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Determination of the thermodynamic parameters of ionic liquid 1-hexyl-3-methylimidazolium chloride by inverse gas chromatography

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ABSTRACT

Some thermodynamic properties for the ionic liquid 1-hexyl-3-methylimidazolium chloride ([HMIM]Cl) were investigated by inverse gas chromatography (IGC) method at temperatures from 343.15 K to 373.15 K. The thermodynamic parameters, including weight fraction activity coefficient, Flory–Huggins interaction parameter, partial molar enthalpy of mixing, molar enthalpy of sorption, activity coefficient at infinite dilution and solubility parameter, were obtained to judge the interactions between [HMIM]Cl and the selected solvents at the studied temperatures. The results showed that dichloromethane, chloroform, carbon tetrachloride, ethanol, and carbinol were the favorite solvents for [HMIM]Cl, while *n*-C₆ to *n*-C₉, cyclohexane, benzene, toluene, *m*-xylene, acetone, ethyl acetate, tetrahydrofuran, ether, methyl, and acetate were bad solvents for [HMIM]Cl.

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1. Introduction

Ionic liquids (ILs) are organic salts composed of unsymmetrical organic cation and inorganic anion, which are liquid at ambient conditions [1–3]. They have emerged as environmentally friendly replacement for the traditionally used volatile organic solvents in many scientific fields. In recent years, a considerable attention by many scientists and engineers has been focused on the systematic applications of ILs [4–7], owing to their multifaceted properties, namely, excellent chemical stability, exceedingly low vapor pressure, high thermal stability, low volatility at room temperature, and wide liquid range and their recyclability [8,9]. The potential advantages of ILs, which are extremely dependent on the nature of anions and cations, can be revealed by studying their thermodynamic properties [10]. The thermodynamic data of ILs will give a better understanding of their behavior in mixtures depending on their ionic structures and the intermolecular interactions. Furthermore, the concept of the solubility parameter [11] has been used to estimate various physicochemical parameters [12] and interpret the different phenomena occurring between materials [13]. The solubility parameter is important in solvent extraction process for understanding the intermolecular interactions.

Several different methods have been used to determine the solubility parameter, such as solubility, miscibility, viscosity, mechanical measurements [14], swelling [15] and group additive methods [16]. However, these methods are often time-consuming and laborious [17]. Inverse gas chromatography (IGC) has been shown to be a simple method to obtain thermodynamic parameters for solvents of binary mixtures or properties of pure substances over a wide temperature range [18,19]. One of the most important and promising classes of ILs is based on the 1-alkyl-3-methylimidazolium cation ([C_nMIM]⁺), which can be used for synthesis of ILs with different anions. 1-Hexyl-3-methylimidazolium chloride ([HMIM]Cl) is one of the most commonly investigated ionic liquids. David Rooney et al. predicted the physical properties and behavior of 1-hexyl-3-methylimidazolium chloride ([HMIM]Cl) by using group contribution methods [20]. Nilesh M. Vaghela et al. investigated the surface active and aggregation behavior of [HMIM]Cl [21]. Alessandro Triolo et al. provided the first experimental evidence about the existence of nanoscale segregation in [HMIM]Cl [22]. However, few articles have been published on determining the thermodynamic parameters of [HMIM]Cl by the IGC method.

The objective of this work was to determine the thermodynamic parameters of [HMIM]Cl with the selected solvents by the IGC method. The thermodynamic parameters, including weight fraction activity coefficient, Flory–Huggins interaction parameter, partial molar enthalpy of mixing, molar enthalpy of sorption, activity coefficient at infinite dilution and the solubility parameter were determined which could be used to judge the interactions between [HMIM]Cl and solvent probes.

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2. Theoretical background

2.1. IGC theory

The specific retention volume of the probes, V_g^0 , which is used to investigate the elution behavior of the tested probes, can be calculated experimentally using the following equation [23,24]:

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

where m is the mass of [HMIM]Cl, T_a is the column temperature, F is the flow rate of the carrier gas measured at room temperature, t_r is the retention time of the probe, t_0 is the retention time of the non-retainable component (such as methane), P_w is the saturated vapor pressure of water at ambient temperature, and P_i and P_0 are inlet and outlet pressures, respectively.

2.2. Thermodynamic parameter

According to the IGC technique, the specific retention volume, V_g^0 , can be used for characterization of the thermodynamic properties of the investigated IL. The weight fraction activity coefficient, Ω_1^* , and the molar heat (enthalpy) of sorption, ΔH_1^S , of the probes are given by the following equations [25]:

$$\ln \Omega_1^* = \ln \frac{273.15R}{P_1^0 V_g^0 M_1} - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (2)$$

$$\Delta H_1^S = -R \partial \ln V_g^0 / \partial (1/T) \quad (3)$$

where T is the column temperature, R is the gas constant, M_1 is the molecular mass of the probe, P_1^0 is the saturated vapor pressure of the probe at temperature T , and B_{11} is the second virial coefficient of the probe in the gaseous state at temperature T , which can be calculated by the equation: $B_{11} / V_c = 0.430 - 0.886(T_c / T) - 0.694(T_c / T)^2 - 0.0375(n - 1)(T_c / T)^{4.5}$, where V_c and T_c are the critical molar volume and the critical temperature of the probe solvents, respectively. V_1 represents the molar volume of the probe, and n is the amount of carbon atoms in the probe.

