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Activity Coefficients at Infinite Dilution in Methylimidazolium Nitrate Ionic Liquids

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Supporting Information

ABSTRACT: The paper reports infinite dilution activity coefficients of a series of polar and nonpolar solutes (alkanes, alcohols, ketones, ethers, aromatic hydrocarbons, halogenated compounds) in 1-butyl-3-methylimidazolium nitrate and 1,1-hydroxypropyl-3-methylimidazolium nitrate ionic liquids at (323, 333, and 343) K. The data were measured by gas—liquid chromatography using the ionic liquid as a stationary phase.

INTRODUCTION

The special properties of ionic liquids (ILs) such as low volatility, high solvating power, wide liquid range, high thermal stability, and high thermal and electrical conductivity have made them interesting solvents for a number of applications such as extraction, reaction media, gas absorption, electrolytes for batteries, and so forth. To evaluate the potentiality of ILs in these applications, it is necessary to know some of their thermophysical and phase equilibrium properties.

ILs with an imidazolium cation and a nitrate anion have been scarcely studied. Only a few properties are available in the literature. The density of these ILs is lower than the density of ILs of other families. For the ILs considered in this study the density values[1] at 20 °C are 1.15 $g \cdot cm^{-3}$ for 1-butyl-3-methylimidazolium nitrate ($[bmim^+][NO_3^-]$) and of 1.27 $g \cdot cm^{-3}$ for the 1-(1-hydroxypropyl)-3-methyl-imidazolium nitrate ($[HO\text{-}C_3mim^+][NO_3^-]$). The viscosity[2] and melting point[3] are higher than other ILs with the same cation and other frequently used anions. The melting point of $[\text{-}mim^+][NO_3^-]$ is much higher than those of $[\text{-}mim^+][BF_4^-]$ and $[\text{-}mim^+][Tf_2N^-]$. For example for the ILs with ethyl substituent in the cation the meltion point for the nitrate IL is of 311 K, higher than the ones of $[emim^+][BF_4^-]$ and $[emim^+][Tf_2N^-]$, (288 and 277) K, respectively. Nitrate-based ILs are completely miscible with water and are much more hygroscopic[4,5] than other imidazolium salts. They also dissolve less CO_2 than other ILs of the same family.[1,6] The nitrate-based ILs also seem to be less resistant to high temperature, since the nitrate group serves as a strong oxidizer and reacts easily with alkyl groups at elevated temperatures, producing common combustion products.[7]

These ILs have been proposed as reaction media for enzymatic reactions.[8] In 2003 Holbrey et al.[9] reported that the incorporation of a secondary hydroxyl-functionality in the cation of an imidazolium-based IL causes some interesting modifications in the properties of the corresponding ILs with an alkyl group. When heated above room temperature, there is a more rapid decrease of viscosity and increase of hydrophilicity and hygroscopicity. The hydrophilicity caused by the hydroxyl group may be advantageous for stabilizing enzymatic catalyst systems in nonaqueous IL environments and may also provide new applications in metal complexation.

In this work the activity coefficients at infinite dilution of several organic polar and nonpolar solvents in two imidazolium-based ILs with a nitrate anion, that is, 1-butyl-3-methyl-imidazolium nitrate ($[bmim^+][NO_3^-]$) and 1-(1-hydroxypropyl)-3-methyl-imidazolium nitrate ($[HO\text{-}C_3mim^+][NO_3^-]$), have been experimentally determined. Figure 1 shows the structure of both ILs.

The only data found in the literature on this family of ILs are the activity coefficients measured by Sobota et al.[10] on 1-ethyl-3-methylimidazolium nitrate.

In the present work inverse gas liquid chromatography has been applied to measure infinite dilution activity coefficients of various solutes in $[bmim^+][NO_3^-]$ and $[HO\text{-}C_3mim+][NO_3^-]$. The same method has been previously applied to other ILs by different authors.[10−13] Infinite dilution activity coefficients provide an insight on the degree of nonideality of solute—IL solutions. They

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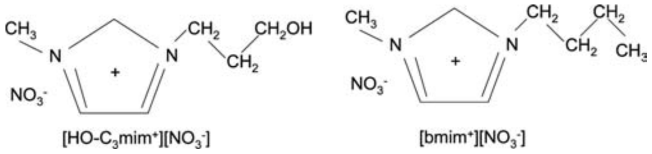

