

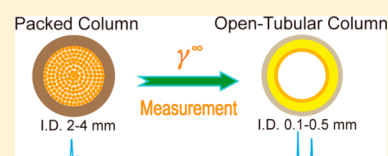
Accurate Measurements of Infinite Dilution Activity Coefficients Using Gas Chromatography with Static-Wall-Coated Open-Tubular Columns

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S Supporting Information

ABSTRACT: Wall-coated open-tubular (WCOT) columns provide higher column efficiency and lower solute interfacial adsorption effect than packed columns. However, previous efforts used to measure the infinite dilution activity coefficient (γ^∞) via a chromatographic technique have used packed columns, because the low carrier gas flow rate (U) and the small stationary phase amount (n_2) in WCOT columns raise large errors. By rationally revising the γ^∞ -calculation equation for static-wall-coated open-tubular column, we observed that U and n_2 are not necessarily needed and the resulting error could be reduced, and WCOT column gas chromatography subsequently became a superior method for the accurate γ^∞ determination. In this study, we validate our revised γ^∞ -calculation equation by measuring γ^∞ in an ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate system, in which 55 organic compounds covering a wide range of functional groups were used as probe solutes and their γ^∞ values in the ionic liquid were determined at 40.0, 50.0, and 60.0 °C. Experimental error analysis shows that our revised equation remarkably reduces the error compared to the common γ^∞ -calculation equation. Our data is consistent with previously reported values obtained via other techniques, which further proves the credibility of our revised equation. The accurately determined γ^∞ values can be directly used to calculate the partial molar excess enthalpy, selectivity, and capacity, which will benefit for the rapid screening of solvents (especially ionic liquids) in separation approaches.



In selection of solvents for extraction and extractive distillation processes, knowledge of the infinite dilution activity coefficient (γ^∞) is very important and useful. The γ^∞ is also very helpful in the calculation of the Henry constants and partition coefficients, estimation of mutual solubilities, predicting the existence of an azeotrope, and development of thermodynamic models.^{1,2} Several methods, e.g., the ebulliometry method, static method, dilutor method, liquid–liquid chromatography, gas–liquid chromatography (GLC), and headspace GLC, have been developed to measure γ^∞ .¹ GLC is a rapid and accurate method and is the most extensively used, in which the solvent used as the stationary phase (SP) is most commonly a nonvolatile liquid.^{1,3} Two general types of columns are usually used in GLC, i.e., packed columns and wall-coated open-tubular (WCOT) columns. WCOT column gas chromatography (we adopted “WGC” as an abbreviation for convenience) has several advantages over packed column gas chromatography (PGC) for γ^∞ measurement. Contrary to the tortuous and intricate geometry of porous solid supports in packed beds, geometrical simplicity in WCOT columns allows more uniform films which would minimize the contribution to peak broadening due to the delay of mass transfer at the SP, yielding very high column efficiencies.⁴ WCOT columns offer lower SP surface-to-volume ratio than packed ones, which would reduce solute adsorption on the SP.⁵ Moreover, split injection is often employed in WGC for attaining infinite dilution condition and turning negligible the extracolumn time.

In PGC, where split injection is not generally applied, the extracolumn time in the injector is 1 order higher and infinite dilution is achieved only through careful regulation of the injected quantity.⁴

Despite the advantages of WGC, PGC is still the dominant method in the γ^∞ determination, due to the difficulty in quantifying the very small values of SP amount and carrier gas flow rate in WGC.^{5–10} Only a few published papers used WGC in γ^∞ determination, in which the carrier gas flow rates were generally measured by gas flow meter and might suffer from large errors.^{11–15} In order to determine the SP amount in WCOT columns, some researchers suggested an indirect calculating method.^{11,12} They assumed the specific retention volume (V_g) of any component (e.g., n -alkanes) on a certain SP was independent with the applied column type; then the amount of SP in a WCOT column could be calculated by backward induction from the SP amount in a packed column. However, the V_g values result from the combination of adsorption and partition processes. Adsorption in different column types is quite different because they offer different SP surface-to-volume ratios. Hence, the assumption is true only when the adsorption is negligible for the selected solutes in

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both columns, which needs further inspection. Moreover, implementing such a complicated procedure is not only troublesome but also inaccurate. Some other researchers increased the SP amount to improve the measurement accuracy.^{13–15} However, thick films are more likely to cause SP loss due to the continuous flowing of carrier gas. In a very recent research, Rosenboom et al. have determined γ^∞ for some organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium acetate by both WGC and PGC. They used the weighing method to determine the SP amount since their WCOT column had a thick SP film (2.63 μm).¹⁶ Therefore, current SP amount and carrier gas flow rate determining methods in WGC are still unsatisfying and WGC is not popularly accepted in the determination of γ^∞ .

