



# Activity coefficients at infinite dilution of organic solutes in 1-octyl-3-methylimidazolium nitrate using gas–liquid chromatography

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## ABSTRACT

Activity coefficients at infinite dilution and gas–liquid partition coefficients ( $K_L$ ) of 25 organic solutes, including alkanes, alkenes, alkylbenzenes, alcohols, acetonitrile, ethylacetate, acetone, tetrahydrofuran, dichloromethane, trichloromethane, and tetrachloromethane in the ionic liquid 1-octyl-3-methylimidazolium nitrate ([OMIM][NO<sub>3</sub>]), have been determined by means of gas–liquid chromatography over a temperature range of 303.15–363.15 K with the ionic liquid as the stationary phase. From the dependence of experimental activity coefficients, the partial molar excess enthalpies at infinite dilution and the solubility parameters of the organic solutes in the ionic liquid [OMIM][NO<sub>3</sub>] have been determined.

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## 1. Introduction

Ionic liquids (ILs) have been applied as replacement for conventional volatile organic solvents as designable “green” solvents to special task in the development of new separation processes. In the supported liquid membrane technology, an ionic liquid can be impregnated in the pore in polymer support or hollow fiber module, the capability of ILs to separate solutes mixtures depends on the selectivity of the solutes in ILs. A feature of ILs is that their physical properties can be tailored by judicious selection of cations, anions, and substitutes.

Selectivities of the solutes at infinite dilution in an ionic liquid, can be calculated from the ratio of activity coefficients at infinite dilution ( $S_{ij}^\infty$ , defined according to the equation:  $S_{ij}^\infty = \gamma_{is}^\infty / \gamma_{js}^\infty$ , where subscript *s* denotes solvent). The activity coefficients at infinite dilution ( $\gamma_{i,3}^\infty$ ) of organic solutes in ionic liquids can be determined by using steady-state gas–liquid chromatography (GLC) with the ionic liquid as stationary phase [1,2]. This work is a continuation of a study on the determination of  $\gamma_{i,3}^\infty$  by GLC for functional ionic liquids. The ionic liquid, 1-octyl-3-methylimidazolium nitrate ([OMIM][NO<sub>3</sub>]), belongs to a group of weak polar ILs. In this work, we determined the activity coefficients at infinite dilution of

organic solutes in [OMIM][NO<sub>3</sub>] using GLC. The obtained data were not available in the literature.

## 2. Experimental

### 2.1. Materials

The ionic liquid 1-octyl-3-methylimidazolium nitrate [OMIM][NO<sub>3</sub>] were purchased from Shanghai Cheng Jie Chemical Co., Ltd. Its percent mass fraction purity was above 99% according to manufacturer's specifications with impurities:  $w(\text{Cl}^-) < 5 \times 10^{-4}$ . The mass fraction of water was checked to be less than  $4 \times 10^{-4}$  by Karl Fischer titration. The solutes provided by some domestic reagent companies were all analytical reagents and were used without further purification. The purities of the solutes used and their suppliers are given in Table 1. Dry nitrogen was used as the carrier gas, and dichloromethane evaporated using a rotary evaporator was used as solvent to coat the ionic liquid onto the solid support. Chromosorb W/AW-DMCS 100/120 mesh was used as solid support for the ionic liquid in the GLC column. The chemical shifts for the <sup>1</sup>H NMR spectrum (parts per million, C<sub>3</sub>D<sub>6</sub>O) appeared as follows: [OMIM][NO<sub>3</sub>],  $\delta$ : 9.462 (s, 1H, CH–N), 7.83–7.92 (d, 2H, CH=CH–N), 4.18–4.217 (t, 2H, CH<sub>2</sub>Me), 3.566 (s, 3H, CH<sub>3</sub>N), 1.711–1.744 (t, 2H, CH<sub>2</sub>N), 1.13–1.16 (m, 2H, CH<sub>2</sub>), 0.722–0.756 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>). The Chromosorb and empty GLC column were purchased from Varian Inc.

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### List of symbols

$B_{ii}$	second virial coefficient
$B_{i2}$	mixed second virial coefficient
$\overline{H}_i^{E,\infty}$	excess molar enthalpy at infinite dilution
$\overline{S}_i^{E,\infty}$	excess molar entropy at infinite dilution
$J$	pressure correction term
$K_L$	gas–liquid partition coefficient
$n_3$	the number of moles of the solvent
$\rho_3$	the density of the solvent
$P_{cij}$	critical pressure
$P_0$	the outlet pressure
$P_i$	the inlet pressure
$P_i^0$	the saturated vapor pressure of the solute
$R$	gas constant
$S_{ij}^\infty$	selectivity at infinite dilution
$V_N$	retention volume of the solute
$V_i^0$	the molar volume of the solute
$V_i^\infty$	the partial molar volume of the solute at infinite dilution
$V_{cij}$	critical volume
$U_0$	the column outlet flow rate
$t_r$	the retention time for the solute
$t_G$	the dead time
$T$	the column temperature
$T_f$	the flow meter temperature
$T_{cij}$	critical temperature
$Y$	residual function

### Greek letters

$\gamma_{i,3}^\infty$	activity coefficient at infinite dilution
$\omega_{ij}$	acentric factor
$\sigma$	standard deviation
$\delta_i$	the solute solubility parameter
$\delta_s$	the solvent solubility parameter

