Thermodynamics and activity coefficients at infinite dilution for organic compounds in the ionic liquid 1-hexyl-3-methylimidazolium chloride

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ABSTRACT

The activity coefficients at infinite dilution, γ_i^∞, for 33 solutes, including alkanes, cycloalkanes, alkenes, aromatic hydrocarbons, acetonitrile, acetone, tetrahydrofuran, ethyl acetate, 1,4-dioxane, chloromethanes, alcohols in the ionic liquid 1-hexyl-3-methylimidazolium chloride, [HMIM][Cl], were determined by gas–liquid chromatography at temperatures range of (313.15–363.15) K. The gas-liquid partition coefficients, K_L were calculated for all solutes. The densities of [HMIM][Cl] were measured at the temperature range from 313.15 K to 363.15 K. The values of the partial molar excess enthalpies at infinite dilution $\left(\overline{H}_i^{E,\infty}\right)$ were derived from the temperature dependence of the γ_i^∞ values. The entropies $\left(T_{ref}\overline{S}_i^{E,\infty}\right)$ and Gibbs energies $\left(\overline{G}_i^{E,\infty}\right)$ of organic solutes in [HMIM][Cl] at a reference temperature T_{ref} = 298.15 K were also calculated from the γ_i^∞ values. The Hildebrand's solubility parameters of the IL [HMIM][Cl] were also determined by the regular solution theory (RST) combined with Flory "combinatorial" equation. The values of selectivity and capacity for n-hexane (i)/benzene (j), cyclohexane (i)/benzene (j) were calculated from γ_i^∞ and compared to literature values for [HMIM]-based or [Cl]-based ILs for the same separation problems.

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1. Introduction

Ionic liquids (ILs) are of great interest to the chemical and related industries because of its unique physical and chemical properties, such as the high stability, non-flammable, negligible vapour pressure, adjustable acidity and alkalinity and flexible design. The replacement of volatile organic solvents by ILs has a promising application prospect in the fields of catalytic synthesis, electrochemical and chemical separation process.

In the application of ILs, it is primarily necessary to analyse the interaction between the ionic liquid and the solute molecules, and then choose the targeted ionic liquid. During this process, activity coefficient at infinite dilution $\left(\gamma_i^\infty\right)$ is an important parameter in the ionic liquid separation process, not only reflects the dissolving ability of ionic liquids, but also describes the relationship between solute and IL [1]. It shows the essential information of the interaction between the solute molecules and the solvent molecules under the ideal condition that the solute molecules are surrounded by the solvent without considering the interactions between the solute molecules [2,3]. In the meantime, the activity coefficient at infinite dilution (γ_i^∞) can not only evaluate the separation properties of solvents, but also be used as an important basis to characterize the interaction between solute and solute molecules, which has important theoretical significance. It has important influences and wide application in chemical process and solution thermodynamics. In addition, it can be directly used in the design of units operation such as distillation, extraction and separation in petroleum and chemical fields. At the same time, ionic liquid has important applications in macromolecules, food, and petroleum processing.

A number of experimental techniques are available for direct measurement of γ_i^∞, including steady-state gas–liquid chromatography (GLC), the dilutor technique (DT method) or inert gas stripping, differential ebulliometry, headspace, and dew point. Each of these techniques has some limitations. The GLC method is fast and accurate and requires only a small amount of the required

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agent. Due to the unique advantages of ILs, it is very suitable as a stationary phase for gas-liquid chromatography. The retention values of various organic and inorganic compounds are determined by gas-liquid chromatography, and γ_i^∞ of each compounds in the ionic liquid is calculated by specific formula. In this paper, the infinite dilution activity coefficients (γ_i^∞) and the gas-liquid partition coefficients (K_L) of 33 organic solutes (alkanes, cycloalkanes, alkenes, aromatic hydrocarbons, acetonitrile, acetone, tetrahydrofuran, ethyl acetate, 1,4-dioxane, chloromethanes, alcohols) in ionic liquid 1-hexyl-3-methylimidazolium chloride ([HMIM][Cl]) have been measured at the temperatures from 313.15 K to 363.15 K by gas-liquid chromatography. By using the relationship between γ_i^∞ and the temperature, the values of the partial molar excess enthalpies at infinite dilution $\left(\bar{H}_i^{E,\infty}\right)$ were obtained. The entropies $\left(T_{ref}\bar{S}_i^{E,\infty}\right)$ and Gibbs energies $\left(\bar{G}_i^{E,\infty}\right)$ of organic solutes at a reference temperature $T_{ref}\bar{S}_i^{E,\infty}$ = 298.15 K were also determined from the γ_i^∞ values. These thermodynamic functions emphasize the interaction between solute and IL and are important information for the extraction of IL. The research results can provide basic data and theoretical basis for the further application of ILs as green solvents.