Inspired by Lebron-Aguilar et al., who had proposed a mathematically revised equation for specific retention volume in static-wall-coated open-tubular column,⁹ we present a revised equation for accurate measurement of γ^∞ in the same kind of column, in which the SP amount and carrier gas flow rate are not necessarily needed so that the difficulties in determining them are avoided and the corresponding errors are reduced. We measured γ^∞ in an organic solute–ionic liquid WGC system to validate this equation. Ionic liquid (IL) was used as SP because of its extremely low vapor pressure, high viscosity, and high thermal stability.¹⁷ Also, ILs are considered as promising substitutes for traditional volatile solvents, and hence, their thermodynamic properties with organic solvents are crucial to their application. The γ^∞ of organic solvents in some ILs have been studied over the past decade via PGC.^{18–26} On the basis of the work of Armstrong and co-workers, static-wall-coated open-tubular IL columns could be self-made in laboratories.^{27–30} All Supelco commercial IL columns are based on the work of Armstrong and co-workers. The simple static-coating technique of ILs further promoted us to determine γ^∞ in ILs by WGC. The IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), whose γ^∞ values have already been determined,^{20,31,32} was chosen for the data comparison.

This study was aimed to validate our revised γ^∞ -calculation equation and test whether the revised equation could effectively reduce errors which occurred when the common γ^∞ -calculation equation was used. Apart from determining γ^∞ , influence of solute adsorption on WCOT columns was also examined. We adopted the concurrent retention mechanism with four [bmim][PF₆] WCOT columns of different SP loadings. This mechanism has not yet been studied for [bmim][PF₆].

THEORY AND CALCULATIONS

Revision of the γ^∞ -Calculation Equation for the GLC Method Using Static-Wall-Coated Open-Tubular Columns. The γ^∞ -calculation equation developed by Everett³³ appears as follows:

$$\ln \gamma_{1,2}^\infty = \ln \left(\frac{n_2 RT}{V_N p_1^0} \right) - p_1^0 \frac{(B_{11} - V_1^0)}{RT} + \frac{(2B_{13} - V_1^\infty)}{RT} \frac{p_0}{J} \quad (1)$$

where $\gamma_{1,2}^\infty$ is the infinite dilution activity coefficient of solute (index 1) in the SP (index 2), V_N is the net retention volume of solute, n_2 is the mole amount of SP inside the column, p_1^0 is the solute vapor pressure, B_{11} is the second virial coefficient of pure solute, B_{13} is the mixed virial coefficient of solute with carrier gas (index 3), V_1^0 is the solute molar volume, V_1^∞ is the solute partial molar volume in the SP at infinite dilution, R is the ideal

gas constant, and T is the column temperature. The pressure correction term J is given by

$$J = \frac{3 \left(\frac{p_i}{p_0} \right)^2 - 1}{2 \left(\frac{p_i}{p_0} \right)^3 - 1} \quad (2)$$

where p_i and p_0 are the inlet and outlet pressures, respectively.

According to eq 1, n_2 and the flow rate of the carrier gas in the column (U , $U = V_N/t'_R$, where t'_R is the adjusted retention time of solute) must be precisely measured. Actually, n_2 is difficult to be measured even in PGC (weighing after extraction usually)⁶ and is the biggest uncertainty for γ^∞ determination. Most often, a soap-bubble flow meter is used at the column outlet of PGC to measure the wet carrier gas flow rate saturated with water vapor at ambient temperature and pressure. This flow rate needs to be corrected for water vapor, ambient temperature, and pressure to get the value of U . When WCOT columns are used, both parameters are very small and the uncertainties increase significantly.

