Activity Coefficients at Infinite Dilution of Alkanols in the Ionic Liquids 1-Butyl-3-methylimidazolium Hexafluorophosphate, 1-Butyl-3-methylimidazolium Methyl Sulfate, and 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) Amide Using the Dilutor Technique

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Activity coefficients at infinite dilution were measured for eight alkanols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol) in the three ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methylimidazolium methyl sulfate ([bmim][CH_3SO_4]), and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide ([hmim][Tf_2N]) between (293.15 and 353.15) K using the dilutor technique. The results are presented and, as far as possible, compared with literature data.

Introduction

The activity coefficient of a solute i at infinite dilution γ_i^∞ in a solvent (also called limiting activity coefficient) results from the intermolecular interactions that the solute experiences at high dilution in that solvent (i.e., solute−solvent interactions) in comparison to those interactions the solute experiences when it is surrounded only by other solute molecules of the same kind (solute−solute interactions). Limiting activity coefficients are important from a theoretical point of view, but also for applications, e.g., in distillation. In recent years, room-temperature ionic liquids have become established as novel solvents for industrial applications.[1−4] Ionic liquids are salts that are liquid at around room temperature. They consist of cations and anions. Therefore, there is almost no limit to the number of combinations which paves the way to design solvents according to the individual requirements of the intended application. Almost all ionic liquids that have been synthesized and investigated so far are low-volatile substances with very small, often negligible vapor pressures that are typical for salts. Therefore, ionic liquids are under investigation as solvents for various separation and liquid extraction processes.[5−8] Activity coefficients at infinite dilution γ_i^∞ are key pieces of information for the realization of many separation processes that employ ionic liquids. For example, the selectivity between components i and j in an ionic liquid $S_{i,j}^\infty$ ($S_{i,j}^\infty = \gamma_i^\infty/\gamma_j^\infty$) and the capacity k_i^∞ ($k_i^\infty = 1/\gamma_i^\infty$) for the separation process can directly be derived from such data.

There are two major methods employed in the determination of limiting activity coefficients with ionic liquids: the retention time method by gas−liquid chromatography (GLC method; two pivotal contributions to that method date back to 1961 and 1965, respectively[9,10]) and the dilutor technique (DT method) or inert gas stripping method. The latter was applied in this study. Already in 1977, Leroi et al. established the dilutor technique for measuring limiting activity coefficients.[11] That method quickly attracted particular attention among the researchers who refined the setup and applied it to a great variety of systems. The development of the dilutor technique, its design principles, and data evaluation and analysis are comprehensively described in the two papers by Hovorka and Dohnal[12] and Krummen et al.[13] (prior to the involvement of ionic liquids).

From 2001 onward, several groups focused on the experimental determination of limiting activity coefficients of various solutes in the, at the time, prevailing ionic liquids. To highlight that research field, we only point at the latest (or initial) contributions, as the other relevant papers mostly are referenced therein. The group of Heintz and co-workers at the University of Rostock, Germany, started with the ionic liquid 4-methyl-*n*-butylpyridinium tetrafluoroborate ([mbpy][BF_4]) using the GLC method.[14] Their most recent contribution deals with [hmim][Tf_2N] within the scope of the coordinated international study on thermophysical properties of a reference ionic liquid under the auspices of IUPAC.[15] The GLC method was also adopted, for example, by the groups of Mutelet at the École Nationale Supérieure des Industries Chimiques (ENSI), Nancy, France,[16] Letcher at the University of KwaZulu-Natal, Durban, South Africa,[17] Domańska at the Warsaw University of Technology, Poland,[18] and Gmehling at the University of Oldenburg, Germany.[19] Gmehling and co-workers, however, employed the dilutor technique as well and published a respective cutting-edge paper already in 2002.[20] Moreover, the paper by Kato and Gmehling evaluates results for identical systems by both the GLC and the dilutor method.[19]

In the present work, activity coefficients at infinite dilution γ_i^∞ of eight alkanols (= solute i), methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol, in three ionic liquids (= solvent), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methylimidazolium methyl sulfate ([bmim][CH_3SO_4]), and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide

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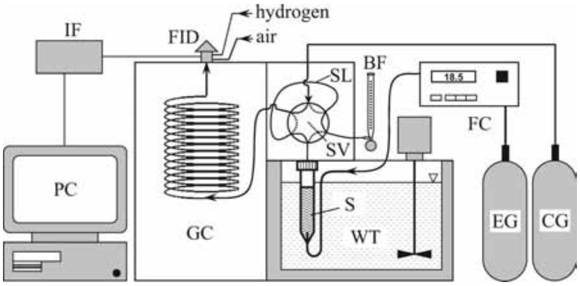

Figure 1. Scheme of the dilutor apparatus. BF, soap bubble flowmeter; CG, GC operating carrier gas; EG, extracting carrier gas; FC, flow controller; FID, flame-ionization detector; GC, gas chromatograph; IF, interface; PC, personal computer; S, saturation cell; SL, sampling loop; SV, six-way sampling valve; WT, water thermostat.

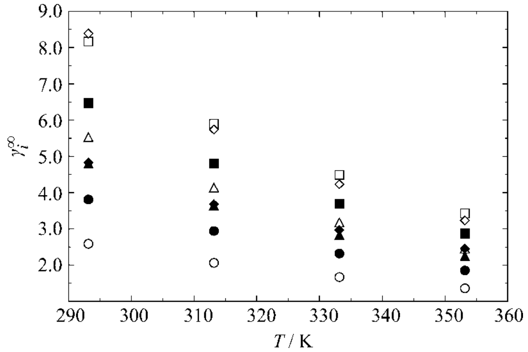

Figure 2. Experimental results for the activity coefficient at infinite dilution γ_i^∞ for eight alkanols in [bmim][PF_6]: ○, methanol; ●, ethanol; Δ, 1-propanol; ▲, 2-propanol; □, 1-butanol; ■, 2-butanol; ◇, 2-methyl-1-propanol; ◆, 2-methyl-2-propanol.

([hmim][Tf_2N]), were determined with the dilutor technique. The experiments were performed at four temperatures, 293.15 K (298.15 K for [bmim][CH_3SO_4]), 313.15 K, 333.15 K, and 353.15 K.

