Measurement of Infinite Dilution Activity Coefficients of Alkanes in Ionic Liquid Using Gas-Liquid Chromatography

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ABSTRACT

The infinite dilution activity coefficients of octane, nonane and decane in 4-methyl-n-butylpyridinium tetrafluoroborate ($C_{10}H_{16}BF_4N$, MW=237.05) were measured by gas-liquid chromatography (GC) using the ionic liquid as stationary phase. The measurements were carried out at several temperatures between 305 and 345 K. The infinite dilution activity coefficients were affected by the flow rate of carrier gas. The infinite dilution activity coefficients were determined by extrapolating the flow rate of carrier gas to zero. The infinite dilution activity coefficients determined in this work somewhat are larger than those of the literature values because the effect of flow rate of carrier gas is not considered in the literature.

The experimental results were correlated by using the ASOG which is one of the successful group contribution activity coefficient models. The group interaction parameters were determined by using the Complex method to minimize the deviation between the experimental and calculated values. The correlated results are in good agreement with the experimental results.

Keywords: infinite dilution activity coefficient, ionic liquid, gas-liquid chromatography, ASOG

1. INTRODUCTION

Ionic liquids have received increased attention in recent years. They are particularly suitable as new solvents or electrolytes because of their low vapor pressures, high boiling points, nonflammability and existence as liquids over wide temperature range. Most works have been invested in the development of synthetic methods and applications of ionic liquids for reaction processes [1,2]. However, the thermodynamic properties of ionic liquids have not been studied systematically. Relatively few papers have been published on the liquid-liquid equilibria [3,4], the vapor-liquid equilibria [5-9] and the extraction [10] of the mixtures containing ionic liquids.

The infinite dilution activity coefficients of solutes are important for design of separation processes when the trace impurities have to be removed. In particular, reliable data of equilibria at infinite dilution are required for purifying ionic liquids by stripping process or for separation of products from ionic liquids used as reaction solvents.

The infinite dilution activity coefficients of octane, nonane and decane in 4-methyl-n-butylpyridinium tetrafluoroborate ($C_{10}H_{16}BF_4N$, MW=237.05) shown in **Fig.1** for the molecular structure were measured by gas-liquid chromatography (GC) using the ionic liquid as stationary phase. GC method is suitable for measurement of the infinite dilution activity coefficients because of a negligible vapor pressure of ionic liquids. Feasibility of the GC method and the procedure of the measurement have been investigated. The experimental results were correlated by using the ASOG which is one of the successful group contribution activity coefficient models.

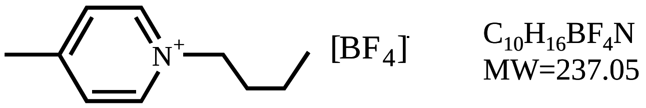
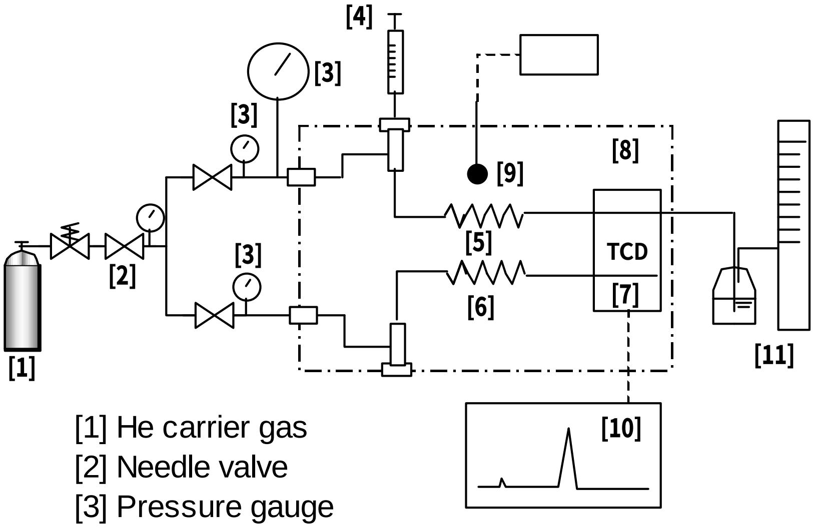


Fig.1 Molecular structure of 4-methyl-n-butylpyridinium tetrafluoroborate

2. EXPERIMENTAL

2.1 Materials

Reagent-grade octane, nonane and decane with a purity of 98 wt% and were supplied by Wako Pure Chemical Industries Co Ltd. The ionic liquid 4-methyl-n-butylpyridinium tetrafluoroborate was supplied by Merck. Chromosorb W AW DMCS (mesh 100/120) was supplied by GL Science Inc. Japan and was used as the support material for the ionic liquid in the GC column.