When the static coating method is used to prepare a WCOT column, the SP amount can be calculated by the concentration of SP solution (used to prepare the column) and the column inner volume since all the SP that is put into the column stays in during the static coating procedure. The n_2 and U can be expressed as follows:

$$n_2 = \frac{W_S}{M} = \frac{c \pi d_i^2}{4M} \quad (3)$$

$$V_N = t'_R U = t'_R \frac{V_M}{t_M} = t'_R \frac{l \pi (d_i - 2d_f)^2}{4t_M} = \frac{k l \pi (d_i - 2d_f)^2}{4} \quad (4)$$

where W_S is the mass of SP in WCOT column, M is the molecular weight of the SP, c is the concentration of SP solution used to prepare the column, l is the column length, d_i is the inner diameter of the pretreated column, d_f is the film thickness of the SP, V_M is the hold-up volume, t_M is the hold-up time, and k is the retention factor. The SP film thickness could be expressed as a function of W_S , the density of SP (ρ), and the internal surface of the column (πd_i) since $d_f \ll d_i$:

$$d_f = \frac{W_S}{\rho \pi d_i} = \frac{c \pi d_i^2}{4 \rho \pi d_i} = \frac{cd_i}{4\rho} \quad (5)$$

Combining eqs 3, 4, and 5, the first item in eq 1 may be rewritten as

$$\frac{n_2 RT}{V_N p_1^0} = \frac{c RT}{k M p_1^0 \left(1 - \frac{c}{2\rho} \right)^2} \quad (6)$$

Similar deduction has been used for the calculation of specific retention volume by Lebron-Aguilar et al. years ago.⁹ Equation 1 could be rewritten as

$$\ln \gamma_{1,2}^\infty = \ln \left(\frac{c RT}{k M p_1^0 \left(1 - \frac{c}{2\rho} \right)^2} \right) - p_1^0 \frac{(B_{11} - V_1^0)}{RT} + \frac{(2B_{13} - V_1^\infty)}{RT} \frac{p_0}{J} \quad (7)$$

Equation 7 is our revised γ^∞ -calculation equation for the GLC method using a static-wall-coated open-tubular column

without need of SP amount and carrier gas flow rate. The values of c , k , T , p_0 , and J can be accurately determined from each experiment. The thermodynamic parameters involved in the calculation of γ^∞ are given in the Supporting Information (Table S-1).

It should be pointed out that the experimentally measured hold-up time (the gross hold-up time) included the extracolumn time t_{ext}^{34} and should be corrected by multiplying a correction factor f [$f = t_M/(t_M + t_{\text{ext}}) = V_M/(V_M + V_{\text{ext}})$, V_{ext} is the extracolumn volume]. We measured the extracolumn volume (Supporting Information, p S-6) of our gas chromatograph (0.016 cm³), and f is 0.98, very close to 1. Indeed, the extracolumn volume is negligible in the modern WGC with a flame ionization detector (FID) since the column directly enters the injector and detector and reasonable streams of gas sweep the injector and detector.³⁴

Concurrent Retention Mechanism. According to Conder et al., retention which combines partition and interfacial adsorption can be expressed as follows:³⁵

$$V_N = V_L K_L + A_{GL} K_{GL} + A_{LS} K_{GLS} \quad (8)$$

where V_N is the net retention volume which is the same as in eq 1, V_L is the volume of SP, and A_{GL} and A_{LS} are the gas–liquid and liquid–solid interfacial areas, respectively. The partition coefficients K_L , K_{GL} , and K_{GLS} correspond to dissolution in the SP and to adsorption at the gas–liquid and liquid–solid interfaces, respectively. Equation 8 can be rewritten as eq 9:

$$V_N/V_L = K_L + A_{GL} K_{GL}/V_L + A_{LS} K_{GLS}/V_L \quad (9)$$

The contributions of partition and adsorption to retention can be separated by a phase loading study. The partition coefficient K_L can be obtained from extrapolation of V_N/V_L against $1/V_L$.³⁵ The real γ^∞ value eliminating the influence of adsorption can be calculated from K_L :

$$\ln \gamma_{1,2}^\infty = \ln \left(\frac{\rho RT}{K_L M p_1^0} \right) - p_1^0 \frac{(B_{11} - V_1^0)}{RT} + \frac{(2B_{13} - V_1^\infty)}{RT} \frac{p_0}{J} \quad (10)$$

Some researchers have adopted this procedure for the measurements of γ^∞ in PGC.^{18,36,37} Conder et al. suggested that the phase loading should be higher than 5–10% in PGC to ensure that a bulk liquid phase is actually presented on the solid support. Although WCOT columns offer significant lower SP surface-to-volume ratio than packed columns, they could only minimize but unlikely eliminate the interfacial adsorption. This procedure is also applicable in WGC. Since the precise length of a WCOT column is hard to be determined, the quantities V_N , V_L , A_{GL} , and A_{LS} in eq 9 could be all expressed in per unit length of column. Therefore, V_N/V_L remains the same, and $1/V_L$ becomes l/V_L . The calculation of V_N/V_L and l/V_L in a static-wall-coated open-tubular column and an example plot of V_N/V_L versus l/V_L are illustrated in the Supporting Information (Figure S-1).