Figure 1. Structure of the ILs 1-butyl-3-methyl-imidazolium nitrate ($[bmim^+][NO_3^-]$) and 1-(1-hydroxypropyl)-3-methyl-imidazolium nitrate ($[HO\text{-}C_3mim^+][NO_3^-]$).

provide useful information to identify the potential of ILs for solvent-aided separation processes[10] and can also be used to adjust parameters of thermodynamic models.[14]

EXPERIMENTAL SECTION

Materials. The ILs were synthesized at the Laboratory of Biocatalysis and Organic Chemistry of Delft University of Technology. The synthesis procedure has been extensively described in a previous publication.[6] The purity of the ILs was analyzed with ^1H NMR and ^{13}C NMR at a frequency of 300.2 MHz using deuterated chloroform as solvent and tetramethylsilane (TMS) as reference in the case of $BmimNO_3$ and heavy water as solvent and *tert*-butyl alcohol (*t*-BuOH) as reference, in the Unity Inova 300 s of Varian. The spectra are shown in the Supporting Information. They present the characteristic peaks from the cationic structures of both ILs without showing peaks from impurities.

The solutes were chromatographic or reagent grade compounds. Since gas—liquid chromatography is itself a separation technique, the experimental results are not influenced by small solute impurities.[15]

Experimental Procedure. The infinite dilution activity coefficients were measured by inverse gas chromatography.[16] Details of the experimental technique are given in previous publications.[17,18]

A series of chromatographic columns were prepared using each IL as stationary phase, and the retention times of different solutes in these chromatographic columns were measured. In the case of $[HO\text{-}C_3mim^+][NO_3^-]$, different columns were prepared, containing untreated and vacuumed IL. Previous to the preparation of the chromatographic columns, the ILs were dried at room temperature for 36 h in a Liofilizator (TRIFICOR) under a vacuum of 0.09 mmHg. The water content was determined by a Karl Fisher titrator (Mettler DL18).

The specific retention volume (V_g^0) at 273.15 K (i.e., the normalized volume of carrier gas necessary to elute solute i out of a column with a mass M_s of the IL solvent) is calculated from the measured retention time t_i of solute i as shown in eq 1.[19]

$$V_g^0 = (t_i - t_a)\cdot F\cdot(273.15/T_f)\cdot((P_f - P_w^s)/P_o)\cdot J_3{}^2/M_S \quad (1)$$

where t_a is the inert gas retention time; F is the carrier gas flow, measured at temperature T_f and pressure P_f in a soap-film meter; $P_w{}^S$ is the saturated vapor pressure of water at T_f; P_o is the pressure at the column exit; and $J_3{}^2$ is the James—Martin correction factor for pressure gradient and gas compressibility inside the column.[20]

Equation 2 gives the thermodynamic relationship between the retention volume ($V_g{}^0$) and the infinite dilution activity coefficient ($\gamma_i{}^\infty$) of solute i in solvent s:[19]

$$\ln \gamma_i^\infty = \ln(R\cdot 273.15/(M_S\cdot P_i^s\cdot V_g^0))\cdot(B_{ii} - v_i)\cdot P_i^s/(R\cdot T) \quad (2)$$

In this expression, the virial equation of state is used to correct the nonideality of the gas phase. B_{ii}, v_i, and P_i^S represent, respectively, the second virial coefficient, the liquid molar volume, and the vapor pressure of solute i at column temperature T; R is the universal gas constant; and M_S is the molecular weight of the solvent. For all of the solutes studied in this work, Hayden—O'Connell model was used to calculate second virial coefficients; saturation pressures were obtained from the Antoine equation, and liquid molar volumes from the correlation of Yen-Woods.[21]

A Varian (model: Star 3400 Cx) gas chromatograph with a TCD detector and a Hewlett-Packard (model: 3392) integrator were used in the measurements. The carrier gas was hydrogen, flowing at (20 to 30) $cm^3\cdot min^{-1}$. A soap-film meter was used to measure the gas flow rates. The value of the atmospheric pressure and the pressure drop inside the column ($4\cdot 10^4$ to $5\cdot 10^4$ Pa) were determined with a quartz transducer (Paroscientific). Temperatures were measured with a platinum resistance thermometer (Systemtechnik AB S1220). Hamilton 25 μL syringes were used to inject the solutes into the carrier gas.