Experimental Section

Apparatus and Method. In the dilutor technique, a highly diluted component (i.e., the solute *i*; here an alkanol) is continuously stripped from a solvent (here the (nonvolatile) ionic liquid) by a constant inert gas flow under isothermal conditions. The composition of the vapor phase is determined by gas chromatography and recorded as a function of time. A typical signal versus time chart of such an experiment will show diminishing peaks of the solute *i* because the solute is depleted by the stripping gas flow. Hence, several authors, particularly from Russia, prefer to use the term "continuous gas extraction".[21,22]

A scheme of the dilutor technique used in the present work is shown in Figure 1. This kind of equipment was already described previously.[23] It is very similar to the arrangement designed and employed by Krummen et al.[13,20]

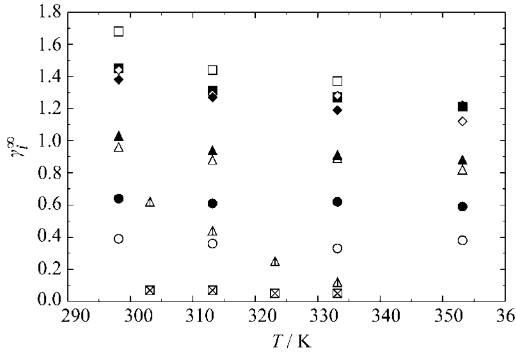

Figure 3. Experimental results for the activity coefficient at infinite dilution γ_i^∞ for eight alkanols in [bmim][CH_3SO_4]: ○, methanol; ●, ethanol; Δ, 1-propanol; ▲, 2-propanol; □, 1-butanol; ■, 2-butanol; ◇, 2-methyl-1-propanol; ♦, 2-methyl-2-propanol; square with an X through it, methanol in [mmim][CH_3SO_4] by Kato and Gmehling;[33] ⍋, 1-propanol in [mmim][CH_3SO_4] by Kato and Gmehling.[33]

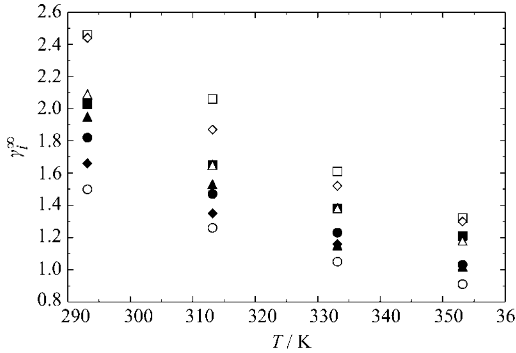

Figure 4. Experimental results for the activity coefficient at infinite dilution γ_i^∞ for eight alkanols in [hmim][Tf_2N] (with N_2 as the extracting carrier gas): ○, methanol; ●, ethanol; Δ, 1-propanol; ▲, 2-propanol; □, 1-butanol; ■, 2-butanol; ◇, 2-methyl-1-propanol; ◆, 2-methyl-2-propanol.

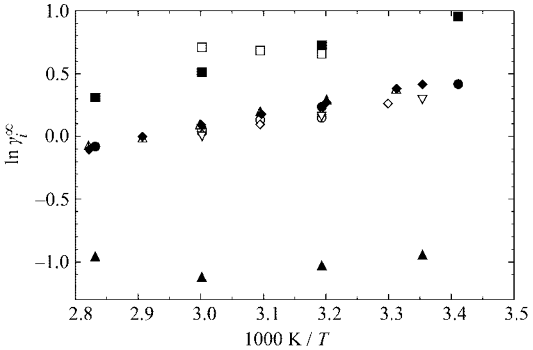

Figure 5. Activity coefficient of methanol at infinite dilution in three ionic liquids. In [bmim][PF_6]: ■, present work; □, Mutelet et al.[39] In [hmim][Tf_2N]: ●, present work (average value of the results obtained with both H_2 and N_2 as extracting carrier gas); ○, Kato and Gmehling,[19] dilutor; ◇, Kato and Gmehling,[19] GLC; ▽, Letcher et al.;[40] ⍋, Heintz et al.;[41] ◆, Heintz et al.[15] In [bmim][CH_3SO_4]: ▲, present work.

An exactly known amount (of about 3 cm^3) of the solvent (i.e., the ionic liquid) is filled into the glass-made saturation cell (S), which has a total volume of 5 cm^3. The saturation cell is immersed in a water thermostat (WT; model U-10, VEB Prüfgerätewerk Medingen, former GDR) with a maximum variance of ± 0.1 K. Since the ionic liquid is nonvolatile at any experimental conditions, an additional presaturation cell[13] that saturates the carrier gas with the solvent, as it is indispensable for volatile solvents, is not needed. Prior to adjusting the water bath to the operational temperature, about 10 μL of the solute is directly added into the saturation cell by a microsyringe. The mass of the prepared saturation cell is determined by an electronic high-precision balance (Ohaus Explorer, model 00640, readability 0.1 mg; Ohaus GmbH, Giessen, Germany). The extracting carrier gas (EG)—helium was chosen for [bmim][PF_6], hydrogen for [bmim][CH_3SO_4], and both hydrogen and nitrogen for [hmim][Tf_2N]—enters the saturation cell via a capillary tube which is plumbed in at the bottom of the saturation cell. The saturation cell itself can be dismounted for weighing. The flow velocity of the carrier gas is administered by an electronic flow controller (FC; model IRG-100, AO Tsvet, Dzerzhinsk, Russia). During the experiment, the flow rate of the extracting carrier gas was maintained at values between (8 and 20) mL·min^{-1},

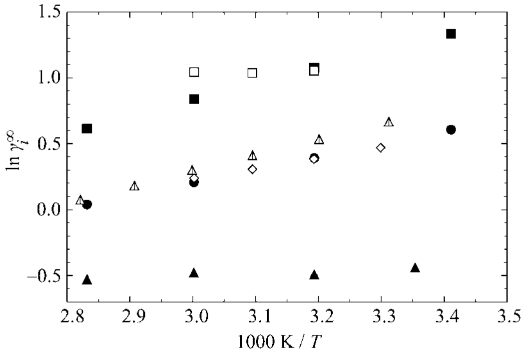

Figure 6. Activity coefficient of ethanol at infinite dilution in three ionic liquids. In [bmim][PF$_6$]: ■, present work; □, Mutelet et al.[39] In [hmim][Tf$_2$N]: ●, present work (average value of the results obtained with both H_2 and N_2 as extracting carrier gas); ◇, Kato and Gmehling,[19] GLC; ⍋, Heintz et al.[41] In [bmim][CH$_3$SO$_4$]: ▲, present work.

