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Solvation parameter model and thermodynamic parameters in a dicationic ionic liquid based on pyrrolidinium

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ABSTRACT

The activity coefficient at infinite dilution, γ^{∞} has been determined for 26 solutes (alkanes, alcohols, amines, aromatics, chloroalkanes, ketones, ethers) in a newly developed dicationic ionic liquid 1,9-di(N-naphthalen-2-ylmethylpyrrolidinium)nonanebis[(trifluoromethyl)sulfonyl]imide ($[C_9(2MNPTpy)_2][(NTf_2)_2^-]$) by inverse gas chromatography at four different temperatures (T = 313, 323, 333 and 343 K). Solvation interactions between solvents and solute molecules have been estimated at T = (313, 343 and 373) K using Abraham solvation parameter. The experiments were carried out at various stationary phase loadings of (5 to 18)%. The selectivity values for cyclohexane/aromatics, octane/linear alcohols, octane/polar solutions were extracted from experimental activity coefficient data at T = 313 K. Compared with other ionic liquids from the literatures, this ionic liquid can be utilized as an efficient solvent for (aromatic + aliphatic) separation.

1. Introduction

Ionic liquids (ILs) are a class of compounds which are made of bulky cations (e.g., imidazolium, pyridinium, phosphonium, ammonium and pyrrolidinium) and organic or inorganic anions (e.g., Cl^-, Br^-, BF_4^-, PF_6^- and Tf_2N^-). These compounds are nonmolecular ionic solvents which have low melting points [1,2]. Because of their interesting physiochemical and solvation properties, ILs have caught much interest in recent years [3–5]. Moreover, ILs exhibit unique properties such as high thermal stability, miscibility, viscosity and negligible vapor pressure [3,6]. These properties are affected by nature of the cations, polarity and size of the anions, as well as length, shape and symmetry of the alkyl chains [6,7].

ILs are suitable as stationary phases in gas chromatography due to their high viscosity, low surface tension, great thermal stability and low vapor pressure [2]. Also when ILs are utilized as the stationary phases, they show dual-nature retention selectivity. This means that they can separate polar molecules similar to the polar stationary phases and nonpolar molecules similar to the nonpolar stationary phases [2,8].

There are three methods to determine multiple solvation interactions between the ILs and the solute molecules. In all three methods ILs have been used as the stationary phase for gas chromatography (GC) columns, with retention data of probe molecules being obtained chromatographically to find out types and magnitudes of the (solute + solvent) interactions. These methods include Rohrschneider–McReynolds classification system [9,10], solvation 39 parameter model [11,12], and measurement of thermodynamic parameters of the ILs such as activity coefficients at infinite dilution [13,14].

The Rohrschneider–McReynolds system is the foremost classification system that codifies stationary phases based on the retention behavior of five probe molecules, namely, benzene, butanol, 2-pentanone, nitropropane, and pyridine. Each probe molecule is used to represent a distinct or combination of interactions between the solutes and the stationary phases [15]. Abraham developed the solvation parameter model (linear solvation free energy relationship [LSFER] model), that describes gas or liquid phase interactions between the liquid phases and the solutes. Activity coefficients at infinite dilution (γ^{∞}) give information about intermolecular energy between the solvent and the solute [13,14,16–18]. Values of γ^{∞} are of significant relevance in separation processes, extractive distillation, selection of solvents for extraction and predicting existence of azeotropes. The inverse gas chromatography technique is known as the best way to determine values of γ^{∞}, since it needs less than even 1 g of IL and can be considered as a cost-efficient method.

Due to the great interest for using ionic liquids as the GC stationary phase and to follow previous works on dicationic ILs [3,16], in this work a novel pyrrolidinium bis(trifluoromethylsulfonyl)imide dicationic ionic liquid has been synthesized (figure 1) and used for separation of poly aromatic compounds. Dicationic

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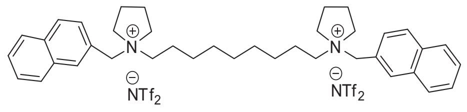

$[C_9(2MNPTpy)_2]$ $[(NTf_2)_2]$

FIGURE 1. Structures of ionic liquids.

ILs show an increase in the viscosity when compared to monocationic ILs [2], while thermal stabilities of the pyrrolidinium and imidazolium based dicationic ILs are also considerably higher than their monocationic analogs [19,20]. Among many other anions, ILs containing bis(trifluoromethylsulfonyl)imide (NTf_2^-) anion possess the lowest surface tension values except bis(pentafluoroethylsulfonyl)imide [2,21,22] and have high thermal stability [23]. The values of γ^{∞} have been determined for 26compounds at various temperatures (313, 343 and 373 K).

