Determination of the solubility parameter of ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate by inverse gas chromatography

Lishuang Deng, Qiang Wang *, Yali Chen, Zhengfang Zhang, Jun Tang

Center for Physical and Chemical Analysis, Xinjiang University, Urumqi 830046, PR China

ABSTRACT

The thermodynamic and physicochemical properties of 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM]PF_6) were investigated by inverse gas chromatography from 343.15 K to 373.15 K. Two groups of solvents with different chemical natures and polarities were used to characterize [OMIM]PF_6–solvent interactions. The specific retention volume, molar heat of sorption, weight fraction activity coefficient, partial molar heat of mixing, Flory–Huggins interaction parameter between [OMIM]PF_6 and the tested solvents, as well as activity coefficients at infinite dilution were determined. The solubility parameters of [OMIM]PF_6 were also determined by plotting the graph of $\delta_1^2/(RT) - \chi_{12}^\infty/V_1$ versus the solubility parameter δ_1 of the probes.

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1. Introduction

Ionic liquids (ILs) are a new class of solvents that have excellent applications in a broad range of scientific and industrial fields. ILs are salts entirely composed of ions and have normal melting point temperatures below the normal boiling point temperature of water. Compared with conventional organic solvents, ILs are used as reaction media, separation solvents, novel electrolytes, and catalysts in synthesis reactions because of their unique properties, such as excellent thermal stability, non-flammability, low vapor pressure, and high thermal solubility. The 1-alkyl-3-methylimidazolium family (C_nMIM^+) of cations appears to be very useful for fine tuning variations in the alkyl chain length, and their appropriate application areas are mainly affected by anions [1–3]. Francisco, M. et al. [4] used the IL 1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate as the solvent for extracting linalool from citrus essential oil. Armstrong et al. [5] used 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium chloride as stationary phases in gas chromatography. The activity coefficients at infinite dilution of some organic solutes in these two ILs were also determined [1,6,7].

The abovementioned applications utilize the molecular interactions offered by the different thermodynamic attributes of the ILs. Numerous studies have investigated various parameters to better understand how ILs work and how they can be applied. The Flory–Huggins interaction parameter [8] is frequently used to predict the thermodynamic state of two pure liquids and estimate the interactions between unlike molecules in mixtures. Meanwhile, the solubility parameter has proven to be useful in various applications [9]. A good solvent for a certain solute should have a solubility parameter value close to that of the solute [10] or should have similar compatibilities. The activity coefficient at infinite dilution is especially important because it describes the extreme case in which only solute–solvent interactions contribute to nonideality.

Several different methods are used to determine the interaction parameters, such as group contribution method, dynamic mechanical analysis, differential scanning calorimetry, and IGC [11,12]. In the present study, IGC was used to examine the physicochemical properties and thermodynamic quantities of ILs by measuring the dynamic adsorption characteristic of the probes. IGC has been proven to be powerful for this type of comparative study [13]. IGC can be used to measure the retention times of various solvents for the further calculation of thermodynamic parameters, which can provide rapid and accurate information for the physicochemical characterization of an IL. In the present study, IGC was used to determine the activity coefficients at infinite dilution [14–17] and partition coefficients [18–20] of ILs. However, reports on thermodynamic data related to [OMIM]PF_6 are limited.

In the present study, the interaction between [OMIM]PF_6 and solvents was determined using IGC from 343.15 K to 373.15 K. Some thermodynamic parameters including the molar heats of sorption at infinite dilution and partial molar heats of mixing were determined. The weight fraction activity coefficients, activity coefficients at infinite dilution, and Flory–Huggins interaction parameters were also obtained to characterize interactions between [OMIM]PF_6 and solvents. The apparent solubility parameters of the [OMIM]PF_6 were also calculated.

* Corresponding author. Tel./fax: +86 991 8582966.
  E-mail address: xjuwq@sina.com (Q. Wang).

2. Experimental

2.1. Chemicals

The IL [OMIM]PF$_6$ used in the experiments was obtained from Changjie Chemical Co., Ltd. China and had a mass fraction purity greater than 0.99. [OMIM]PF$_6$ was purified by vacuum evaporation to remove the traces of volatile impurities prior to use. A homologous series of n-hexane to n-nonane (n-C$_6$, n-C$_7$, n-C$_8$, n-C$_9$) compounds was used as nonpolar solvents to calculate the solubility parameter. Diethyl ether, acetone, ethanol, methanol, chloroform, ethyl acetate, and other test solutes were used as polar solvents. An overview of the chemicals used in this study is summarized in Table 1.

2.2. Procedures

The stationary phase used in the experiments was prepared by dissolving a weighed sample of [OMIM]PF$_6$ (precision, ±0.0001 g) in dichloromethane, followed by depositing the resulting solution onto a weighed amount of silicon alkylation 102 monomer support (60–80 mesh). The mixture was allowed to slowly dry under a rotary evaporator and stirred to ensure a homogeneous mixture. The stationary phases consisted of 10% (w/w) [OMIM]PF$_6$. The coated support was packed into stainless steel columns 0.2 cm in inner diameter and 60 cm long and subsequently conditioned at 453.15 K under nitrogen for 8 h prior to use.