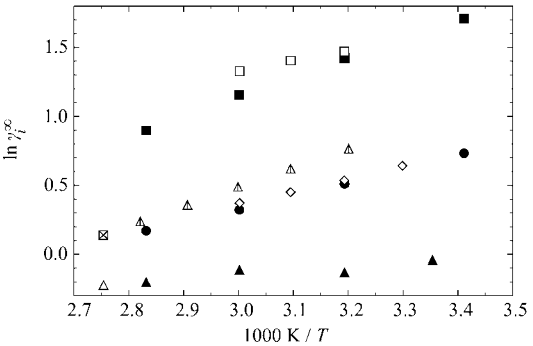

Figure 7. Activity coefficient of 1-propanol at infinite dilution in three ionic liquids. In [bmim][PF$_6$]: ■, present work; □, Mutelet et al.[39] In [hmim][Tf$_2$N]: ●, present work (average value of the results obtained with both H_2 and N_2 as extracting carrier gas); ◇, Kato and Gmehling,[19] GLC; ⍋, Heintz et al.;[41] square with an X through it, Braun.[38] In [bmim][CH$_3$SO$_4$]: ▲, present work; △, Braun.[38]

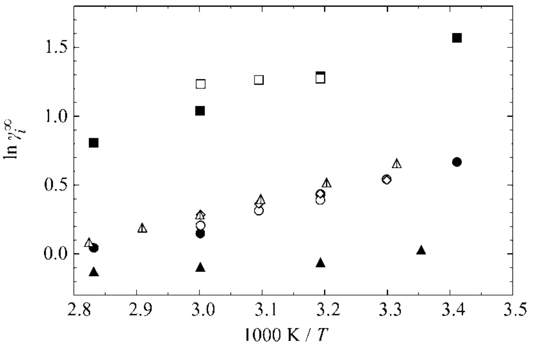

Figure 8. Activity coefficient of 2-propanol at infinite dilution in three ionic liquids. In [bmim][PF$_6$]: ■, present work; □, Mutelet et al.[39] In [hmim][Tf$_2$N]: ●, present work (average value of the results obtained with both H_2 and N_2 as extracting carrier gas); ○, Kato and Gmehling,[19] dilutor; ◇, Kato and Gmehling,[19] GLC; ⍋, Heintz et al.[41] In [bmim][CH$_3$SO$_4$]: ▲, present work.

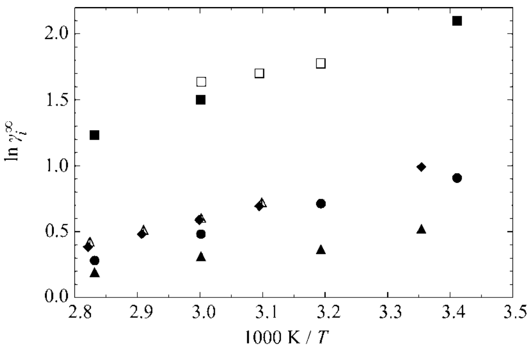

Figure 9. Activity coefficient of 1-butanol at infinite dilution in three ionic liquids. In [bmim][PF$_6$]: ■, present work; □, Mutelet et al.[39] In [hmim][Tf$_2$N]: ●, present work (average value of the results obtained with both H_2 and N_2 as extracting carrier gas); ⍋, Heintz et al.;[41] ♦, Heintz et al.[15] In [bmim][CH$_3$SO$_4$]: ▲, present work.

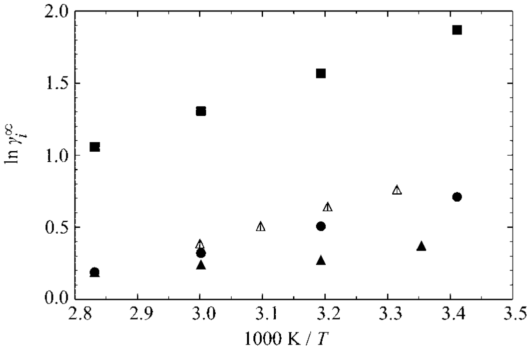

Figure 10. Activity coefficient of 2-butanol at infinite dilution in three ionic liquids. In [bmim][PF$_6$]: ■, present work. In [hmim][Tf$_2$N]: ●, present work (average value of the results obtained with both H_2 and N_2 as extracting carrier gas); ⍋, Heintz et al.[41] In [bmim][CH$_3$SO$_4$]: ▲, present work.

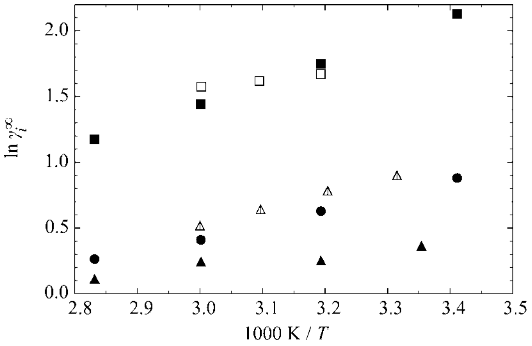

Figure 11. Activity coefficient of 2-methyl-1-propanol at infinite dilution in three ionic liquids. In [bmim][PF$_6$]: ■, present work; □, Mutelet et al.[39] In [hmim][Tf$_2$N]: ●, present work (average value of the results obtained with both H_2 and N_2 as extracting carrier gas); ⍋, Heintz et al.[41] In [bmim][CH$_3$SO$_4$]: ▲, present work.

dependent on the chosen temperature, with an accuracy not worse than 0.05 mL·min^{-1}. The gas flow is additionally monitored by a soap bubble flowmeter (BF) that is placed at the outlet of the equipment. The saturation cell is directly connected to an electrically operated six-way sampling valve (SV) equipped with a high-precision sampling loop (SL). The volume of the sampling loop is about 0.5 cm^3. The sampling valve is kept at 80 °C to avoid any condensation of the solute. The controlled operation of the sampling valve guarantees an exact and reproducible sampling in periodic intervals. The sample is analyzed by gas chromatography (GC; model Tsvet-500M, AO Tsvet). The gas chromatograph was equipped with a Varian Chrompack capillary column CP-Sil 5CB (CP 8677: length: 30 m, diameter: 0.53 mm, film thickness: 3 μm; Varian, Inc., Palo Alto, CA, USA) and a flame-ionization detector (FID). The gas chromatograph was operated with helium for the measurements with [bmim][PF$_6$] and with hydrogen for the other. The gas flow through the gas chromatograph was kept at 10 mL·min^{-1} during the entire measurements. When hydrogen was applied, the settings for the flame-ionization detector had to be modified (hydrogen flow reduced from (30 to 20) mL·min^{-1}, that of synthetic air was kept at 300 mL·min^{-1} all the time). For the analysis of the alkanols, the column temperature was set to 50 °C, and the flame-ionization detector operated at 120 °C. The vapor phase was analyzed in intervals

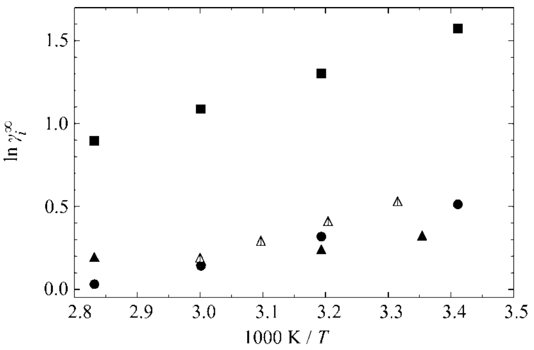

Figure 12. Activity coefficient of 2-methyl-2-propanol at infinite dilution in three ionic liquids. In [bmim][PF$_6$]: ■, present work. In [hmim][Tf$_2$N]: ●, present work (average value of the results obtained with both H$_2$ and N$_2$ as extracting carrier gas); △, Heintz et al.[41] In [bmim][CH$_3$SO$_4$]: ▲, present work.

of 6 min over a period of about (5 to 7) h. The obtained signals were recorded by a personal computer (PC) via an interface (IF). Ultimately, the signals are analyzed using the software "MultiChrom v. 1.5" (ZAO Ampersand, Moscow, Russia).

