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Gas permeabilities, solubilities, diffusivities, and diffusivity correlations for ammonium-based room temperature ionic liquids with comparison to imidazolium and phosphonium RTIL data

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ABSTRACT

Like our previous work with imidazolium- and phosphonium-based ionic liquids, we report diffusivities over a range of viscosities (71–532 cP) and develop a predictive diffusivity correlation. Reported are the permeability, solubility, and diffusivity data for nine gases in nine ammonium RTILs liquids at 30 °C, as determined with a lag-time technique. The gas solubilities and diffusivities of the ammonium RTILs are of the same magnitude as those for the phosphonium and imidazolium RTILs. The ammonium RTILs used, in this study, included cations with both *N*-alkyl groups and branched alkyl groups. We also report on ammonium-based RTILs derived from quaternary ammonium surfactants. These surfactants-derived ammonium-based RTILs offer a relatively inexpensive alternative to imidazolium-based RTILs. We compare and contrast the thermodynamic (solubility) and transport (diffusivities) phenomena in the ammonium-based RTILs with both the imidazolium and the phosphonium RTILs in the context of being working fluids in a chemical process. From this comparison came certain "universal" trends for diffusivity in RTILs. Specifically, diffusivity scales roughly with the inverse of the square-root of viscosity and inversely with solute molar volume to the power of 1–1.3. This means that diffusivity, in RTILs, is less dependent on viscosity, and more dependent on solute size than predicted by the conventional Stokes–Einstein model. The gases tested were carbon dioxide, nitrogen, oxygen, methane, ethylene, propylene, 1-butene, butane, and 1,3-butadiene.

1. Introduction

This paper is the continuation of transport phenomena studies in room temperature ionic liquids (RTILs). In our previous work we measured transport in imidazolium-based [1] and phosphonium-based RTILs [2]. We reported thermodynamic and transport properties such as Henry's law constant and gas diffusivities. The gas permeabilities of imidazolium-based and phosphonium-based RTILs were similar with the exception that the imidazolium CO_2-permeabilities are significantly higher than the phosphonium ones. The gas solubilities and diffusivities of the phosphonium-based and the imidazolium-based RTILs were of the same order of magnitude. Strong correlations were found for gas diffusion in imidazolium-based ($r^2 = 0.97$) and phosphonium-based ($r^2 = 0.92$) ionic liquids. Both, imidazolium-based and phosphonium-based RTILs had similar diffusivity correlations with respect to viscosity and gas molar volumes.

The objective of our present work is to further our research into using RTILs as separating agents and support media for chemical reactions. We will report diffusivities, permeabilities, solubilities, and Henry's law constant for ammonium-based ionic liquids over a range of viscosities (71–532 cP). The molecular weight range for the tested ammonium-based ionic liquids was 396.4–648.8. We will develop a predictive diffusivity correlation for ammonium-based ionic liquids. There is a need for this correlation because the assumptions for classical models developed by Stokes–Einstein or Wilke–Chang do not fit the physical characteristics of RTILs [1]. There were two motivations for the present work. The first one is to make available transport properties for an economical alternative to imidazolium-based RTILs. Ammonium-based ionic liquids cost 20% of the cost of the imidazolium-based RTILs ($2/g versus $10/g for RTILs consisting of the Tf_2N anion, based on 0.5–1 kg laboratory-scale purchases or synthesis by our laboratory; however, economy of scale should apply for commercial quantities). The second motivation is the possible electrochemical applications for these RTILs, because of their physical properties like conductivity and non-volatility [3]. We will compare and contrast the thermodynamic and transport phenomena properties of the ammonium-based ionic liquids with the two previously studied RTIL classes.