2. Experimental

2.1. Materials and chemicals

The ionic liquid, 1,9-di(N-naphthalen-2-ylmethylpyrrolidinium)nonanebis[(trifluoromethyl) sulfonylimide (figure 1) was prepared in CCERCI[1] and characterized by its 1H and 13C NMR (400 MHz) and spectra are recorded on a FT-NMR Bruker Ultra Shield as CDCl3 solutions using TMS as internal standard reference. Elemental analyses were performed using a Thermo Finnigan Flash EA 1112 instrument. The water content be estimated by Karl-Fischer titration 852 Titrando Metrohn. Pyrrolidine and 2-(bromomethyl)naphthalene were purchased from Merck and Fluka, respectively. 1,9-dibromononane and $Li[NTf_2]$[2] were procured from Sigma–Aldrich. The solutes were supplied by Merck and Fluka without further purification. Table 1 lists the source and purity of the compounds used. Chromosorb W/AW (mesh 60/80) was purchased from Fluka.

2.2. Experimental procedure

Inverse gas chromatography experiments were performed using a Varian CP-3800 gas chromatograph (Middelburg, Netherlands) equipped with a flame ionization detector (FID) and a 1041 injector. The injector and detector temperatures were kept at 523 K during all experiments. Hydrogen was used as the carrier gas and its flow rate was adjusted such to reach the optimum level. Methane was used to determine the dead time. A personal computer directly recorded the detector signals, while the corresponding chromatograms were extracted using Galaxie software.

Column packings, containing (5, 10, 15 and 18)% stationary phase (IL) on Chromosorb W/AW (mesh 60/80), were prepared using dichloromethane as the solvent. After evaporation of the solvent under vacuum condition, the support was equilibrated at $T = 373$ K for 18 h. Before measurements, each packed column is conditioned during 4 h at $T = 433$ K with a flow rate of $15\ cm^3 \cdot min^{-1}$. The solid support material was filled in a stainless steel column with an inner diameter of 1.8 in and length of 1 m. The weight of the packing material was calculated from weights of the packed and empty columns. In order to remain within infinite dilution conditions, (0.1 to 0.3) μl of headspace vapor of the samples was injected into the columns. To check the reproducibility, each experiment was repeated at least three times.

TABLE 1
Sources and purity of compounds.

Solute	Company	Purity (W/W%)
Hexane	Merck	95
Heptane	Fluka	⩾99.5
Octane	Merck	⩾99
Decane	Sigma–Aldrich	99.5
Dodecane	Fluka	⩾99.5
Tridecane	Fluka	⩾99.5
Cyclohexane	Merck	99.8
Benzene	Merck	⩾99
Toluene	Merck	99.8
o-Xylene	Merck	⩾99
m-Xylene	Merck	⩾99
p-Xylene	Merck	⩾99
Methanol	Merck	99.9
Ethanol	Merck	⩾99
1-Propanol	Fluka	⩾99
1-Pentanol	Fluka	⩾99.5
1-Butanol	Sigma–Aldrich	⩾99
2-Propanol	Merck	99.7
Cyclohexanol	Sigma–Aldrich	99
Butyraldehyde	Fluka	⩾99
Octyl aldehyde	Aldrich	99
Benzaldehyde	Fluka	⩾99
2-Pentanone	Sigma–Aldrich	99.8
Cyclopentanone	Aldrich	⩾99
Cyclohexanone	Sigma–Aldrich	99.5
Cycloheptanone	Aldrich	99
Acetophenone	Fluka	98
Triethylamine	Sigma–Aldrich	99.5
Pyridine	Sigma–Aldrich	99.8
Carbontetrachloride	Fluka	99
1,2-Dichloroethane	Fluka	⩾99
1,4-Dioxane	Fluka	⩾98
Acetonitrile	Merck	⩾99
Benzonitrile	Fluka	98
Ethylacetate	Merck	99
Acetic acid	Fluka	⩾99
Dimethylformamide	Merck	99.9
1-Nitropropane	Merck	99
1-Chlorooctane	Aldrich	99
1-Bromooctane	Aldrich	99
Nitrobenzene	Fluka	99
$[C_9(nmpy)_2]$–$[(NTf_2)_2^-]$	Synthesized in CCERCI	98

3. Calculation

3.1. Rohrschneider–McReynolds classification system

The Rohrschneider–McReynolds system is defined in equation (1) [2] in terms of five probes and their corresponding phase constants; namely, benzene (X'), butanol (Y'), 2-pentanone (Z'), nitropropane (U'), and pyridine (S') with the overall difference in Kovats retention index (ΔI).

$$\Delta I = aX' + bY' + cZ' + dU' + eS'. \tag{1}$$

The value of each phase constant (i.e., X', Y', Z', U' and S') is calculated by subtracting the retention index of the probe on a Squalane stationary phase from the retention index of the probe on the stationary phase being characterized.

3.2. Abraham's solvation parameter model

The Abraham's solvation model utilizes a large number of probe molecules to describe the simultaneous interactions between the solvent and the solutes. An LSER model is given by equation (2) [12], where K_L describes (gas + liquid) partition coefficient.

$$\text{Log } K_L = c + eE + sS + aA + bB + lL. \tag{2}$$

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[1] Chemistry and Chemical Engineering Research Center of Iran.

[2] Lithium bis(trifluoromethylsulfonyl)imide.