Provided that phase equilibrium is achieved in the stripping cell, the recorded signals can be evaluated to give the activity coefficient of the solute at infinite dilution in the ionic liquid.

Data Reduction. The periodically repeated analysis of the vapor phase in a dilutor experiment, as employed here, results in a chromatographic chart that shows monotonously diminishing peaks of the single solute. The decrease of the solute concentration in the vapor phase is directly related to the peak area, and the determination of the limiting activity coefficient γ_i^∞ basically resorts to the variation of the relative peak areas.

For a complete and very detailed description of the thermodynamic principles following the ideas of Leroi et al.[11] the reader is referred to the paper by Krummen et al.[13] On the assumptions that the solute is infinitely diluted, the Poynting correction can be skipped (reasonable at moderate pressures), the solubility of the carrier gas in the liquid phase can be neglected, the fugacity coefficient of the solute $\varphi_i^{\mathrm{v}} \approx 1$ (the behavior of the extracting carrier gas is considered ideal), and the solvent is nonvolatile, Krummen et al. established for γ_i^∞

$$\gamma_i^\infty = -\frac{n_{\mathrm{L}}RT}{\varphi_i^{\mathrm{s}} p_i^{\mathrm{s}}\left(\frac{\dot{V}}{\alpha} + V_{\mathrm{G}}\right)} \tag{1}$$

with

$$\alpha = \ln\left(\frac{A_i}{A^0}\right)\cdot\frac{1}{t} \tag{2}$$

The property α of eq 2 is determined by a linear regression of the logarithm of the ratio of peak area A_i at time t and initial peak area A^0. A calibration is spared since no absolute but only relative peak areas as a function of time are needed, and—as the amount of solute in a sample is very small—the detector's response is assumed to be linear. The other properties that are directly drawn from the experiment are the operational temperature T, the amount of solvent n_{L} in the saturation cell, the vapor space volume in the saturation cell V_{G}, and ultimately the carrier gas flow rate $\dot{V}$. Apart from the experiment, the universal gas constant R, the saturation vapor pressure of the solute p_i^{s}, and its saturation fugacity coefficient φ_i^{s} are retrieved. For many solutes, such as alkanols, $\varphi_i^{\mathrm{s}} = 1$ is tolerable as a first approximation. The saturation properties are to be calculated referring to appropriate sources, such as, for example, the Antoine equation for p_i^{s} and to determine φ_i^{s} using the second virial coefficient B_{ii} and eq 3.

$$\varphi_i^{\mathrm{s}} = \exp\left[\frac{B_{ii}p_i^{\mathrm{s}}}{RT}\right] \tag{3}$$

Ultimately, the amount of solvent usually is determined by high-precision weighing. Krummen et al. attribute the dilutor technique in their design to a relative error for γ_i^∞ of about ± 2.5 %.[13,20]

Another thermodynamic property that can be derived from the same kind of data analysis is the distribution ratio at infinite dilution K_i^∞.[12,22,23]

$$K_i^\infty = \lim_{c_i \to 0} \frac{c_i^{\mathrm{liq}}}{c_i^{\mathrm{vap}}} \tag{4}$$

Drozd and Novák proposed the following relation for the concentration of the solute c_i^{vap} in the gas phase[24]

$$c_i^{\mathrm{vap}} = c_i^{\mathrm{vap},0}\exp\left[-\frac{V_{\mathrm{g}}}{KV_{\mathrm{L}} + V_{\mathrm{G}}}\right] \tag{5}$$

where $K = (c_i^{\mathrm{liq}}/c_i^{\mathrm{vap}})$ is the distribution ratio. V_{g} is the volume of the carrier gas that has passed the saturation cell; V_{L} is the volume of the solvent; and V_{G} is the vapor space volume in the cell. $c_i^{\mathrm{vap},0}$ is the initial concentration of the solute in the gas phase (i.e., for $V_{\mathrm{g}} = 0$). c_i^{vap} is the respective solute concentration after the gas volume V_{g} has passed the saturation cell. At a constant flow rate $\dot{V}$ of the stripping gas, the volume V_{g} of the gas passed through the solution inside the saturation cell is proportional to the time t elapsed from the start of the extraction until the sampling (cf. eq 6).

$$V_{\mathrm{g}} = \dot{V}\cdot t \tag{6}$$

With these assumptions, eq 5 can be rewritten as

$$\ln\left(\frac{c_i^{\mathrm{vap}}}{c_i^{\mathrm{vap},0}}\right) = -\frac{\dot{V}t}{KV_{\mathrm{L}} + V_{\mathrm{G}}} \tag{7}$$

For highly or infinitely diluted solutions, the ratio of the solute concentrations in eq 5 can be replaced by the corresponding peak areas A_i and A^0. Replacing the concentration ratio by the ratio of peak areas as well as introducing the appropriate indices for "limiting" gives

$$\ln\left(\frac{A_i}{A^0}\right)\cdot\frac{1}{t} = -\frac{\dot{V}}{K_i^\infty V_{\mathrm{L}} + V_{\mathrm{G}}} \tag{8}$$

The left side of eq 8 is equal to eq 2 and thus can similarly be determined by linear regression.

$$\alpha = -\frac{\dot{V}}{K_i^\infty V_{\mathrm{L}} + V_{\mathrm{G}}} \tag{9}$$

The limiting distribution ratio K_i^∞ for a solute can be combined with the limiting activity coefficient γ_i^∞ as follows: First, K_i^∞ is rewritten from eq 9 as

$$K_i^\infty = \frac{1}{V_{\mathrm{L}}}\left[-\frac{\dot{V}}{\alpha} - V_{\mathrm{G}}\right] \tag{10}$$

Substituting eq 10 into eq 1 gives

$$\gamma_i^\infty = \frac{\rho_{\mathrm{L}}RT}{\varphi_i^{\mathrm{s}} p_i^{\mathrm{s}} M_{\mathrm{L}} K_i^\infty} \tag{11}$$

M_{L} is the molar mass of the solvent.

In this study, the limiting activity coefficients γ_i^∞ were calculated using eq 11 via the limiting distribution ratio K_i^∞. The experimental uncertainty ΔK_i^∞ for the limiting distribution ratio K_i^∞ was estimated from the error in measuring the gas flow rate $\dot{V}$, the volume of the solvent (i.e., the ionic liquid) in the saturation cell V_L, and the errors of the peak areas A^0 and A_i. The experimental uncertainty ΔK_i^∞ for the limiting distribution ratio K_i^∞ does not depend on the solute but on the solvent. The vapor space volume V_G is made as small as possible, and its contribution becomes only important (cf. eq 5) for $K_i^\infty < 100$.[23] Here, we considered V_G for calculating K_i^∞ but discounted the uncertainty of V_G for the determination of ΔK_i^∞.