Other Thermodynamic Properties. The infinite dilution partial molar excess enthalpy ($h_1^{E,\infty}$) could be calculated according to the Gibbs–Helmholtz equation using the temperature dependence of the real γ^∞ value:

$$\frac{\partial \ln \gamma^\infty}{\partial (1/T)} = \frac{h_1^{E,\infty}}{R} \quad (11)$$

The infinite dilution selectivity and capacity which indicate the suitability of a solvent for separating mixtures of component i and j by extraction or extractive distillation are given by³⁸

$$S_{i,j}^\infty = \frac{\gamma_i^\infty}{\gamma_j^\infty} \quad (12)$$

$$k_i^\infty = \frac{1}{\gamma_i^\infty} \quad (13)$$

■ EXPERIMENTAL SECTION

Materials and Chemicals. The fused-silica capillary tubing (0.25 mm i.d.) used for preparing WCOT column was obtained from Lanzhou ZhongKeKaiDi Chemical New-tech Co., Ltd. (China). [bmim][PF₆] (99%) was purchased from Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (China). Prior to the use for column preparation, [bmim][PF₆] was dried under vacuum at room temperature for several days to remove trace moisture. The water content of the IL, as determined by Karl Fischer titration, was less than 100 ppm. All the test solutes were purchased from Shanghai Aladdin Reagent Co., Ltd. (China) or Sigma-Aldrich and used without further purification.

WCOT Column Preparation. Due to the poor wettability of untreated silica with [bmim][PF₆], it is necessary to improve the adhesion of the capillary wall. Before coating, fused-silica capillary tubing was subjected to a sodium chloride pretreatment.^{39,40} A suspension of NaCl in methanol–dichloromethane mixture was passed through the capillary at a constant velocity (around 3 cm/s) by nitrogen pressure for 4 h, leaving NaCl deposited on the inner wall. Then the capillary was emptied and dried by a nitrogen flow at a constant velocity (around 1 cm/s) and coated by the static method.^{39,41} The pretreated capillary was filled with a degassed [bmim][PF₆]–dichloromethane solution in an appropriate concentration. To seal the column end, epoxy adhesive was used. To prevent the possible dissolving of epoxy in the SP solution, a short plug of deionized water was sucked in before the suction of epoxy. The adhesive requires about 5–10 min to harden, after which the column was placed in an air thermostat bath at 30.0 °C. Dichloromethane was slowly evaporated under vacuum applied to the other end for about 12 h. Coated columns were conditioned with helium from 30.0 to 100.0 °C at 0.5 °C/min overnight. Four columns with different film thicknesses of [bmim][PF₆] were prepared, and their parameters are given in Table 1.

Apparatus and Experimental Procedure. The measurements were carried out using a Shimadzu GC-2010 gas chromatograph. Split injection and FID were utilized and held at 250.0 °C. Helium was used as carrier gas, and its flow rates

Table 1. Specifications of Static-Wall-Coated Open-Tubular [bmim][PF₆] Columns

column no.	1	2	3	4
capillary tube i.d. (mm)	0.25	0.25	0.25	0.25
column length l (m)	15.00	15.00	15.00	15.00
[bmim][PF ₆] solution concn c (mg/mL)	2.24	3.32	5.54	10.98
column film thickness d_f at 30.0 °C (μm)	0.10	0.15	0.25	0.50
column efficiency (plates/m) ^a	1300	1100	1600	800

^aColumn efficiencies were tested with naphthalene at 100.0 °C.

