Gas-liquid chromatography measurements of activity coefficients at infinite dilution of hydrocarbons and alkanols in 1-alkyl-3-methylimidazolium bis(oxalato)borate

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ARTICLE INFO

ABSTRACT

The activity coefficients at infinite dilution, γ_i^∞ for various solutes: alkanes, cycloalkanes, 1-alkenes, 1-alkynes, benzene, alkylbenzenes, and alcohols in the ionic liquids 1-butyl-3-methylimidazolium bis(oxalato)borate [BMIM][BOB] and 1-hexyl-3-methyl-imidazolium bis(oxalato)borate [HMIM][BOB] have been determined by gas-liquid chromatography at the temperatures ranging from 308 to 348 K. The partial molar excess enthalpies at infinite dilution $H_i^{E,\infty}$ of the solutes in the ionic liquids were also derived from the temperature dependence of the γ_i^∞ values. The selectivities for the hexane/benzene, cyclohexane/benzene and hexane/hexene separation problems were calculated from experimental infinite dilution activity coefficient values and compared to the other ionic liquids, taken from the recent literatures.

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1. Introduction

This work is a continuation of our investigations on the determination of activity coefficients at infinite dilution for many organic solutes in ionic liquids using gas-liquid chromatography. Our previous work includes measurements of γ_i^∞ for organic solutes in the ionic liquids (ILs): 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [EMIM][FAP] [1] and 1-ethyl-3-methylimidazolium tetracyanoborate [EMIM][TCB] [2]. Due to their unique properties such as no flammability, wide liquid range, stability at high temperatures, and negligible vapor pressure, so not surprisingly, one of the most significant applications for ionic liquids is using them as solvents for clean liquid–liquid extraction replacement for conventional volatile, flammable and toxic organic solvents [3,4]. Activity coefficients at infinite dilution of a solute i (γ_i^∞) is a suitable and widely accepted approach for quantify the volatility of the solute as well as to provide information on the intermolecular energy between solvent and solute [5,6]. Since ILs have a negligible vapor pressure, the gas-liquid chromatography (GLC) using the ionic liquid as stationary phase has been proven to be a good method for measuring activity coefficients at infinite dilution γ_i^∞.

Until now, there are so many publications about the ILs based on some common anions, such as bis(trifluoromethanesulfonyl)imide[NTf_2^-] [7–13], tetrafluoroborate [BF_4^-] [14–17], hexafluorophosphate [PF_6^-] [18] and trifluoromethanesulfonate [$CF_3SO_3^-$] [19–21]. In order to expand our knowledge about the nature of ILs, influence of the anion structure on the thermodynamic properties of the disubstituted imidazolium based ionic liquid with bis(oxalato)borate [BOB^-] anion was studied in this work. For this study, activity coefficients at infinite dilution, γ_i^∞ values for 23 solutes: alkanes, cycloalkanes, 1-alkenes, 1-alkynes, benzene, alkylbenzenes, and alcohols in the ionic liquids 1-butyl-3-methylimidazolium bis(oxalato)borate [BMIM][BOB] and 1-hexyl-3-methyl-imidazolium bis(oxalato)borate [HMIM][BOB] have been determined over the temperatures range from (308 to 348) K. The partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, of these solutes in the ionic liquids were also derived from the temperature dependence of the γ_i^∞ values. This work also intends to provide information about the slight modification in the length of these substituents and its influence on the value of γ_i^∞ and selectivity of ionic liquids based on the bis(oxalato)borate anion.

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2. Experimental

2.1. Materials

1-Alkyl-3-methylimidazolium bis(oxalato)borate (R = butyl, hexyl) were synthesized from 1-alkyl-3-methylimidazolium bromide (R = butyl, hexyl) with lithium bis(oxalato)borate (LiBOB) according to the procedures [22]. A silver nitrate test was performed on the RTIL and indicated that a less than 50 ppm of bromide ion impurity existed in the RTIL. The ionic liquids were purified and dried under high vacuum at 343 K for 24 h to remove organic solvents and water, and its structure was confirmed by ^{1}H NMR, ^{13}C NMR and 11B NMR spectroscopy. The water content was determined by Karl–Fischer titration, and it was found to be less than 100 ppm. The purity of the ionic liquids was >99%.

The hydrocarbons provided by Beijing Chemical Reagents Company were of analytical grade. Since the GLC process separated the solutes from any impurities, the solutes were used without further purification.101 AW (80/100 mesh, the inert and white diatomite) purchased from Shanghai Reagent Corporation was used as a solid support for the ionic liquid in the GC column. Before use, the support material was subjected to vacuum treatment with heating to remove traces of adsorbed moisture.