[1] He carrier gas
[2] Needle valve
[3] Pressure gauge
[4] Micro syringe
[5] Column
[6] Reference column
[7] TCD detector
[8] Column Oven
[9] Thermocouple
[10] Recorder
[11] Buble flow meter

Fig.2 Schematic diagram of experimental apparatus

2.2 Apparatus and Procedure

The schematic diagram of the experimental apparatus is shown in **Fig.2**. The solvent dichloromethane was used to coat the ionic liquid onto the solid support. Chromosorb 3.56 g was dispersed in the solution of the ionic liquid 1.84 g and dichloromethane. The mixture was evaporated by using a vacuum pump to remove dichloromethane. The coated solid support was introduced into a stainless steel column (3 mm I.D. x 2 m Length, 304SS) with help of a vibrator in order to provide uniform packing. The experiments were performed by a gas-liquid chromatography (Shimazu GC-14B) with a thermal conductivity detector (TCD), a recorder (Shimazu C-R3A) and a low temperature control unit (Shimazu CRG-15). Helium was used as carrier gas. The flow rate of carrier gas U was determined using a soap bubble flowmeter. The hydrocarbons were injected into the GC with air using a micro syringe. Air was assumed to be a nonretentional component because the solubility of air in 4-methyl-n-butylpyridinium tetrafluoroborate is very low. The retention times were measured by the TCD.

The standardized retention volume V_N can be obtained by [11]

$$V_{\mathrm{N}} = JU(t_{\mathrm{R}} - t_{\mathrm{G}})\frac{T_{\mathrm{col}}}{T_{\mathrm{f}}}\left[1 - \frac{p_{\mathrm{w}}^{\mathrm{o}}}{p_{\mathrm{out}}}\right] \quad (1)$$

where T_{col} and T_{f} are the column and the flowmeter temperatures, respectively. t_{R} and t_{G} are the retention times of solute and air, respectively. $p^{\mathrm{o}}_{\mathrm{w}}$ and p_{out} are the saturation pressure of water at T_{f} and the pressure of column outlet, respectively. The factor J to correct the influence of the pressure drop along the column is given by [11]

$$J = \frac{3}{2}\frac{(p_{\mathrm{in}}/p_{\mathrm{out}})^2 - 1}{(p_{\mathrm{in}}/p_{\mathrm{out}})^3 - 1} \quad (2)$$

where p_{in} is the inlet pressure of the GC column.

According to Cruickshank et al. [12], the infinite dilution activity coefficient γ_1^{∞} is derived from the standardized retention volume V_{N} as follows:

$$\ln\gamma_1^{\infty} = \ln\left(\frac{n_2 R T_{\mathrm{col}}}{V_{\mathrm{N}} p_1^{\mathrm{o}}}\right) - \frac{B_{11} - V_1^{\mathrm{o}}}{RT_{\mathrm{col}}} p_1^{\mathrm{o}} + \frac{2B_{13} - V_1^{\infty}}{RT_{\mathrm{col}}} J p_{\mathrm{out}} \quad (3)$$

where n_2 is the amount of substance for the ionic liquid (subscript 2) used as the stationary phase in the column. R is the gas constant. p_1^{o} is the vapor pressure of the pure solute (subscript 1). The second and third terms in equation (3) are the correction terms for the nonideality of the solute and the carrier gas (subscript 3). B_{11} is the second virial coefficient of the pure solute, B_{13} is the cross virial coefficient between the solute and the carrier gas. V_1^{o} is the liquid molar volume of the pure solute, and V_1^{∞} is the partial molar volume of solute in the ionic liquid at infinite dilution.

The liquid molar volumes of the pure solutes V_1^{o} were estimated using the densities of pure solutes given in the literature [13]. The partial molar volumes of solutes in the ionic liquid at infinite dilution V_1^{∞} were assumed to be equal to V_1^{o}. B_{11} were calculated using the method of Tsonopolous [14]. The critical properties needed for the calculation of B_{11} were cited from the literature [14]. The values of B_{13} were also calculated using the method of Tsonopolous. The properties $P_{\mathrm{c}ij}$, $T_{\mathrm{c}ij}$, $V_{\mathrm{c}ij}$, $Z_{\mathrm{c}ij}$ and ω_{ij} were calculated by using the equations given in the literature [14]