were adjusted to obtain suitable retention times. The hold-up time (t_M) was estimated by a zero carbon atom alkane method where the retention times for n -alkanes including methane were measured.^{34,42,43}

$$t_R(n) = A + \exp(B + Cn^D) \quad (14)$$

where n is the carbon number of the n -alkane, $t_R(n)$ is the retention time of the n -alkane, and A , B , C , and D are the nonlinear regression parameters. The hold-up time t_M is obtained for a value of n equals zero. Since t_M determined by eq 14 was almost consistent with the values directly determined by methane, methane was injected together with each sample to determine the hold-up time. In order to approach infinite dilution, a small volume (0.005 μ L) of solute–dichloromethane solution (10%, v/v) was injected at a high split ratio (100:1). Solute injected directly or injected in dichloromethane solutions showed no noticeable retention time difference. All solutes were injected individually by a 0.5 μ L syringe (0.005 μ L diluted solution completing up to 0.5 μ L with methane).

The temperature of the column was controlled to within 0.1 °C. The outlet pressure p_o was kept equal to the ambient pressure and measured by a mercury barometer. The pressure at the inlet of the column p_i was measured by a pressure sensor. The column inlet pressure was controlled to within 0.1 kPa and ambient pressure 0.4 kPa. At least three injections were made for each solute, and retention times were reproducible to within 0.03 min. Relative standard deviations for measured γ^∞ values were less than 2%, reflecting good repeatability of our experimental data. The retention times for n -octane, benzene, and 1-nitropropane (retention time short, medium, and long) were measured at 40.0 °C every day during the γ^∞ measurements, and no noticeable changes were observed. It confirmed the stability of our experimental conditions and showed no SP loss by the helium stream.

RESULTS AND DISCUSSION

Influence of Concurrent Retention Mechanism in WGC. In order to correct for interfacial adsorption, four static-wall-coated open-tubular [bmim][PF₆] columns with different film thicknesses (Table 1) were used. Actually, extrapolation of V_N/V_L against $1/V_L$ is a slightly curved plot since interfacial area is a function of V_L .³⁵ But in most WCOT columns where SP film thickness is several orders of magnitude smaller than the column i.d., the interfacial area differences are very small between columns with different film thicknesses. For the four columns we used, the differences are within 0.3%. Taking into account that nonlinear extrapolation may be subject to human prejudice, linear extrapolation may better be used here. However, interfacial areas may vary with different phase loadings in packed columns due to the irregular geometry of the porous solid supports. Therefore, linear extrapolation is more suitable for WGC. The values of uncorrected and corrected γ^∞ together with values of K_L are presented in the Supporting Information (Table S-2).

The error for calculated γ^∞ value from our revised equation (eq 7) may be obtained from the propagation law of errors (detailed in the Supporting Information, pp S-11–S-12).⁴⁴ The estimated error limits for c , k , and T were 0.2%, 2%, and 0.3%, respectively. Taking into account that thermodynamic parameters p_1^0 and ρ were also subject to an error, the resulting error in the γ^∞ value was around 3%. If the common γ^∞ -calculation equation was used, n_2 and U should be measured. After all γ^∞

measurements were completed, the coated SP was washed out by a large volume of methanol and n_2 was analytically obtained by a UV spectrometer. The error limit of n_2 was about 2%. The values of U were at a range of 0.5–1.5 mL/min, measured by a soap bubble flow meter and corrected for water vapor, ambient temperature, and ambient pressure. The error limit of U was about 6% at 0.5 mL/min. The error limits of t'_R and T were 0.5% and 0.3%, respectively. Consequently, the resulting error in the γ^∞ value calculated by the common γ^∞ -calculation equation was about 7%. Therefore, our revised equation for WGC not only avoids the complex measurement procedure of n_2 and U but also remarkably reduces the error in the γ^∞ determination.