Structures of investigated ILs are presented below:

R=butyl, hexyl
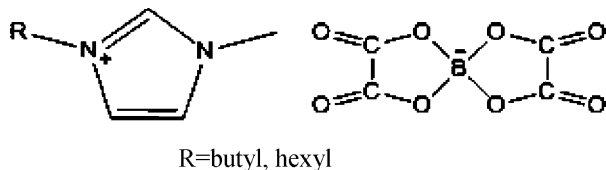
2.2. Experimental procedure

The detailed experimental procedure used in this work can be found in previous published works [1,2]. The column used in the experiment was constructed of stainless steel with length of 2 m and an inner diameter of 2 mm. Dichloromethane was used as solvent to coat ILs onto the solid support 101 AW (80/100 mesh) by a rotary evaporator to ensure the homogeneous spread of the IL onto the surface of support. The solid support was weighed before and after the coating process. The amounts of stationary phase ([BMIM][BOB] and [HMIM][BOB]) were 1.75 mmol and 1.89 mmol, respectively. The uncertainty of the mass of the stationary phase measurement was within ±0.0001 g. To avoid possible residual adsorption effects of the solutes on solid support, the amount of ionic liquids ([BMIM][BOB] and [HMIM][BOB]) were all 30.00 mass percent of the support material. Experiments were performed on a GC-7900 gas chromatograph apparatus, supplied by Shanghai Techcomp Limited Company in China equipped with a heated on-column injector and a flame ionization detector. The carrier gas flow rate was determined using a GL-102B Digital bubble/liquid flow meter with an uncertainty of ±0.1 cm^3 min^{-1}, which was placed at the outlet of the column. The carrier gas flow rate was adjusted to obtain adequate retention times. The pressure drop (P_i–P_o) varied between (35 and 150) kPa depending on the flow rate of the carrier gas. The pressure drop was measured by a pressure transducer implemented in the GC with an uncertainty of ±0.1 kPa. The atmospheric pressure was measured using a membrane manometer with an uncertainty of ±0.2 kPa. Solute injection volumes ranged from 0.1 to 0.3 ul and were considered to be at infinite dilution on the cloumn. The injector and detector temperature were kept at 473 and 523 K, respectively during all experiments. The temperature of the oven was measured with a Pt100 probe and controlled to within 0.1 K. The GLC technique and equipment was tested for the system hexane in hexadecane as stationary phase at 298 K, and

the results were within 2.0% of the literature values [23]. The procedure of the experimental error estimation was described in our previous work [1]. Values of γ_i^∞ are estimated to be accurate to within ±4%.

3. Theoretical basis

The equation developed by Everett [24] and Cruickshank et al. [25] was used in this work to calculate the γ_i^∞ of solutes in the ionic liquid:

$$\ln \gamma_{13}^\infty = \ln \left(\frac{n_3 RT}{V_N P_1^*} \right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_o J(2B_{12} - V_1^\infty)}{RT} \quad (1)$$

V_N is the standardized retention volume of the solute, P_o is the outlet pressure, n_3 is the number of moles of the ionic liquid on the column packing, T is the column temperature, P_1^* is the saturated vapor pressure of the solute at temperature T, B_{11} is the second virial coefficient of the pure solute, V_1^* is the molar volume of the solute, V_1^∞ is the partial molar volume of the solute at infinite dilution in the solvent (assumed as the same as V_1^*) and B_{12} (where 2 refers to the carrier gas, nitrogen) is the cross second virial coefficient of the solute and the carrier gas. The values of B_{11} and B_{12} were calculated using the McGlashan and Potter equation [26]:

$$\frac{B}{V_c} = 0.430 - 0.886 \left(\frac{T_c}{T} \right) - 0.694 \left(\frac{T_c}{T} \right)^2 - 0.0375(n-1)\left(\frac{T_c}{T} \right)^{4.5} \quad (2)$$

where n refers to the number of carbon atoms of the solute. Using the Hudson and McCoubrey combining rules [27,28], V_{12}^C and T_{12}^C were calculated from the critical properties of the pure component.

The net retention volume V_N was calculated with the following usual relationship:

$$V_N = JU_0(t_r - t_G)\frac{T_{col}}{T_f}\left(1 - \frac{P_{ow}}{P_o}\right) \quad (3)$$

where t_r is the retention time, t_G is the dead time, U_0 is the flow rate, measured by digital bubble/liquid flow meter, T_{col} is the column temperature, T_f is flowmeter temperature, P_{ow} is saturation vapor pressure of water at T_f and P_o is the pressure at the column outlet.

The factor J appearing in Eqs. (1) and (3) corrects for the influence of the pressure drop along the column and is given by [29]:

$$J = \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \quad (4)$$

where P_i and P_o are the inlet and the outlet pressure of the GC column, respectively.

The vapor pressure values were calculated using the Antoine equation and constants were taken from the literature [30]. Critical data and ionization energies used in the calculation of T_{12}^C, were obtained from literature [30–32].

4. Results and discussion

Tables 1 and 2 list the values of γ_i^∞ of different solutes (alkanes, cycloalkanes, 1-alkenes, 1-alkynes, benzene, alkylbenzenes, and alcohols) in the ionic liquids [BMIM][BOB] and [HMIM][BOB] in the temperature range from 308 to 348 K and partial molar excess enthalpies at infinite dilution $H_i^{E,\infty}$, determined from the Gibbs–Helmholtz equation:

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)} \right) = \frac{H_i^{E,\infty}}{R} \quad (5)$$

Figs. 1–8 show the natural logarithm of the activity coefficients in the ionic liquid as a function of the inverse absolute temperature