Materials. All three ionic liquids [bmim][PF$_6$] ($C_8H_{15}F_6N_2P$, purum, mass fraction ≥ 0.98, yellowish color, relative molar mass $M = 284.18$), [bmim][CH$_3$SO$_4$] ($C_9H_{18}N_2O_4S$, purum, mass fraction ≥ 0.98, dark yellow to brownish color, $M = 250.32$), and [hmim][Tf$_2$N] ($C_{12}H_{19}N_3F_6O_4S_2$, purissimum, mass fraction ≥ 0.99, colorless to slightly yellow color, $M = 447.42$) were supplied by Solvent Innovation GmbH, Cologne, Germany. All alkanols (i.e., methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol) were purchased from AO Reachim, Kharkov, Ukraine, in chromatography grade and were supplied in sealed vials. The chromatograms from the experiment showed no further peaks, indicating the absence of significant impurities.

Prior to the experiments, the ionic liquid samples were purified by exposure to continuous flow of dry nitrogen over (4 to 5) days at about 50 °C. Traces of water and other volatile impurities could be eluted by this procedure. Subsequently, a gas chromatographic vapor phase analysis (using a flame-ionization detector) of an experiment with a processed pure ionic liquid sample at 80 °C revealed no volatile components. As checked by Karl Fischer titration, the water content of the initial sample was below 0.1 mass % for [bmim][PF$_6$], below 0.05 mass % for [bmim][CH$_3$SO$_4$], and below 0.05 mass % for [hmim][Tf$_2$N], respectively.

The applied gases (helium (purity ≥ 99.995 %), nitrogen (purity ≥ 99.999 %), hydrogen (≥ 99.995 %), and synthetic air (20.8 % O_2)) came all from OOO Monitoring, Saint-Petersburg, Russia.

Results and Discussion

The new experimental results for the limiting distribution ratio K_i^∞ are given in Table 1. From these results, the limiting activity coefficients γ_i^∞ are calculated. The calculation requires the solvent density ρ_L, the saturation vapor pressure p_i^s, and the corresponding fugacity coefficient φ_i^s. The solvent density ρ_L was calculated using the linear regression

$$\rho_L = a + b(T/K) \qquad (12)$$

with coefficients a and b fitted to literature data. The literature sources and the resulting coefficients are given in Table 2.

The vapor pressures p_i^s and fugacity coefficients φ_i^s of methanol and ethanol were determined from the software package “ThermoFluids”.[28] That package resorts to the reference equation of state by de Reuck and Craven for methanol[29] and by Dillon and Penoncello for ethanol,[30] respectively. A different procedure had to be executed to obtain the saturation properties for the other alkanols because these substances are not implemented in “ThermoFluids”.

These vapor pressures p_i^s were calculated using the empirical equations compiled by Reid, Prausnitz, and Poling.[31] The corresponding fugacity coefficients were calculated with the virial equation of state that was truncated after the second virial coefficient. All required second virial coefficients were calculated from a method by Tsonopoulos.[32] The numerical values for p_i^s and φ_i^s which were used to calculate the activity coefficient at infinite dilution by eq 11 are given in Table 3.

Table 1. Distribution Ratios at Infinite Dilution K_i^∞ for a Series of Alkanols i in the Ionic Liquids [bmim][PF$_6$], [bmim][CH$_3$SO$_4$], and [hmim][Tf$_2$N] at Temperatures between (293 and 353 K)

solute i	solvent	K_i^∞			
		T/K = 293.15	T/K = 313.15	T/K = 333.15	T/K = 353.15
methanol	[bmim][PF$_6$]	352 ± 8	173 ± 4	96 ± 3	58 ± 2
ethanol		523 ± 12	236 ± 6	121 ± 4	70 ± 3
1-propanol		1056 ± 25	430 ± 10	203 ± 7	111 ± 4
2-propanol		583 ± 14	247 ± 6	121 ± 4	68 ± 3
1-butanol		2276 ± 57	847 ± 19	364 ± 13	184 ± 7
2-butanol		1114 ± 30	431 ± 10	197 ± 7	105 ± 4
2-methyl-1-propanol		1476 ± 35	563 ± 13	253 ± 9	132 ± 5
2-methyl-2-propanol		610 ± 14	247 ± 6	116 ± 4	63 ± 3
		T/K = 298.15	T/K = 313.15	T/K = 333.15	T/K = 353.15
methanol	[bmim][CH$_3$SO$_4$]	1840 ± 86	1004 ± 45	492 ± 23	208 ± 10
ethanol		2350 ± 110	1142 ± 51	458 ± 22	222 ± 11
1-propanol		4470 ± 200	2044 ± 68	731 ± 25	337 ± 12
2-propanol		2020 ± 64	960 ± 28	380 ± 12	174 ± 5
1-butanol		7844 ± 390	3490 ± 172	1204 ± 57	525 ± 24
2-butanol		3587 ± 136	1590 ± 52	577 ± 18	252 ± 7
2-methyl-1-propanol		6027 ± 326	2526 ± 95	845 ± 30	384 ± 11
2-methyl-2-propanol		1561 ± 48	719 ± 20	292 ± 9	128 ± 4
		T/K = 293.15	T/K = 313.15	T/K = 333.15	T/K = 353.15
methanol[a]	[hmim][Tf$_2$N]	379 ± 15	180 ± 7	94 ± 3	54 ± 2
ethanol[a]		686 ± 27	297 ± 11	145 ± 4	79 ± 3
1-propanol[a]		1795 ± 75	674 ± 20	299 ± 7	146 ± 5
2-propanol[a]		915 ± 40	366 ± 14	187 ± 6	90 ± 3
1-butanol[a]		4757 ± 243	1576 ± 65	638 ± 24	302 ± 11
2-butanol[a]		2266 ± 102	792 ± 25	338 ± 9	159 ± 5
2-methyl-1-propanol[a]		3314 ± 169	1094 ± 38	457 ± 13	208 ± 7
2-methyl-2-propanol[a]		1118 ± 46	415 ± 16	192 ± 5	95 ± 3
methanol[b]		390 ± 15	180 ± 7	97 ± 3	55 ± 1
ethanol[b]		698 ± 27	301 ± 11	146 ± 4	80 ± 2
1-propanol[b]		1786 ± 72	688 ± 26	298 ± 8	147 ± 4
2-propanol[b]		917 ± 40	375 ± 14	190 ± 5	95 ± 3
1-butanol[b]		4823 ± 256	1548 ± 58	648 ± 24	303 ± 9
2-butanol[b]		2263 ± 96	802 ± 31	335 ± 9	159 ± 5
2-methyl-1-propanol[b]		3244 ± 147	1104 ± 43	448 ± 13	208 ± 6
2-methyl-2-propanol[b]		1131 ± 45	428 ± 16	190 ± 5	96 ± 3

[a] Extracting carrier gas: hydrogen. [b] Extracting carrier gas: nitrogen.