The relative contribution from interfacial adsorption could be obtained from the experimental value of V_N and the calculated value of V_N . Since [bmim][PF₆] is ionic, its adsorption on the pretreated capillary inner wall (NaCl) is strong enough for solutes to compete. In this case, the liquid–solid adsorption may be negligible and interfacial adsorption mostly occurs on the gas–liquid interfacial surface. The relative percent contributions of interfacial adsorption to retention for four [bmim][PF₆] WCOT columns at 40.0 °C are presented in the Supporting Information (Table S-3). As expected, increasing film thickness effectively reduces adsorption contribution. Alkanes exhibit the strongest interfacial adsorption compared to other solutes. Their adsorption contribution can reach 60% with the 0.10 μ m [bmim][PF₆] column. The strong interfacial adsorption contribution of alkanes in [bmim][PF₆] may be attributed to the specific physicochemical behavior of alkanes in IL, which had been investigated by Berthod et al.⁴⁵ Alkanes tend to adhere to one another in an IL (the hydrophobic effect), thereby changing the local ordering of the IL, that is analogous to the effect found in dilute aqueous solutions of certain nonelectrolytes. Cycloalkanes, alkenes, and alcohols also show relatively strong interfacial adsorption. Unfortunately, we were unable to compare the adsorption contributions in WGC with those in PGC since the concurrent retention mechanism had not yet been studied for [bmim][PF₆] packed columns. However, we could speculate that the adsorption contributions in PGC were higher than ours as WCOT columns offer significant lower SP surface-to-volume ratio.

Infinite Dilution Activity Coefficients and Partial Molar Excess Enthalpies. We compared our γ^∞ values (Table S-2, Supporting Information) and our $h_1^{E,\infty}$ values (Table S-4, Supporting Information) with previously reported data. Mutelet et al. measured γ^∞ values for plenty of solutes in [bmim][PF₆] by PGC without correction for interfacial adsorption.²⁰ The γ^∞ values for solutes retained largely by adsorption (such as alkanes, cycloalkanes, and alkenes) may be inappropriate for comparison. We only compared the γ^∞ values for solutes with less adsorption contributions (Table 2), and the average deviations are within experimental error. The γ^∞ values for alcohols were also reported by other groups by the dilutor method³¹ or PGC.³² Their γ^∞ values in Table 3 together with ours showed rather good agreement. In order to further validate our data, the values of $h_1^{E,\infty}$ for alcohols are compared in Table 4. The agreement of our $h_1^{E,\infty}$ values with those obtained by eq 11 and especially those obtained by the direct calorimetric method⁴⁶ (except for Mutelet et al.'s) justifies the reliability of our data and further demonstrates the credibility of our revised equation.

Table 2. Comparison of Our γ^∞ Values with Those Obtained by PGC^a

solutes	γ^∞					
	40.0 °C		50.0 °C		60.0 °C	
	ref 20	this work	ref 20	this work	ref 20	this work
1-hexyne	6.00	5.84	5.52	5.83	6.11	5.77
1-heptyne	8.62	9.09	9.49	8.85	9.41	8.59
benzene	1.82	1.86	1.96	1.88	2.13	1.89
toluene	2.97	2.90	3.09	2.93	3.37	2.97
ethylbenzene	4.81	5.05	5.26	5.00	5.70	4.93
<i>o</i> -xylene	3.91	3.90	4.20	3.91	4.58	3.93
<i>m</i> -xylene	4.80	4.77	5.17	4.78	5.51	4.79
<i>p</i> -xylene	4.51	4.39	4.96	4.44	5.21	4.54
diethyl ether	5.68	5.30	5.69	5.21	5.43	5.20
2-pentanone	1.39	1.55	1.71	1.58	1.87	1.63
dichloromethane	0.79	1.30	0.90	1.30	1.04	1.32
trichloromethane	1.30	1.29	1.46	1.33	1.63	1.39
tetrachloromethane	5.51	5.46	5.43	5.50	5.81	5.52
1-nitropropane	1.05	1.07	1.13	1.03	1.23	1.01
acetonitrile	0.51	0.51	0.55	0.51	0.60	0.52
1,4-dioxane	0.97	0.92	1.01	0.93	1.14	0.95
thiophene	1.37	1.34	1.47	1.36	1.60	1.38

^aMutelet et al. (ref 20).

It can be observed from Table S-2 (Supporting Information) that the γ^∞ values for *n*-alkanes are significantly higher than others due to the hydrophobic effect of *n*-alkanes in [bmim][PF₆].⁴⁵ The γ^∞ values increase with an increasing of alkyl chain length for *n*-alkanes and other homologues, which is a typical behavior for ILs including those based on the imidazolium cation.⁴⁷ Cyclization, double bonds, triple bonds, and other polar functional groups can enhance the interaction with the polar cation and anion of [bmim][PF₆] thereby effectively reducing the γ^∞ values. Aromatics, which have six π -delocalized electrons accessible to interact with the [bmim]⁺ cation, have even smaller γ^∞ values than alkynes with the same carbon number. Among the 55 solutes we used, propanol, acetone, nitromethane, nitroethane, acetonitrile and 1,4-dioxane have the smallest γ^∞ values ($\gamma^\infty < 1$), i.e., the solute–[bmim][PF₆] interaction is stronger than the solute–solvent interaction. Indeed, these solutes all contain a negatively charged oxygen or nitrogen atom which would interact strongly with [bmim]⁺ cation by H-bond. For alcohols, which also contain an oxygen atom, their γ^∞ values are larger than unity