2.3. Results and Discussion

The measurements were carried out at 5 temperatures between 305 and 345 K. The temperature of the GC column oven was maintained within ±0.04 K. At a given temperature, each experiment was repeated five times to check the reproducibility. The volumes of the solute samples injected into the GC were from 0.02 to 1 μL. As shown in **Fig.3**, the retention times were affected by the volume of samples. The sample volumes were adjusted to be less than 0.5 μL, in which region the retention times were independent of the sample sizes, to keep the condition of infinite dilution. The flow rate of carrier gas was adjusted to be $(0.5\text{-}5)\times10^{-7}$ $m^3\cdot s^{-1}$ and the pressure drop of the column was in 0.2-0.8 MPa consequently. As shown in **Fig.4** the infinite dilution activity coefficients were also affected by the flow rate of carrier gas. It is considered that the diffusivity of the solute in the ionic liquid is so small that equilibrium condition was not achieved at finite flow rate conditions. The infinite dilution activity coefficients were determined by extrapolating the flow rate of carrier gas to zero. The values of the infinite dilution activity coefficients of different solutes (octane, nonane and decane) in 4-methyl-n-butylpyridinium tetrafluoroborate obtained at different temperature are listed in **Table 1** and are shown in **Figs.5-7**. The values of γ_1^{∞} determined in this work follow the same trend as the values obtained by Heintz and co-workers [8]. However, the values of γ_1^{∞} determined in this work are larger, as shown in **Figs. 5-7**, than those of the literature values, because the values were not determined by extrapolating the flow

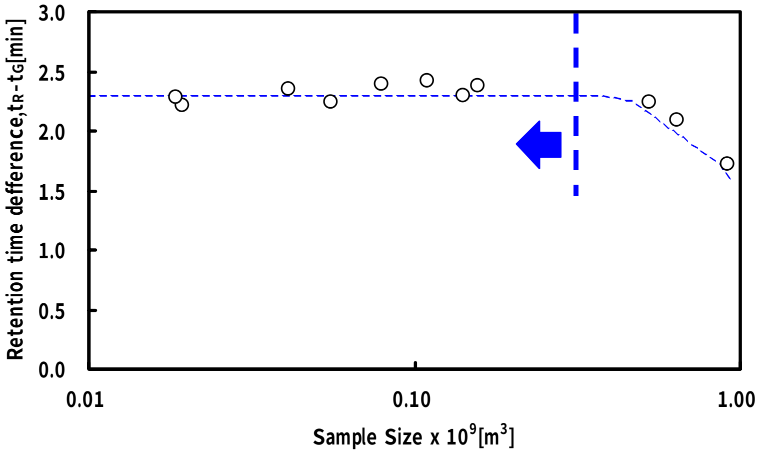


Fig.3. Sample size effect on retention time difference t_R-t_G of octane in 4-methyl-n-butyl pyridinium tetrafluoroborate at 335K.

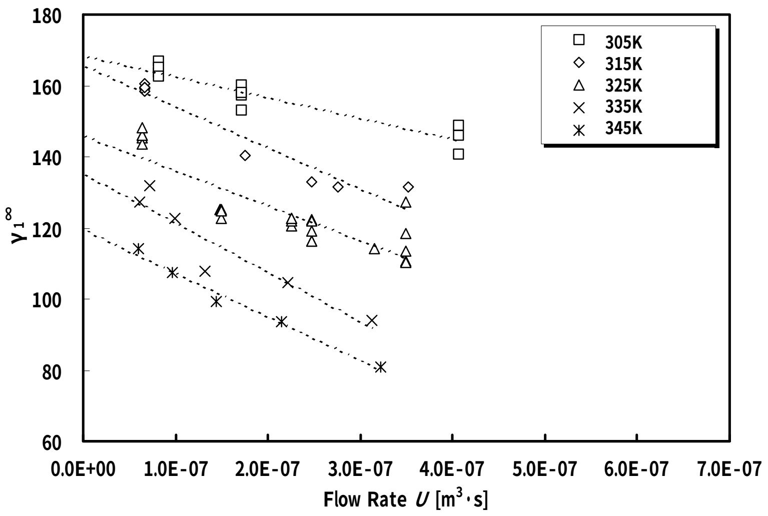


Fig.4. Effect of flow rate of carrier gas on γ_1^{∞} of octane in 4-methyl-n-butyl pyridinium tetrafluoroborate.

rate of carrier gas in the literature.

