15$ K. The temperature of the column was maintained constant to within ±0.02 K. At a given temperature, each experiment was repeated two to four times to check the reproducibility. Retention times