The stationary phase for each chromatographic column was prepared by dissolving weighed amounts of solvent (IL) and inert support (Chromosorb W, 60/80 mesh) in methanol, at different chromosorb/IL mass ratios. Methanol was then evaporated from the solution in an inert atmosphere, using a rotoevaporator. Chromatographic columns 2 m long were prepared by packing stainless steel tubing (1/8 in. outside diameter) with each stationary phase. The amount of ILs in the solid support ranged from (0.84 to 1.41) g ((20 to 35) by mass).

The retention time of a selected solute (hexane for $[bmim^+][NO_3^-]$ and methanol for $[HO\text{-}C_3mim^+][NO_3^-]$) was measured systematically every 2 h to check for the stability of the experimental conditions.

From a propagation of error analysis the $\gamma_i{}^\infty$ values reported are estimated to be accurate within ± 5 %. This error was calculated on the basis of the following absolute deviations in the measured variables: (± 13 Pa for column pressure drop, ± 0.7 $cm^3\cdot min^{-1}$ for the carrier gas flow, ± 0.1 K for temperatures, ± 0.002 g for the solvent mass in the column, and ± 0.12 s for the retention times).

RESULTS AND DISCUSSION

The activity coefficients of several polar and nonpolar organic solutes in the ILs $[HO\text{-}C_3mim^+][NO_3^-]$ and $[bmim^+][NO_3^-]$ are respectively listed in Tables 1 and 2. For $[HO\text{-}C_3mim^+][NO_3^-]$, two sets of measurements were performed. The first set corresponds to a stationary phase prepared with undried IL having a water content of 1.1123 % in mass fraction, and the second one with IL dried up to a water content of 0.248 % in mass fraction. For some of the polar and nonpolar solutes, the measurements were repeated in both stationary phases. The results reported in Table 1 show a small influence of the water content in the infinite dilution activity coefficient values, in general lower than the experimental uncertainty (± 5 %).

Columns with different IL loadings ((20 to 35) % by mass) were prepared to check for adsorption effects. The dispersion in the $\gamma_i{}^\infty$ values measured in these columns lay within the experimental uncertainty. In general the $\gamma_i{}^\infty$ values were higher in the columns with lower IL loading. If adsorption effects were present, the opposite behavior would have been observed.

The values for $[bmim^+][NO_3^-]$ are consistent with those reported in the literature[10] for 1-ethyl-3-methyl-imizazolium nitrate. Figure 2 shows experimental infinite dilution activity coefficients of heptane and cyclohexane in various 1-alkyl-3-methyl

Table 1. Infinite Dilution Activity Coefficients in [HO-C$_3$mim$^+$][NO$_3^-$]

	γ_i^{∞} (water, w = 0.011123)			γ_i^{∞} (water, w = 0.00248)		
solute	T/K = 323	T/K = 343	T/K = 363	T/K = 323	T/K = 343	T/K = 363
decane	828.5	871.9	878.4			
dodecane	1208.8	1199.1	1144.8			
benzene	6.57	6.72	6.86	6.46	6.67	
toluene	12.65	12.79	13.07	12.1	11.48	12.64
methanol	0.69	0.68	0.68	0.62	0.65	0.66
ethanol	1.41	1.33	1.28	1.27	1.26	1.25
1-propanol	2.3	2.16	2.08			
2-propanol	2.36	2.29	2.21			
chloroform	1.54	1.85	2.16			
1,2-dichloroethane	3.03	3.18	3.5	2.97	3.15	3.43
trichloroethylene	9.13	9.67	10.47		9.63	10.24
ethyl acetate	9.52	10.04	10.15	9.23	9.61	9.95
methyl ethyl ketone	4.76	5.15	5.1			
ethyl benzene	26.31	25.89	24.97	25.52	24.62	24.59
acetone	2.72	2.84	2.85	2.58	2.79	2.78

Table 2. Infinite Dilution Activity Coefficients in [bmim$^+$][NO$_3^-$]