Table 2. Correlation Coefficients for Equation 12 Describing the Solvent Density ρ_L[a]

solvent	a/g·cm^{-3}	b/g·cm^{-3}	data source
[bmim][PF$_6$]	1.6167	$-8.447 \cdot 10^{-4}$	ref 25
[bmim][CH$_3$SO$_4$]	1.4119	$-6.772 \cdot 10^{-4}$	ref 26
[hmim][Tf$_2$N]	1.6415	$-9.052 \cdot 10^{-4}$	ref 27

[a] Note: The samples of [bmim][PF$_6$] and [bmim][CH$_3$SO$_4$] employed in the present study were taken from a larger sample that was used for gas solubility investigations at the University of Kaiserslautern (cf. refs 25 and 26).

Table 4 contains the new data for the limiting activity coefficient γ_i^∞ of all (eight) alkanols in the three ionic liquids including the estimated experimental uncertainty. The experi-

Table 3. Saturation Vapor Pressures p_i^s and Saturation Fugacity Coefficients φ_i^s of the Solutes i Investigated

T/K	293.15	298.15	313.15	333.15	353.15
solute i			p_i^s/kPa		
methanol	13.032	16.981	35.518	84.713	181.11
ethanol	5.925	7.951	18.033	47.128	108.57
1-propanol	2.019	2.807	7.008	20.374	51.095
2-propanol	4.223	5.801	13.976	38.798	93.099
1-butanol	0.6324	0.9093	2.487	8.014	21.870
2-butanol	1.632	2.310	6.014	18.089	46.107
2-methyl-1-propanol	0.9509	1.386	3.858	12.309	32.683
2-methyl-2-propanol	4.016	5.596	13.821	38.630	92.049
			φ_i^s		
methanol	0.9863	0.9845	0.9778	0.9658	0.9497
ethanol	0.9961	0.9951	0.9912	0.9825	0.9689
1-propanol	0.9967	0.9960	0.9931	0.9872	0.9782
2-propanol	0.9939	0.9926	0.9877	0.9779	0.9636
1-butanol	0.9986	0.9983	0.9968	0.9935	0.9879
2-butanol	0.9975	0.9969	0.9944	0.9889	0.9802
2-methyl-1-propanol	0.9976	0.9970	0.9943	0.9886	0.9799
2-methyl-2-propanol	0.9938	0.9924	0.9869	0.9762	0.9608

Table 4. Activity Coefficients at Infinite Dilution γ_i^∞ for a Series of Alkanols i in the Ionic Liquids [bmim][PF$_6$], [bmim][CH$_3$SO$_4$], and [hmim][Tf$_2$N]

solute i	solvent	γ_i^∞			
		T/K = 293.15	T/K = 313.15	T/K = 333.15	T/K = 353.15
methanol	[bmim][PF$_6$]	2.59 ± 0.06	2.06 ± 0.05	1.67 ± 0.06	1.36 ± 0.06
ethanol		3.81 ± 0.09	2.94 ± 0.07	2.32 ± 0.08	1.85 ± 0.07
1-propanol		5.53 ± 0.13	4.14 ± 0.10	3.18 ± 0.11	2.45 ± 0.09
2-propanol		4.80 ± 0.12	3.64 ± 0.09	2.83 ± 0.10	2.25 ± 0.09
1-butanol		8.17 ± 0.20	5.90 ± 0.13	4.49 ± 0.16	3.43 ± 0.12
2-butanol		6.47 ± 0.17	4.80 ± 0.11	3.69 ± 0.13	2.87 ± 0.10
2-methyl-1-propanol		8.39 ± 0.20	5.74 ± 0.13	4.23 ± 0.14	3.23 ± 0.11
2-methyl-2-propanol		4.83 ± 0.11	3.68 ± 0.09	2.97 ± 0.10	2.45 ± 0.10
		T/K = 298.15	T/K = 313.15	T/K = 333.15	T/K = 353.15
methanol	[bmim][CH$_3$SO$_4$]	0.39 ± 0.02	0.36 ± 0.02	0.33 ± 0.02	0.38 ± 0.02
ethanol		0.64 ± 0.03	0.61 ± 0.03	0.62 ± 0.03	0.59 ± 0.03
1-propanol		0.96 ± 0.04	0.88 ± 0.03	0.89 ± 0.03	0.82 ± 0.03
2-propanol		1.03 ± 0.03	0.94 ± 0.03	0.91 ± 0.03	0.88 ± 0.03
1-butanol		1.68 ± 0.08	1.44 ± 0.07	1.37 ± 0.06	1.21 ± 0.06
2-butanol		1.45 ± 0.05	1.31 ± 0.04	1.27 ± 0.04	1.21 ± 0.03
2-methyl-1-propanol		1.44 ± 0.08	1.29 ± 0.05	1.28 ± 0.05	1.12 ± 0.03
2-methyl-2-propanol		1.38 ± 0.04	1.27 ± 0.04	1.19 ± 0.04	1.22 ± 0.04
		T/K = 293.15	T/K = 313.15	T/K = 333.15	T/K = 353.15
methanol[a]	[hmim][Tf$_2$N]	1.54 ± 0.06	1.27 ± 0.05	1.08 ± 0.03	0.93 ± 0.03
ethanol[a]		1.85 ± 0.07	1.49 ± 0.06	1.24 ± 0.03	1.05 ± 0.03
1-propanol[a]		2.08 ± 0.09	1.68 ± 0.05	1.38 ± 0.03	1.19 ± 0.04
2-propanol[a]		1.95 ± 0.09	1.56 ± 0.06	1.17 ± 0.04	1.08 ± 0.03
1-butanol[a]		2.50 ± 0.13	2.02 ± 0.08	1.63 ± 0.06	1.33 ± 0.05
2-butanol[a]		2.03 ± 0.09	1.67 ± 0.05	1.37 ± 0.04	1.20 ± 0.04
2-methyl-1-propanol[a]		2.39 ± 0.12	1.88 ± 0.07	1.49 ± 0.04	1.30 ± 0.05
2-methyl-2-propanol[a]		1.68 ± 0.07	1.40 ± 0.05	1.15 ± 0.03	1.04 ± 0.04
methanol[b]		1.50 ± 0.06	1.26 ± 0.05	1.05 ± 0.03	0.91 ± 0.02
ethanol[b]		1.82 ± 0.07	1.47 ± 0.06	1.23 ± 0.03	1.03 ± 0.03
1-propanol[b]		2.09 ± 0.08	1.65 ± 0.06	1.38 ± 0.04	1.18 ± 0.03
2-propanol[b]		1.95 ± 0.09	1.53 ± 0.06	1.15 ± 0.03	1.02 ± 0.03
1-butanol[b]		2.46 ± 0.13	2.06 ± 0.08	1.61 ± 0.06	1.32 ± 0.04
2-butanol[b]		2.03 ± 0.09	1.65 ± 0.06	1.38 ± 0.04	1.21 ± 0.04
2-methyl-1-propanol[b]		2.44 ± 0.11	1.87 ± 0.07	1.52 ± 0.04	1.30 ± 0.04
2-methyl-2-propanol[b]		1.66 ± 0.07	1.35 ± 0.05	1.16 ± 0.03	1.03 ± 0.03