According to the IGC technique, the partial molar enthalpy of mixing at infinite dilution, ΔH_1^∞ , and the values of heats of vaporization, ΔH_v , can be calculated according to the following thermodynamic relations [26,27]:

$$\Delta H_1^\infty = R \partial \ln \Omega_1^* / \partial (1/T) \quad (4)$$

$$\Delta H_v = \Delta H_1^\infty - \Delta H_1^S \quad (5)$$

From the retention data determined with the inverse gas chromatography technique, the activity coefficients at infinite dilution for probe 1 in IL 2 can be calculated with the following expression [8]:

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

where n_2 is the number of moles of stationary phase component within the column, and B_{13} is the mutual virial coefficient between probe 1 and the carrier gas (dried N_2 , denoted by "3"). The V_1^0 is the molar volume of the probes, and the partial molar volume of the solute at infinite dilution

Table 1

The specific retention volume of the probes, V_g^0 , at different temperatures.

Probe	V_g^0 (mL)			
	343.15 K	353.15 K	363.15 K	373.15 K
<i>n</i> -C ₆	2.502	1.937	1.547	1.258
<i>n</i> -C ₇	8.764	6.386	4.753	3.728
<i>n</i> -C ₈	24.15	16.60	11.72	8.462
<i>n</i> -C ₉	56.73	36.98	24.88	17.17
Cyclohexane	7.612	5.708	4.324	3.369
Benzene	49.48	34.77	25.03	18.05
Toluene	95.20	64.78	44.97	31.75
<i>m</i> -Xylene	186.7	114.6	78.04	53.79
Dichloromethane	77.94	53.94	38.14	27.55
Acetone	25.24	18.21	13.31	9.72
Chloroform	391.8	256.6	173.1	118.7
Ethyl acetate	24.90	17.18	12.21	8.75
Tetrahydrofuran	26.36	19.07	14.14	10.51
Ether	1.954	1.551	1.346	0.998
Carbon tetrachloride	71.72	48.60	33.66	23.78
Methyl acetate	17.62	12.60	9.353	6.836
Ethanol	756.5	487.2	322.5	218.8
Carbinol	686.0	456.4	310.0	215.2

V_1^∞ was assumed to be equal to V_1^0 . The factor J that corrects for the influence of the pressure drop along the column was given by [28]:

$$J = \frac{3(P_i/P_0)^2 - 1}{2(P_i/P_0)^3 - 1} \quad (7)$$

2.3. Flory–Huggins interaction parameter

On the grounds of the Flory–Huggins theory, the interaction parameter, χ_{12}^∞ , at infinite dilution, which reflects the strength of the interaction between [HMIM]Cl and the probes, can be calculated from the following relation [29,30]:

$$\chi_{12}^\infty = \ln \left(273.15RV_2/P_1^0 V_g^0 V_1 \right) - 1 - P_1^0 (B_{11} - V_1) / RT \quad (8)$$

where R and V_2 are the gas constant and the specific volume of the IL, respectively. V_1 represents the molar volume of the probe, and P_1^0 is the saturated vapor pressure of the probe at the column temperature.

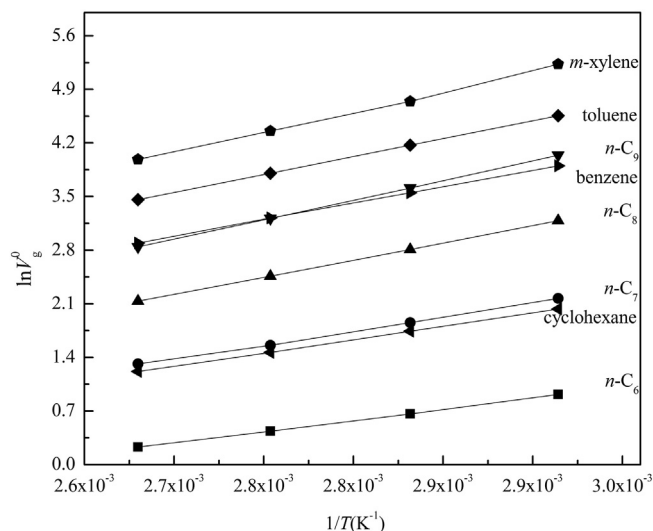


Fig. 1. Plot of $\ln V_g^0$ versus $1/T$ for the probes: ■ *n*-C₆; ● *n*-C₇; ▲ *n*-C₈; ▼ *n*-C₉; ► benzene; ◆ toluene; * *m*-xylene; ◄ cyclohexane.

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