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Nomenclature

A	nominal membrane area
D_i	diffusivity
L	membrane or film thickness
P_i	gas partial pressure
R	ideal gas constant
S_i	solubility
T	system temperature
V_i	molar volume
V_L	permeate chamber volume
τ	tortuosity
ϕ	porosity
μ_i	viscosity

Subscripts

0	at the membrane feed interface
L	at the membrane permeate interface
1	solute
RTIL	solvent

The ammonium-based RTILs in this study had three root cations. Two of RTILs tested had cations of the form $[N_{(1)RRR}{}^{+}]$ were R was either equal to 4 or 8. These two RTILs, therefore, had bulky cations similar to those found in phosphonium-based RTILs. The second root was of the form $[N_{(R)113}{}^{+}]$, where “3” refers to an isopropyl group and R was equal to 4, 6, or 10. The third root was of the form $[N_{(R)111}{}^{+}]$, were R was equal to 4, 6, 8, 10, 12, and 14. RTILs in this study with this cation root were liquids at 25 °C for $R \leq 10$. $[N_{(R)111}{}^{+}]$-based RTILs with $R \geq 8$ can be made from surfactants. While we synthesized $[N_{(R)111}{}^{+}]$-based RTILs for R equal to 6, 8, 10, 12, and 14, we report on dissolved gas transport/thermodynamic properties in only those with R equal to 4, 6, and 10. All of the ammonium-based RTILs tested contained the counter anion of bis(trifluoromethyl)sulfonyl)imide, $[Tf_2N^-]$.

A number of other researchers have studied gas diffusivity in RTILs include carbon dioxide [4,5], hydrocarbons in imidazolium-based RTILs [5], and refrigerants [6]. To the best of our knowledge there are no published studies of gas diffusivity in ammonium-based RTILs.

2. Experimental material and procedures

2.1. Materials

To eliminate free convection during diffusion measurements, glass fiber disk filters (Pall P/N 66209) were used to immobilize the RTILs. These filters have a thickness of 660 μm, pore size of 1 μm, and 90% porosity. The membranes formed by the disk filters and the RTILs were backed with hydrophobic porous PTFE (Pall P/N P5PQ047), pore size 0.5 μm for mechanical support. The area of the membranes was 9.6 cm^2. Ultrahigh purity carbon dioxide, nitrogen, methane, and oxygen were obtained from NexAir (Memphis, TN). Butane and the alkenes (ethylene, propylene, 1-butene, and 1,3-butadiene) used in this study were either obtained from Conley Gas (La Porte, TX) or Specialty Gases of America (Toledo, OH).

Table 1 contains a list of ionic liquids tested in this study. Trimethyl(butyl)ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(4)111}{}^{+}][Tf_2N^-]$ was obtained from Ionic Liquid Technologies (Germany); trimethyl(hexyl)ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(6)111}{}^{+}][Tf_2N^-]$, trimethyl(decyl) ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(10)111}{}^{+}][Tf_2N^-]$, and triethyl(hexyl)ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(6)222}{}^{+}][Tf_2N^-]$ were in-house manufactured (Ole Miss); dimethyl(butyl(*i*-propyl)ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(4)113}{}^{+}][Tf_2N^-]$, dimethyl (hexyl(*i*-propyl)ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(6)113}{}^{+}][Tf_2N^-]$, dimethyl(decyl(*i*-propyl)ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(10)113}{}^{+}][Tf_2N^-]$, and trioctyl(methyl) ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(1)888}{}^{+}][Tf_2N^-]$ were obtained from Oak Ridge National Laboratories (ORNL, Dr. Gary A. Baker); tributyl(methyl)ammonium bis(trifluoromethyl)sulfonyl)imide $[N_{(1)444}{}^{+}][Tf_2N^-]$ was obtained from the Department of Chemistry and Biochemistry at the University of Mississippi (Dr. Charles Hussey). The subscript numbers in the ionic liquid notation indicate the number of carbon atoms in the alkyl group of the ammonium cation.

Kilaru et al. [7] give details on the synthesis methods for the in-house and ORNL RTILs. Table 1 also contains the molar volume, viscosity, and halide (as chloride) content of the RTILs used in this study; all of these properties were measured according to the procedures detailed in ref. [7] (molar volume), ref. [8] (halide content), and ref. [9] (viscosity). It is important to say that the $N_{(R)111}$ RTILs, with $R \geq 8$, were made from surfactants. The $N_{(R)111}$ RTILs with alkyl chains of 10 or less carbons ($R \leq 10$) are liquids at 25 °C; the alkyl chain of 12 carbons ($R = 12$) melts at approximately 38 °C, and the alkyl chains of 14 carbons ($R = 14$) melts at approximately 45 °C.