	γ_i^{∞}		
solute	T/K = 323	T/K = 343	T/K = 363
hexane	122.92		62.52
heptane	179.22	110.81	92.03
cyclohexane	53.78		42.57
isooctane	205.48	132.51	115.93
benzene	3.52		2.99
toluene	5.18		4.82
1-hexene	51.45		44.22
methanol	0.47		0.46
ethanol	0.78		0.72
1-propanol	0.96	0.90	0.90
2-propanol	1.06		1.06
chloroform	0.52	0.63	0.76
1,2-dichloroethane	1.38	1.45	1.59
trichloroethylene	2.76	3.01	3.33
ethyl acetate	4.54	4.58	5.05
methyl ethyl ketone	2.58	2.57	2.66
ethyl benzene	8.19	7.78	7.19
acetone	2.14		1.93
carbon tetrachloride	3.60	4.00	4.59

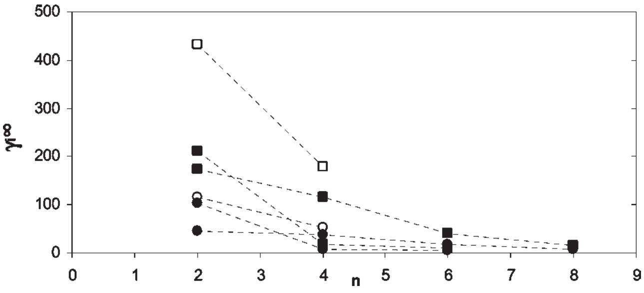

Figure 2. Infinite dilution activity coefficients of heptane and cyclohexane in various 1-alkyl-3-methyl-imidazolium ILs, as a function of the number of carbon atoms in the alkyl change. Symbols: heptane in □, [-mim$^+$][NO$_3^-$]; gray ■, [-mim$^+$][Tf2N$^-$]; ■, [-mim$^+$][BF4$^-$]; cyclohexane in ○, [-mim$^+$][NO$_3^-$]; gray ●, [-mim$^+$][Tf2N$^-$]; ●, [-mim$^+$][BF4$^-$]. Data source: [emim$^+$][NO$_3^-$], ref 10; [-mim$^+$][BF$_4^-$], ref 11; [-mim$^+$][Tf$_2$N$^-$], ref 12, 13, and 21; [bmim$^+$][NO$_3^-$], this work.

imidazolium ILs having NO$_3$, BF$_4$, and Tf$_2$N anions, as a function of the number of carbon atoms in the alkyl chain. The γ_i^{∞} values measured by Sobota et al.[10] for [emim$^+$][NO$_3^-$] and those obtained in this work for [bmim$^+$][NO$_3^-$] seem to follow the general tendency found in the ILs with [BF$_4^-$][11] and [Tf$_2$N$^-$] anions;[12,13,22] that is, the γ_i^{∞} values decrease as the length of the IL alkyl chain increases. The high γ_i^{∞} values of alkanes indicate low solubility in the ILs and weak solute—IL interactions. Cyclic alkanes, alkenes, and aromatic molecules interact more strongly with the ILs, as indicated by the lower γ_i^{∞} values. Polar and associating compounds, such as alcohols and chloroform, show the strongest solute—IL interactions, causing even negative deviations to Raoult's law. For a given family of solutes, the γ_i^{∞} values increase with the increasing number of carbon atoms in the solute molecule.

For most of the solutes studied the change of γ_i^{∞} with temperature was rather small. This implies low values of the solute partial molar excess enthalpy at infinite dilution and suggests a predominance of entropic effects.

■ CONCLUSIONS

Infinite dilution activity coefficients were measured for a series of polar and nonpolar organic solutes in two different 3-methylimidazolium nitrate ILs: 1-butyl-3-methyl-imidazolium nitrate and 1-(1-hydroxypropyl)-3-methyl-imidazolium nitrate.

Water content of up to 1.1 mass % in the ILs seems to have a negligible effect on the values of the infinite dilution activity coefficients. The differences found in using dried and undried ILs lay within the experimental uncertainty.

The results obtained are consistent with γ_i^{∞} values found in the literature for 1-ethyl-3-methyl-imizazolium nitrate and follow a behavior similar to that observed in other imidazolium-based ILs.

The specific interactions that these ILs exhibit with different families of solutes make them potentially attractive solvents for separation processes. Even when ILs of this family have been proven to be excellent media for homogeneous enzymatic catalysts, according to the obtained results, this homogeneous process will only be possible when the substrates poses a certain polarity that make them soluble in the IL media.

ASSOCIATED CONTENT

S Supporting Information. ^{13}C and ^{1}H NMR spectra data of the ILs. This material is available free of charge via the Internet at http://pubs.acs.org.

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