[a] Extracting carrier gas: hydrogen. [b] Extracting carrier gas: nitrogen.

mental uncertainties that were calculated from the uncertainties of the corresponding limiting distribution ratio K_i^∞ amount at average to about 3.0 % for [bmim][PF$_6$], 3.9 % for [bmim][CH$_3$SO$_4$], and 3.5 % for [hmim][Tf$_2$N]. Using the saturation vapor pressure p_i^s for calculating γ_i^∞ instead of the saturation fugacity f_i^s shifts γ_i^∞ to lower values (on average by 1.5 %, at maximum by 5.0 % for methanol at $T = 353.15$ K). Replacing hydrogen as the extracting carrier gas with nitrogen in the experiments with [hmim][Tf$_2$N] resulted for γ_i^∞ in an average relative deviation of 1.5 %. That difference, however, is smaller than the experimental uncertainty. For all systems investigated here, the limiting activity coefficient γ_i^∞ decreases with increasing temperature T. A decreasing γ_i^∞ means a stronger attraction (or a smaller repulsion) between the solute and the solvent. Such behavior is more likely for alkanes or cycloalkanes than for alcohols since the acidic proton of the OH group is attracted to the anion. Delocalized electrons can interact with the polar cation and/or the anion of the ionic liquids as well. For all alkanols except 2-methyl-2-propanol, γ_i^∞ decreases in the following order of solvents for the temperature range investigated:

[bmim][PF$_6$] > [hmim][Tf$_2$N] > [bmim][CH$_3$SO$_4$].

For 2-methyl-2-propanol, higher γ_i^∞ values were determined in [bmim][CH$_3$SO$_4$] than in [hmim][Tf$_2$N] at T = (333.15 and 353.15) K. The different alkanols behave differently in the three liquids. As expected, methanol, being the most acidic species of all alkanols investigated, gives the lowest γ_i^∞ values in all three ionic liquids at all temperatures investigated and reveals the smallest temperature effect of all alkanols.

The γ_i^∞ versus T plot in Figures 2 to 4 illustrates that two opposing effects originate from the structure of the alkanols: γ_i^∞ increases with increasing chain length but decreases with increasing branching of the alkane skeleton. The limiting activity coefficients of the alkanols are particularly low for the solvent [bmim][CH$_3$SO$_4$], and the effect of temperature is only weak. This indicates that there are rather strong attractive forces between an alkanol molecule and the [CH$_3$SO$_4$]$^-$ anion. Moreover, the [bmim][CH$_3$SO$_4$] data scatter distinctly more than the others. We further observed that during the experiments with methanol at (333.15 and 353.15) K the solute could not be stripped completely, but a small amount remained. A significant thermal degradation already at these temperatures is rather unlikely according to the results from the respective studies by Fernández et al.[34] and Holbrey et al.[35] on alkyl-sulfate ionic liquids. More likely, however, might be the beginning of a reaction between the [CH$_3$SO$_4$]$^-$ anion and the alkanol in the manner described by Himmler et al.[36] or an acid-catalyzed hydrolysis as reported by Kurz already in 1962.[37] The limiting activity coefficient data for methanol in [mmim][CH$_3$SO$_4$] (cf. Figure 3) from Kato and Gmehling are outstandingly low compared to other solvents investigated in their work as well.[33]

A comparison between the new experimental results and literature data is given in Figures 5 to 12, where ln γ_i^∞ is plotted versus the inverse temperature.

These figures illustrate the course of the limiting activity coefficient γ_i^∞ from the viewpoint of each solute amended with literature data.

Until now, only Braun employed [bmim][CH$_3$SO$_4$] for such investigations.[38] The reported γ_i^∞ value (by the GLC method) for 1-propanol at $T = 363.15$ K is in good agreement with our results extrapolated to that temperature.

Mutelet et al. determined the infinite dilution activity coefficient for methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-1-propanol in [bmim][PF$_6$] at (313.15, 323.15, and 333.15) K by the GLC method.[39] Surprisingly, and in contrary to the new experimental data, the results of Mutelet et al. reveal a slight increase of the infinite dilution activity coefficient of methanol in [bmim][PF$_6$] with increasing temperature. The deviations between the new data and the results by Mutelet et al. at (313.15 and 333.15) K amount on average to 11.4 %.

There are four literature sources for the infinite dilution activity coefficient of alkanols in [hmim][Tf$_2$N]: Letcher et al. used the GLC method for methanol;[40] Kato and Gmehling employed both the GLC method and the dilutor technique;[19] and two studies came from the group of Heintz at the University of Rostock.[15,41] The Rostock group exclusively employed the GLC technique. One publication covers all alkanols investigated also in the present work,[41] and the more recent publication is a contribution to the aforementioned IUPAC study.[15] As can be seen from Figure 5, the γ_i^∞ data by Letcher et al. are about 6 % lower than our results, and those γ_i^∞ data reported by Kato and Gmehling (cf. Figures 5 to 8) are in good agreement with our data. It can also be seen from Figures 5 to 8 that there is a difference between the results from the dilutor and the GLC experiments. The overall average relative deviation between Kato and Gmehling's and our data at (313.15 and 333.15) K amounts to 5 % (at maximum 15 % for 2-propanol using the GLC technique at 313.15 K). The 2006 paper by Heintz et al. provides reference data for all alkanols.[41] Compared with our own measurements, these data are systematically shifted to higher values, and the deviation becomes more pronounced at lower temperatures. If eq 4 from their paper[41] is used to calculate the infinite dilution activity coefficients at the temperatures investigated in the present work, the average relative deviation to our new data is 5.5 % for methanol but 23.1 % for 1-propanol. However, for 1-propanol, the average relative deviation between our data at (313.15 and 333.15) K and those data reported by Kato and Gmehling (GLC technique) only amounts to 4.3 %.[19] In their subsequent 2007 paper, Heintz et al. examined the question whether the experimental results for γ_i^∞ depend on the amount of ionic liquid that covers the solid support in the GLC column[15]—the solutes were methanol and 1-butanol, and the solvent was [hmim][Tf$_2$N]. They performed several experiments at a single temperature for different column characteristics and concluded that the differences in the experimental results are not caused by the amount of solvent that covers the support but that there is a scattering of the data sets that has to be attributed to the technique itself. Their results are displayed for comparison in Figures 5 and 9 for methanol and 1-butanol, respectively. The symbols refer to the arithmetic mean from all experiments at a certain temperature. The average relative deviation between the arithmetic mean of those data and our new results amounts to 8.2 %. Braun also determined γ_i^∞ for 1-propanol in [hmim][Tf$_2$N] at $T = 363.15$ K, and the result again matches the extrapolation from our measurements quite well.[38]