Table 1. Infinite dilution activity coefficients of octane, nonane and decane in 4-methyl-n-butylpyridinium tetrafluoroborate at 305 – 345 K

Solute	305 K	315 K	325 K	335 K	345 K
Octane	168.5 (306.6)*	166.0 (315.9)	145.9 (325.3)	135.7 (34.7)	119.6 (344.1)
Nonane	274.0 (306.6)	252.0 (316.0)	234.0 (325.3)	209.1 (334.8)	193.2 (344.2)
Decane	423.8 (306.6)	392.2 (316.0)	390.4 (325.4)	309.3 (334.8)	294.3 (344.2)

*Measured experimental temperatures are given in parentheses.

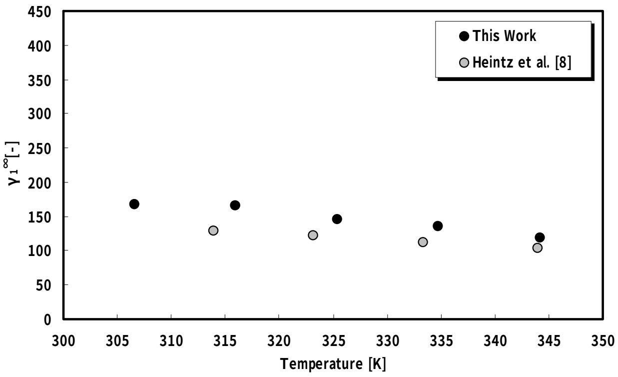


Fig.5. Infinite dilution activity coefficient of octane in 4-methyl-n-butyl pyridinium tetrafluoroborate.

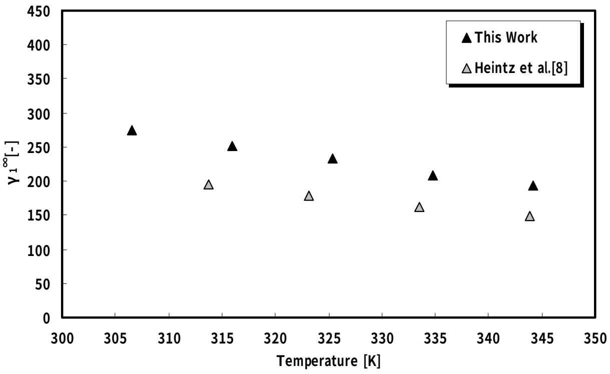


Fig.6. Infinite dilution activity coefficient of nonane in 4-methyl-n-butyl pyridinium tetrafluoroborate.

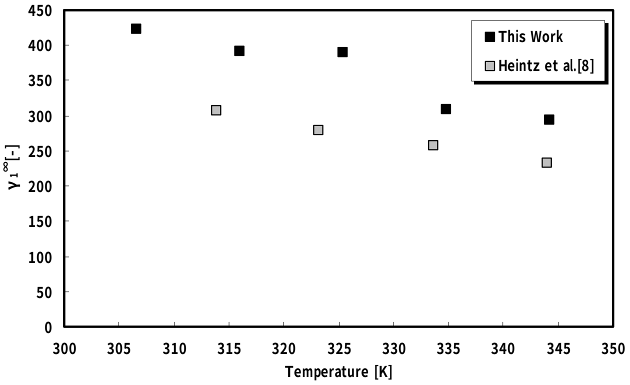


Fig.7. Infinite dilution activity coefficients of decane in 4-methyl-n-butylpyridinium tetrafluoroborate.

3. CORRELATION

The experimental results were correlated by using the ASOG [15] which is one of the successful group contribution activity coefficient models. The activity coefficient of component *i* is given by equations (4) to (9).

$$\ln\gamma_i = \ln\gamma_i^{\mathrm{FH}} + \ln\gamma_i^{\mathrm{G}} \tag{4}$$

$$\ln\gamma_i^{\mathrm{FH}} = \ln\frac{\nu_i^{\mathrm{FH}}}{\sum_j \nu_j^{\mathrm{FH}} x_j} + 1 - \frac{\nu_i^{\mathrm{FH}}}{\sum_j \nu_j^{\mathrm{FH}} x_j} \tag{5}$$

$$\ln\gamma_i^{\mathrm{G}} = \sum_k \nu_{k,i}(\ln\Gamma_k - \Gamma_k^{(i)}) \tag{6}$$

$$\ln\Gamma_k = -\ln\sum_p X_p a_{k,p} + 1 - \sum_p \frac{X_p a_{p,k}}{\sum_m X_m a_{p,m}} \tag{7}$$