The IGC experiments were carried out using a commercial Hewlett-Packard 6890 gas chromatograph equipped with a flame ionization detector. Chemstation Software (Ver A.06.01) was used to directly record detector signals. The injector and detector temperatures were both kept at 523.15 K in all experiments. Dried nitrogen was used as a carrier gas with a flow rate of about 10 mL·min^{-1} measured at the end of the column using a soap bubble flow meter. The temperatures of the oven ranged from 343.15 to 373.15 K in 10 K increments (uncertainty $u(T) = 0.1$ K). Methane was used to determine the column hold-up time for calculating the specific retention times of other probe solvents. Each experiment was repeated at least thrice to ensure reproducibility.

3. IGC theory

3.1. Thermodynamic parameters

IGC can be used to determine the retention time t_r of the probe injected into the column that was then used to calculate the specific retention volume (V_g^0) according to the following equation [21]:

$$V_g^0 = \frac{237.15}{mT_a} F \frac{P_0 - P_w}{P_0} (t_r - t_0) \frac{3}{2} \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \tag{1}$$

where m is the IL mass; t_r is the retention time of the probe; t_0 is the retention time of the non-interacting probe (such as methane); F is the flow rate of the carrier gas measured at room temperature; P_w is the saturated vapor pressure of water at ambient temperature; and P_i and P_0 are the inlet and outlet pressures, respectively.

The following equations were used to calculate the molar heat (enthalpy) of the probe's absorption ΔH_1^S in the IL, the partial molar enthalpy of mixing at infinite dilution ΔH_1^∞, the values of heat of vaporization ΔH_v, and relationship between the infinite dilution activity coefficient Ω_1^∞ of the solvent and the retention volume [22,23]:

$$\Delta H_1^S = -R\partial \ln V_g^0 / \partial(1/T) \tag{2}$$

$$\Delta H_1^\infty = R\partial \ln \Omega_1^\infty / \partial(1/T) \tag{3}$$

$$\Delta H_V = \Delta H_1^\infty - \Delta H_1^S \tag{4}$$

$$\ln \Omega_1^\infty = \ln \frac{273.15R}{P_1^0 V_g^0 M_1} - \frac{P_1^0}{RT}(B_{11} - V_1). \tag{5}$$

Moreover, the retention data determined using IGC experiments revealed the activity coefficients at infinite dilution for solute 1 in IL 2 which was calculated using the following expression [24]:

$$\ln \gamma_{12}^\infty = \ln\left(\frac{n_2 RT}{V_n P_1^0}\right) - P_1^0\left(\frac{B_{11} - V_1^0}{RT}\right) + \frac{2B_{13} - V_1^\infty}{RT} J P_0 \tag{6}$$

where R is the gas constant, T is the oven temperature, n_2 is the number of moles of stationary phase component within the column, P_1^0 is the probe vapor pressure at temperature T, P_0 is the pressure at the column outlet, and B_{11} is the second virial coefficient of the solute in the gaseous state at temperature T. Moreover, $B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n - 1)(T_c/T)^{4.5}$, where V_c and T_c are the critical molar volume and critical temperature of the solute, respectively; n is the number of carbon atoms in the solutes; and B_{13} is the mutual virial coefficient between solute 1 and the carrier gas (nitrogen; denoted by "3"). The molar volume V_1^0 was determined from experimental densities, and the partial molar volumes of the solutes at infinite dilution V_1^∞ were assumed

Table 1
Chemical sample specifications.

Chemical name	CAS No.	Source	Purity	Purification method	Purity measurement
[OMIM]PF$_6$	304680-36-2	Chengjie, China	Water content <0.2%	Vacuum evaporation	Karl Fischer titration
n-C$_6$	110-54-3	Bodi, China	Mass fraction >0.995	None	Gas chromatography
n-C$_7$	142-82-5	Bodi, China	Mass fraction >0.995	None	Gas chromatography
n-C$_8$	111-65-9	Bodi, China	Mass fraction >0.995	None	Gas chromatography
n-C$_9$	111-84-2	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Benzene	71-43-2	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Toluene	108-88-3	Bodi, China	Mass fraction >0.995	None	Gas chromatography
m-xylene	108-38-3	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Ethanol	64-17-5	Hongyan, China	Mass fraction >0.995	None	Gas chromatography
Methanol	67-56-1	Hongyan, China	Mass fraction >0.995	None	Gas chromatography
Dichloromethane	75-09-2	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Acetone	67-64-1	Hongyan, China	Mass fraction >0.995	None	Gas chromatography
Chloroform	67-66-3	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Ethyl acetate	141-78-6	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Tetrahydrofuran	109-99-9	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Diethyl ether	60-29-7	Hongyan, China	Mass fraction >0.995	None	Gas chromatography
Tetrachloromethane	56-23-5	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Methyl acetate	79-20-9	Bodi, China	Mass fraction >0.995	None	Gas chromatography
Cyclohexane	110-82-7	Bodi, China	Mass fraction >0.995	None	Gas chromatography