2.2. Diffusivity measurement procedure

A lag-time technique measured the permeabilities, diffusivities, and the solubilities of the gases in the RTILs. Morgan et al. [1] describe in detail this technique and validation of the analytical method. The following is a brief summary of the apparatus and the experimental technique. The technique analyzes the transient and steady-state permeation through an immobilized RTIL membrane. By doing this dual analysis, we are able to separate permeability in its components; solubility and diffusivity. The procedure is to

Table 1
Physical properties of ammonium-based ionic liquids (Kilaru et al. [7–9]).

Ionic liquid	Chemical formula	Molar volume (cm^3/mol)	Viscosity at 30 °C (cP)	Chloride content (wt%)[a]
$[N_{(4)111}{}^{+}]$ $[Tf_2N^-]$	$[(CH_3)_3(C_4H_9)N^+][(CF_3SO_2)_2N^-]$	289.6	71	<0.03 (unknown)
$[N_{(6)111}{}^{+}]$ $[Tf_2N^-]$	$[(CH_3)_3(C_6H_{13})N^+][(CF_3SO_2)_2N^-]$	324.5	100	<0.03 (bromide)
$[N_{(10)111}{}^{+}]$ $[Tf_2N^-]$	$[(CH_3)_3(C_{10}H_{21})N^+][(CF_3SO_2)_2N^-]$	393.2	173	<0.03 (bromide)
$[N_{(4)113}{}^{+}]$ $[Tf_2N^-]$	$[(CH_3)_2(C_3H_7)(C_4H_9)N^+][(CF_3SO_2)_2N^-]$	315.4	85	<0.01 (bromide)
$[N_{(6)113}{}^{+}]$ $[Tf_2N^-]$	$[(CH_3)_2(C_3H_7)(C_6H_{13})N^+][(CF_3SO_2)_2N^-]$	353.1	126	<0.05 (bromide)
$[N_{(10)113}{}^{+}]$ $[Tf_2N^-]$	$[(CH_3)_2(C_3H_7)(C_{10}H_{21})N^+][(CF_3SO_2)_2N^-]$	424.6	183	<0.05 (bromide)
$[N_{(1)444}{}^{+}]$ $[Tf_2N^-]$	$[(C_4H_9)_3(CH_3)N^+][(CF_3SO_2)_2N^-]$	383.5[b]	386[b]	<0.03 (chloride)[c]
$[N_{(1)888}{}^{+}]$ $[Tf_2N^-]$	$[(C_8H_{17})_3(CH_3)N^+][(CF_3SO_2)_2N^-]$	600.6	532	0.38 (iodide)
$[N_{(6)222}{}^{+}]$ $[Tf_2N^-]$	$[(C_2H_5)_3(C_6H_{13})N^+][(CF_3SO_2)_2N^-]$	365.8	167	<0.03 (iodide)

[a] Halide content reported using the unit “Halide as mg-Cl/mg”, calculated from the relation (moles of halide detected) × (molecular weight of chloride)/(mass of RTIL tested) × 100. The probable halide impurity is indicated next to the reported value.

[b] Ref. [3].

[c] Data from this work.

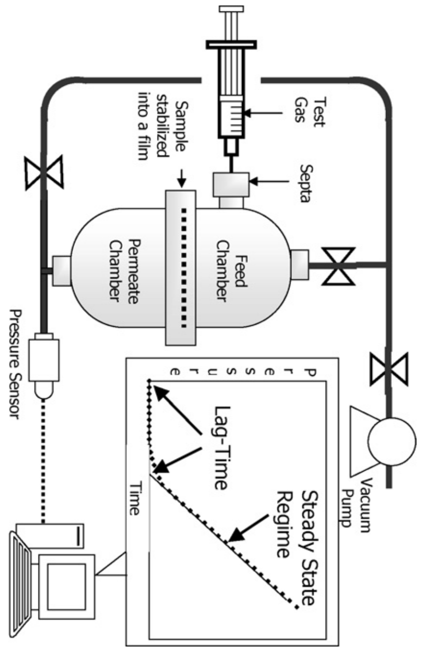

Fig. 1. Sketch of the lag-time experimental set-up. The insert indicates the typical pattern of the permeation data, showing both the lag-time and steady-state regime.

immobilize the ionic liquid into the glass fiber disk filters; this eliminates free convection. Fig. 1 shows a schematic of the diffusion cell experimental set-up. The equipment consist of an in-house manufactured stainless steel dual chamber mounted in a thermally control insulated box. The feed (upper) and permeate (lower) chamber are separated by the RTIL stabilized in the glass fiber disk. The feed chamber has septa port for receiving the gas tested. We filled a 10 mL syringe with the gas to be tested and left this syringe inside the thermally control insulated box for a period of 10–20 min. After the syringe had the same temperature of the system (30 °C), we proceeded to make a 5 mL injection. We started to record the data for period of 120–360 min depending on the gas being tested. A 0–34.5 kPa (0–5 psia) gas transducer measured the gas permeation by monitoring the pressure increase in the permeate chamber.