$$X_k = \frac{\sum_i x_i \nu_{k,i}}{\sum_i x_i \sum_l \nu_{l,i}} \tag{8}$$

$$\ln a_{k,p} = m_{k,p} + n_{k,p}/T \tag{9}$$

where γ_i, γ_i^{FH} and γ_i^{G} are the activity coefficient of component *i*, the size contribution term and the group contribution term, respectively. ν_i^{FH} is the number of atoms except for hydrogen atoms in molecule *i*, $\nu_{k,i}$ is the number of atoms except for hydrogen atoms in group *k* of molecule *i*. X_k and x_i are the group mole fraction of group *k* and the mole fraction of component *i* in liquid phase, respectively. Γ_k and $\Gamma_k^{(i)}$ are the group activity coefficient of group *k* and the group activity coefficient of group *k* in pure component *i*. $a_{k,p}$ is the group Wilson parameter depends on temperature. $m_{k,p}$ and $n_{k,p}$ are the group interaction parameter depend on only the kind of group pairs. In general ionic liquids reported in recent researches consist of the limited kinds of cations and anions. For example, most of the cations are based on imidazolium or pyridinium, and the anions are also limited to few kinds ($[\mathrm{Cl}]^-$, $[\mathrm{BF_4}]^-$, $[\mathrm{PF_6}]^-$, $[\mathrm{Tf_6N}]^-$). The ASOG is one of the suitable methods for the ionic liquids to express the interaction between hydrocarbons because the activity coefficients can be calculated from the limited group pairs. In this case, three groups are considered and 12 group interaction parameters are needed.

The group interaction parameters were determined by using the Complex method to minimize the deviation between the experimental and calculated values. The objective function F_{obj} used was as follows:

$$F_{\mathrm{obj}} = \sum_i^N ((\gamma_{i,\mathrm{exp}}^{\infty} - \gamma_{i,\mathrm{calc}}^{\infty})/\gamma_{i,\mathrm{exp}}^{\infty})^2 \tag{10}$$

The values of the parameters are listed in **Table 2**. As shown in **Fig.8**, the correlated results are in good agreement with the experimental results.

Table 2. Group interaction parameters for ASOG

k	CH_2		Pyridinium		BF_4	
P	m	n	m	n	m	n
CH_2	0	0	1.21	−494.44	−3.18	356.14
Pyridinium	2.18	−0.01	0	0	3.00	−1.04
BF_4	−20.00	0.00	−20.00	0.00	0	0

4. CONCLUSIONS

The infinite dilution activity coefficients of octane, nonane and decane in 4-methyl-n-butylpyridinium tetrafluoroborate were measured by GC in 305-345 K. The values of the infinite dilution activity coefficients were affected by the sample size of solutes and the flow rate of carrier gas. Therefore, they were determined to satisfy the infinite dilution condition. Moreover, the ASOG group interaction parameters were determined to correlate the present data. The correlated results are in good agreement with the experimental results.

LIST OF SYNBOLS

a : *group Wilson parameter*
B_{11} : *second virial coefficient of the pure solute*
B_{13} : *cross virial coefficient of the solute and the carrier gas*
F_{obj} :*objective function*
J :*J factor*
m, n : *group interaction parameter*
n_2 : *amount of substance for the ionic liquid*
p : *pressure*
p_1^{o} : *vapor pressure of the pure solutes*
$p_{\mathrm{w}}^{\mathrm{o}}$: *saturation pressure of water at flow meter temperature*
P_{c} :*critical pressure*
R :*gas constant*
T : *temperature*
T_{c} :*critical temperature*
t_{G} :*retention time of air*
t_{R} :*retention time of the solutes*
U :*flow rate of carrier gas*
V_{c} :*critical volume*
V_{N} : *standardized retention volume*
V_1^{o} : *liquid molar volume of the pure solute*
V_1^{∞} : *partial molar volume of solute in the ionic liquid at infinite dilution*
X : *group mole fraction*
Z_{c} :*critical compressibility factor*

x *: mole fraction in liquid phase*
Γ *: group activity coefficient*
γ *: activity coefficient*
ν *: number of atoms except for hydrogen atoms*
ω_c *:acentric factor*
<Subscript>
calc *:calculated*
col *:column*
exp *:experimental*
f *:flow meter*
i, j *:component i, j*
in *:inlet of GC column*
k, p, m *:group k, p, m*
out *:outlet of GC column*
<Superscript>
FH *:size contribution*
G *:group contribution*
(i) *:standard state (pure component i)*
∞ *:infinite dilution*

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