Table 4. Comparison of Our $h_1^{E,\infty}$ Values for Alcohols with Those Obtained via Different Methods

solutes	$h_1^{E,\infty}$ (kJ/mol)				
	ref 20 ^a	ref 32 ^b	ref 31 ^c	ref 46 ^d	this work
methanol	−2.12	8.23	9.20		6.93
ethanol	0.48	9.36	10.30	9.87	9.35
1-propanol	6.24	10.81	11.60	10.42	10.47
2-propanol	1.67	11.52	10.90	10.37	9.96
1-butanol	6.05	12.87	12.30	11.89	10.81
2-butanol		11.23	11.60		10.19
2-methyl-1-propanol	4.13	12.56	13.70		10.76
2-methyl-2-propanol			9.70		8.60

^aPGC (Mutelet et al.). ^bPGC (Shimoyama et al.). ^cDilutor method (Dobryakov et al.). ^dCalorimetric method (Li et al.); values were taken at 45.0 °C.

due to their well-known self-association effect.⁴⁸ Branching of the alkyl chain on an alkanol will reduce the γ^∞ value. In the series of chloromethanes, the γ^∞ values strongly increase from dichloromethane (CH₂Cl₂) to tetrachloromethane (CCl₄), as already observed with other ILs.^{18,37} This phenomenon can be interpreted by the properties of [bmim][PF₆], which have been characterized by the linear solvation energy relationship (LSER) model⁴⁹ (pp S-15–S-17, Supporting Information). The regressed parameters show the dominant interactions of [bmim][PF₆] are dipolarity/polarizability and hydrogen-bond basicity. For CCl₄ with low dipolarity/polarizability and hydrogen-bond acidity (Table S-6, Supporting Information), their γ^∞ values are large. CH₂Cl₂ has higher dipolarity/polarizability than CHCl₃ but lower hydrogen-bond acidity than CHCl₃ (Table S-6, Supporting Information); the γ^∞ value of CH₂Cl₂ is close to that of CHCl₃ (1.30, 1.29) at 40.0 °C. Since both LSER parameters of [bmim][PF₆] decrease with increasing temperature, the γ^∞ values for CH₂Cl₂ and CHCl₃ increase as temperature increases (1.32, 1.39, respectively, at 60.0 °C). The slower increasing for CH₂Cl₂ can be explained by its larger dipolarity/polarizability.

The infinite dilution partial molar excess enthalpy $h_1^{E,\infty}$ calculated from γ^∞ values are listed in Table S-4 (Supporting Information). The $h_1^{E,\infty}$ values for *n*-alkanes and *n*-alkenes are positive and increase with increasing carbon number, indicating the dissociation effects outweigh association effect in mixing with [bmim][PF₆]. The introduction of cyclization, double bonds, and triple bonds decreases the positive values. The large positive $h_1^{E,\infty}$ values for alcohols can be thought as the large

Table 3. Comparison of Our γ^∞ Values for Alcohols with Those Obtained via PGC or the Dilutor Method

solutes	γ^∞											
	40.0 °C				50.0 °C				60.0 °C			
	ref 20 ^a	ref 32 ^b	ref 31 ^c	this work	ref 20 ^a	ref 32 ^b	ref 31 ^c	this work	ref 20 ^a	ref 32 ^b	ref 31 ^c	this work
methanol	1.93	2.21	2.06	2.16	1.98	2.00	1.84	2.03	2.03	1.82	1.67	1.84
ethanol	2.87	3.10	2.94	3.14	2.82	2.78	2.58	2.85	2.84	2.50	2.32	2.53
1-propanol	4.35	4.12	4.14	4.43	4.07	3.62	3.58	3.88	3.77	3.21	3.18	3.48
2-propanol	3.57	3.77	3.64	3.85	3.54	3.29	3.18	3.42	3.43	2.89	2.83	3.06
1-butanol	5.91	5.80	5.90	6.30	5.48	4.98	5.1	5.53	5.14	4.31	4.49	4.91
2-butanol		4.45	4.80	5.11		3.89	4.17	4.50		3.43	3.69	4.04
2-methyl-1-propanol	5.31	5.25	5.74	6.01	5.05	4.52	4.94	5.23	4.83	3.93	4.23	4.69
2-methyl-2-propanol			3.68	4.00			3.31	3.60			2.97	3.28