The selectivity $\left(S_{ij}^\infty\right)$ and the capacity $\left(k_{ij}^\infty\right)$ at infinite dilution directly calculated from γ_i^∞ offer an important means to evaluate the performance of ILs as solvents in various separation problems. The S_{ij}^∞ and k_{ij}^∞ at T = 323.15 K for IL [HMIM][Cl] have been also calculated for *n*-hexane (*i*)/benzene (*j*), cyclohexane (*i*)/benzene (*j*). The results were analysed in comparison to previously published literature data for [HMIM]-based or [Cl]-based ILs for the same separation problems.

2. Experimental

2.1. Experimental Materials

The ionic liquid [HMIM][Cl] was supplied by Shanghai Chengjie Chemical Co., Ltd. and had a purity of mass fraction greater than 0.99. According to manufacturer's specifications, with the following certified mass fraction of impurities: w (Cl$^-$) <4 × 10^{-4}, water <10^{-3}. Before use, the IL was subjected to vacuum evapouration at T = (323–333) K over 24 h to remove any volatile chemicals and water from the ionic liquid. Karl Fischer titration indicates that the concentration of water in ionic liquid is less than 0.0004. The chemical structures of [HMIM][Cl] is given in Fig. 1. The solutes were obtained from Beijing Chemical Reagents Company and were used without further purification because the GLC technique separated any impurities on the column. The list of materials, the sources and purities are showed in Table 1S in the Supplementary Material.

2.2. Density measurements

The density of the [HMIM][Cl] was measured using an Anton Paar DMA 4500 M digital vibrating-tube densimeter (Graz, Austria) in the temperature range from 313.15 K to 363.15 K at atmospheric
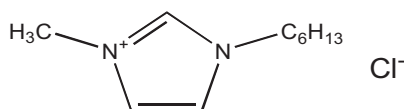
pressure. Measurement is based on the oscillating U-tube method that has been invented at a research institute in Graz, Austria. Two integrated Pt 100 platinum thermometers together with Peltier elements provide an extremely precise thermostatting of the sample. The measuring range is (0–3) g·cm^{-3}, repeatability density is 0.00001 g·cm^{-3} [4].

2.3. Apparatus and experimental procedure

The SP-3420A gas chromatograph with thermal conductivity detector was used for the experiment. The data were collected and processed using CT-22 USB Chromatography Data Acquisition Unit. The column preparation and the packing method used in this work are the same as those described by Ge [5-9]. The GC column (stainless steel) with length of 1 m and an internal diameter of 2 mm was used. Chromosorb W/AW-DCMS 800/100 mesh was used as the solid support and was supplied by SUPELCO. In this work, acetone was used as the solvent to coat the ionic liquid into the solid support. After coating, the solvent was evaporated using a rotary evaporator. The Chromosorb was weighed on an electronic balance of precision of ±0.0001 g before and after the coating process. The solvent column packing were 35.49% (0.4528 g) and 45.35% (0.8122 g) mass fraction of percent of [HMIM][Cl] with a precision of ±0.0001 g. The large column packing was used to prevent possible residual adsorption of solute onto the column packing. The column was filled with the help of an ultrasound vibrator and heated under nitrogen for 12 h at the column temperature of 120 °C. The measurement were carried out at GC column temperature range of (313.15 to 363.15) K. The temperature of injector was set as a value higher than boiling point of the compounds studied and all solutes were in the gaseous state before entering the column. Dry nitrogen was used as the carrier gas. The flow rate of carrier gas was determined using a flowmeter which was installed at the outlet after the detector. The flow rate was set for a series of runs. It was stabilized for at least 30 min before and the γ_i^∞ determinations were made. The volume of the samples injected into the GC probes was about (0.1–1.0)μL, and the peaks were found to be symmetrical, independent of the carrier gas flow rate. The temperature of the column was maintained constant within ±0.05 K. Each experiment was repeated at least three times to check the repeatability. The deviation of the retention time of the three measurements was within ±0.05 min. At each temperature, values of the dead time, t_G, equivalent to the retention time of a completely non-retained component were also measured. The measured dead time in the temperature range has a deviation of ±0.01 min.

To check the stability of the experimental conditions, such as the possible elution of the stationary phase by the carrier gas stream, the measurements of retention time were repeated systematically every (6–8) h for hexane and benzene. No change of the retention time was observed during 80 h of continuous operation.

3. Theory

3.1. Activity coefficients at infinite dilution (γ_i^∞)

In (gas–liquid) chromatography, the activity coefficients at infinite dilution γ_i^∞ were obtained by the equation proposed by Cruickshank et al. [10] and Everett [11].

$$\ln\gamma_i^\infty = \ln\left(\frac{n_3RT}{V_Np_i^0}\right) - \frac{B_{ii}-v_i}{RT}p_i^0 + \frac{2B_{i2}-v_i^\infty}{RT}J_2^3p_0 \tag{1}$$

where γ_i^∞ is the activity coefficient of solute *i* at infinite dilution in the stationary phase (3), p_i^0 is the vapour pressure of the pure liquid

Fig. 1. The chemical structures of 1-hexyl-3-methylimidazolium chloride ([HMIM] [Cl]).