Table 5 lists the partial molar excess enthalpies at infinite dilution $\Delta H_i^{\mathrm{E},\infty}$ that were obtained from the experimental data by

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial\left(\frac{1}{T}\right)}\right) = \frac{\Delta H_i^{\mathrm{E},\infty}}{R} \tag{13}$$

Within the experimental uncertainty, no influence of temperature on $\Delta H_i^{\mathrm{E},\infty}$ could be detected. There is only a slight influence of the alkanol on that property. For the alkanols investigated here, the partial molar excess enthalpy at infinite dilution $\Delta H_i^{\mathrm{E},\infty}$ depends on the solvent being about 10 kJ·mol^{-1} for [bmim][PF$_6$], about 2 kJ·mol^{-1} for [bmim][CH$_3$SO$_4$], and about 8 kJ·mol^{-1} for [hmim][Tf$_2$N]. As is shown in Table 5, that thermodynamic property was reported by other authors as well. In some cases, the new data agree well with literature

Table 5. Partial Molar Excess Enthalpies at Infinite Dilution $\Delta H_i^{\mathrm{E},\infty}$ of Solute i in an Ionic Liquid Solvent ([bmim][PF$_6$], [bmim][CH$_3$SO$_4$], and [hmim][Tf$_2$N] in the Present Work from Experiments with Two Different Extraction Gases, Hydrogen and Nitrogen)

	$\Delta H_i^{\mathrm{E},\infty}$/kJ·mol^{-1}			
	solvent			
solute i	[bmim] [PF$_6$]	[bmim] [CH$_3$SO$_4$]	[hmim] [Tf$_2$N]	source
methanol	9.2	–[a]	7.1 (H$_2$)	this work
			7.2 (N$_2$)	
			6.208	ref 19[b]
			6.8	ref 40
			7.8	ref 41
			8.4	ref 15[c]
			6.4	ref 15[d]
			7.8	ref 15[e]
			8.4	ref 15[i]
			7.380	ref 15[j]
	−2.1212			ref 39
ethanol	10.3	1.2	8.1 (H$_2$)	this work
			8.1 (N$_2$)	
			6.478	ref 19
			10.1	ref 41
	4.7894			ref 39
1-propanol	11.6	2.2	8.1 (H$_2$)	this work
			8.1 (N$_2$)	
			7.536	ref 19
			11.4	ref 41
	6.2385			ref 39
2-propanol	10.9	2.4	9.0 (H$_2$)	this work
			9.7 (N$_2$)	
			8.071	ref 19[b]
			9.5	ref 41
	1.6701			ref 39
1-butanol	12.3	4.8	9.1 (H$_2$)	this work
			9.1 (N$_2$)	
			9.0	ref 41
			10.8	ref 15[c]
			9.9	ref 15[d]
			9.3	ref 15[e]
			9.0	ref 15[f]
			9.6	ref 15[g]
			9.0	ref 15[h]
			9.6	ref 15[i]
			9.320	ref 15[j]
	6.0499			ref 39
2-butanol	11.6	2.7	7.6 (H$_2$)	this work
			7.5 (N$_2$)	
			10.0	ref 41
2-methyl-1-propanol	13.7	3.6	8.9 (H$_2$)	this work
			9.0 (N$_2$)	
			10.1	ref 41
	4.1334			ref 39
2-methyl-2-propanol	9.7	2.1	7.1 (H$_2$)	this work
			6.9 (N$_2$)	
			9.1	ref 41

[a] Value was discarded due to strong scattering of γ_i^∞ values. [b] Combined from both GLC and dilutor measurements. [c] Ionic liquid content of support material's mass: mass fraction $w = 0.32$; 1st run. [d] Ionic liquid content of support material's mass: $w = 0.32$; 2nd run. [e] Ionic liquid content of support material's mass: $w = 0.48$; 1st run. [f] Ionic liquid content of support material's mass: $w = 0.48$; 2nd run. [g] Ionic liquid content of support material's mass: $w = 0.48$; 3rd run. [h] Ionic liquid content of support material's mass: $w = 0.48$; 4th run. [i] Ionic liquid content of support material's mass: $w = 0.60$; 1st run. [j] Determined by calorimetry.

results (e.g., for 1-butanol in [hmim][Tf_2N], when compared to the results by Heintz et al.[15]), while in other cases there are large differences (e.g., the values reported by Mutelet et al. for [bmim][PF_6][39]). Heintz et al. attributed an uncertainty of ± 10 % to the published numbers for $\Delta H_i^{\mathrm{E},\infty}$ due to the experimental uncertainty for the limiting activity coefficient γ_i^∞.[41] Letcher and Reddy assigned an uncertainty of ± 1 $\mathrm{kJ \cdot mol^{-1}}$ to the experimental results for $\Delta H_i^{\mathrm{E},\infty}$.[17] There seems to be some tendency that increasing the chain length of an alkanol results in somewhat higher $\Delta H_i^{\mathrm{E},\infty}$ values. However, that trend proves ambiguous, but the smallest $\Delta H_i^{\mathrm{E},\infty}$ values are found for methanol and 2-methyl-2-propanol. Heintz et al. reported similar findings from their studies with [hmim][Tf_2N].[15,41] Their results are in reasonable accordance with our results, and additionally the bandwidth of the $\Delta H_i^{\mathrm{E},\infty}$ values confirms that a better accuracy is all but impossible. A more authoritative statement, however, has to rely on more data over an as well broader temperature range.

Conclusions

The (calibration-free) dilutor method was employed to measure distribution ratios at infinite dilution K_i^∞ for eight alkanol solutes in three ionic liquid solvents ([bmim][PF_6], [bmim][CH_3SO_4], and [hmim][Tf_2N]). The subsequent analysis accessed solvent density ρ_L as well the vapor pressure p_i^s and the fugacity coefficient φ_i^s of the solute and ultimately resulted in the limiting activity coefficient γ_i^∞. The limiting activity coefficients uniformly decrease with increasing temperatures for all systems. Furthermore, increasing alkyl chain length leads to higher γ_i^∞ values, but branching of the alkyl skeleton results in an opposite effect. A bit astonishing are the comparatively low γ_i^∞ values for [bmim][CH_3SO_4] compared to the other ionic liquids, but the few available literature results agree with our results. There is evidently a stronger interaction between the alkanol and the $[CH_3SO_4]^-$ anion, but also chemical interactions might be responsible for that finding. Basically, the results from the present study might provide information, whether a certain ionic liquid qualifies as a selective solvent for separation processes which at present is a matter of particular interest in chemical engineering.

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