### Subscripts

$i,3$	solute and solvent
2	carrier gas

**Table 1**  
Supplier and purity of the chemicals used.

Solutes	Supplier	Purity (%GC)
Pentane	Tianjin Bodi	99.0
Hexane	Beijing Chemical	99.0
Heptane	Tianjin Bodi	99.0
Octane	Tianjin Bodi	99.0
Nonane	Sinopharm Chemical	98.0
Isooctane	Shantou Xilong	98.0
Cyclohexane	Shantou Xilong	98.0
Methylcyclohexane	Beijing Chemical	99.0
Benzene	Beijing Chemical	99.5
Toluene	Beijing Jinlong	99.5
Ethylbenzene	Beijing Yili	99.0
<i>o</i> -Xylene	Tianjin Chemical	98.5
<i>m</i> -Xylene	Sinopharm Chemical	95.0
<i>p</i> -Xylene	Sinopharm Chemical	99.0
Methanol	CaLledon Laboratories	99.5
ethanol	Beijing Chemical	98.0
1-Propanol	Shantou Xilong	99.0
2-Propanol	Tianjin Chemical	99.0
Acetonitrile	Tianjin Chemical	99.0
Ethyl acetate	Beijing Chemical	99.0
Acetone	Beijing Chemical	98.0
Tetrahydrofuran	Beijing Chemical	99.0
Dichloromethane	Beijing Chemical	99.5
Trichloromethane	A Tuozi Chemical	99.0
Tetrachloromethane	Tianjin Chemical	99.5

## 2.2. Apparatus and procedure

The experiments were carried out with gas–liquid chromatography (Varian CP-3800) with a thermal conductivity detector (TCD). The GC glass packed columns had a length of 1 m and internal diameter of 4 mm. Before use, the IL and the Chromosorb were subjected to vacuum evaporation at (323–333) K over 24 h to remove traces of solvents or moisture. The mass of the stationary phase (1-octyl-3-methylimidazolium nitrate) was 5.9112 g with a precision of  $\pm 0.0001$  g. To avoid possible residual adsorption effects of the solutes on Chromosorb, the mass fraction of the IL was about 60% of the support material. The column was filled uniformly with the help of an ultrasound vibrator.

The retention time  $t_r$  of each injected sample was recorded by GLC. The volume of the injected sample into the GLC probes was about (0.1–1)  $\mu$ L. The experiments were processed over a temperature range from (303.15 to 363.15) K and the carrier flow rates range from (10 to 25) mL/min. Operations at a specified temperature were repeated at least three times to check the reproducibility. The deviation of the retention time of the three measurements was all within  $\pm 0.05$  min. The value of the dead time  $t_G$  was determined with methane [3] as the non-retainable pure component under the assumption that the effect of the methane solubility in the ionic liquid was negligible. The dead time measured in the temperature range had a deviation of  $\pm 0.01$  min. The absolute values of  $(t_r - t_G)$  varied from (1 to 500) min depending on the individual solute and temperature.

## 2.3. Theoretical basis

In gas–liquid chromatography, the activity coefficient at infinite dilution  $\gamma_{i,3}^\infty$  and the gas–liquid partition coefficient  $K_L = (c_i^L/c_i^G)$  for a volatile solute ( $i$ ) partitioning between an involatile solvent (3) and a carrier gas (2) can be obtained from the following equations [3]:

$$\ln \gamma_{i,3}^\infty = \ln \left( \frac{n_3 RT}{V_N P_i^0} \right) - \frac{P_i^0 (B_{ii} - V_i^0)}{RT} + \frac{P_0 J (2B_{i2} - V_i^\infty)}{RT} \quad (1)$$

$$\ln K_L = \ln \left( \frac{V_N \rho_3}{m_3} \right) - \frac{P_0 J (2B_{i2} - V_i^\infty)}{RT} \quad (2)$$

$$V_N = J U_0 (t_r - t_G) \frac{T}{T_f} \left[ 1 - \frac{P_w^0}{P_0} \right] \quad (3)$$

where  $T$  and  $P_i^0$  are temperature of the column and the saturated vapor pressure of the pure liquid solute  $i$ , respectively;  $m_3$ ,  $\rho_3$ , and  $n_3$  are the mass, the density and the number of moles of the solvent, respectively;  $V_N$  is the standardized retention volume obtained by Eq. (3);  $t_r$  is the retention time;  $t_G$  is the dead time;  $U_0$  is the flow rate of the carrier gas, measured by a soap bubble flow meter;  $T_f$  is the flow meter temperature;  $P_w^0$  is the saturation vapor pressure of water at  $T_f$ ; and  $P_0$  is the pressure at the column outlet;  $B_{ii}$  is the second virial coefficient of the pure solute;  $B_{i2}$  is the cross second virial coefficient for the solute–carrier gas interaction;  $V_i^0$  is the liquid molar volume of the pure solute; and  $V_i^\infty$  is the partial molar volume of the solute in the ionic liquid at infinite dilution.

Values of  $P_i^0$  were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al. [4]. Molar volumes of solutes  $V_i^0$  were estimated by using their experimental densities, and partial molar volumes of solute at infinite dilution  $V_i^\infty$  were assumed to be equal to  $V_i^0$ .  $B_{ii}$  and  $B_{i2}$  were estimated according to the Tsonopolous's method [5–7]. The critical parameters needed for the calculations are available from the literature [8] and listed in Table 2. The cross critical constants  $P_{cij}$ ,  $T_{cij}$ ,  $V_{cij}$ ,  $Z_{cij}$  and acentric factor  $\omega_{ij}$  were calculated by using equations given

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