^aPGC (Mutelet et al.). ^bPGC (Shimoyama et al.); values at these temperatures were interpolated by $\ln \gamma^\infty = a/T + b$. ^cDilutor method (Dobryakov et al.); values for 50.0 °C were interpolated.

energy required for the breakdown of the alcohol self-association before mixing. The $h_1^{E,\infty}$ values for linear alkanols increase with increasing alkyl chain length, and the values for branched alkanols are smaller than the corresponding linear alcohol. For the aromatics, $h_1^{E,\infty}$ becomes negative as -0.70 kJ/mol for benzene. However, increasing the alkyl chain in the aromatic ring compensates for this effect, and in ethylbenzene $h_1^{E,\infty}$ is again positive. For aldehydes, ethers, ketones, esters, chloromethanes, and other polar compounds, $h_1^{E,\infty}$ is negative in accordance with the low γ^∞ values due to strong ion-induced dipole interaction with [bmim][PF₆].²⁶

Selectivity of [Bmim][PF₆]. Solute γ^∞ values can be directly used to calculate the selectivity and capacity for different separation problems according to eqs 12 and 13. We calculated S_{ij}^∞ and k_i^∞ of [bmim][PF₆] for the separation of aromatics and aliphatics since it is a potential useful industry process.^{50,51} Large S_{ij}^∞ values and favorable k_i^∞ values in Figure 1 indicate that [bmim][PF₆] can be a possible entrainer for this

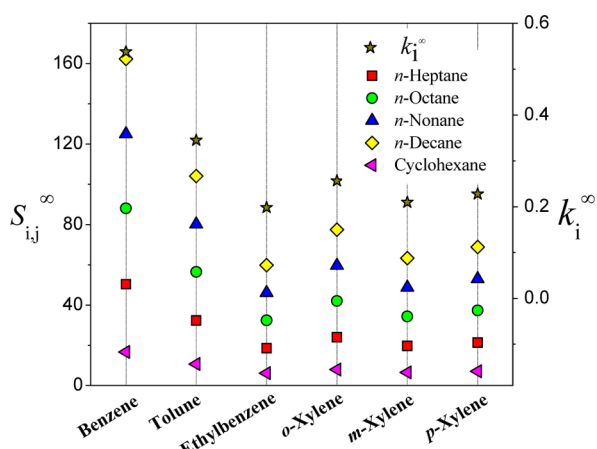


Figure 1. Infinite dilution selectivity of [bmim][PF₆] for the separation of aromatics and aliphatics and infinite dilution capacity of aromatics at 40.0 °C.

application. In [bmim][PF₆], k_i^∞ (solubility) for aromatics decrease with temperature in most cases (a slight increase for ethylbenzene) while k_i^∞ for aliphatics increase with temperature. Therefore, selectivities for extraction of aromatics from aliphatics decrease with temperature. Similar behavior has been observed with most ILs,² which indicates that separation of aromatics from aliphatics using IL should better be operated at a lower temperature.

CONCLUSIONS

The advantages of WCOT columns over packed columns are obvious, e.g., higher column efficiency and lower solute adsorption effect. However, large errors are involved in the determination of γ^∞ by WGC, i.e., the small values of carrier gas flow rate (U) and SP amount (n_2). In this study, we presented a revised equation (eq 7) for GC using static-wall-coated open-tubular columns which can avoid the measurement of U and n_2 and thus reduce the corresponding errors. Such an equation will vigorously promote the development of WGC for accurate γ^∞ determination. We measured γ^∞ of various solutes in [bmim][PF₆] by WGC and demonstrated the validity of our revised equation. Solute adsorption effects in WCOT columns were examined for [bmim][PF₆]. Results show that the interfacial adsorption plays a significant role in the retention

mechanism of n -alkanes. The calculated selectivity indicates that [bmim][PF₆] could be used as an effective entrainer for the separation of aromatics and aliphatics.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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