The lag-time technique assumes that transport through an immobilized RTIL membrane occurs by a solution-diffusion mechanism [1]. The steady-state regime of the permeation data has the following expression [1] for the pressure rise in the permeate chamber with time t:

$$P_{iL} = \frac{\phi}{\tau}\frac{D_iART}{LV_L}P_{i0}S_i\left(t - \frac{L^2\tau^2}{6D_i}\right) \qquad (1)$$

The quantity $(L^2\tau^2)/(6D_i)$ is the lag time, and this simple linear expression allows for the determination of both the solubility and the diffusivity by computing the slope and the abscissa intercept from the experimental permeation data. Here D_i is the gas diffusivity, ϕ is the porosity of the glass support, τ is the tortuosity of the glass support, L is the film thickness, P_{i0} is the initial gas partial pressure in the feed chamber, P_{iL} is the gas partial pressure in the permeate chamber at time t, S_i is the gas solubility (in mol/L atm), V_L is the permeate chamber volume, A is the nominal membrane area, R is the ideal gas constant, and T is the system temperature.

3. Results and discussions

3.1. Gas permeabilities

Table 2 contains the gas permeabilities for the ammonium-based RTILs tested. The ammonium-based RTILs gas permeabilities have similar magnitudes as the previously tested imidazolium-based [1] and phosphonium-based RTILs. [2] The permeabilities of carbon dioxide (CO_2) are an exception, however. The CO_2-permeabilities in the ammonium-based RTILs are similar to the permeability values for phosphonium-based RTILs reported by Ferguson and Scovazzo [2]; and significantly less (averages in barrers, 700 versus 1100) than the respective values for imidazolium-based RTILs reported by Morgan et al. [1]. The CO_2/N_2 and CO_2/CH_4 selec-

Table 2

Permeabilities and selectivities for several gases in ammonium ionic liquids at 30 °C. The listed uncertainties are the standard error resulting from averaging three or more experimental runs.

	Permeability (mL (STP)/(cm s mmHg)) × 10^9 = 1 barrer								
Gas	$[N_{(4)111}{}^+]$ $[Tf_2N^-]$	$[N_{(6)111}{}^+]$ $[Tf_2N^-]$	$[N_{(10)111}{}^+]$ $[Tf_2N^-]$	$[N_{(4)113}{}^+]$ $[Tf_2N^-]$	$[N_{(6)113}{}^+]$ $[Tf_2N^-]$	$[N_{(10)113}{}^+]$ $[Tf_2N^-]$	$[N_{(1)444}{}^+]$ $[Tf_2N^-]$	$[N_{(1)888}{}^+]$ $[Tf_2N^-]$	$[N_{(6)222}{}^+]$ $[Tf_2N^-]$
Oxygen	98 ± 23	97 ± 4.5	106 ± 11	82 ± 2	83 ± 9	96 ± 4	74 ± 2	116 ± 4	68 ± 2
Nitrogen	41 ± 1	46.2 ± 0.25	53.9 ± 5	NA	44 ± 5	68 ± 13	35 ± 3	55 ± 4	32 ± 3
Carbon dioxide	831 ± 15	943 ± 55	800 ± 29	724 ± 6	619 ± 11	633 ± 13	524 ± 9	619 ± 51	630 ± 10
Methane	63 ± 2	102 ± 8	105 ± 2	69 ± 0.7	74 ± 16	114 ± 3	69 ± 3	139 ± 6	64 ± 4.3
Ethylene	217 ± 25	294 ± 2	320 ± 7	243 ± 9	249 ± 26	303 ± 34	NA	361 ± 16	227 ± 6.7
Propylene	389 ± 36	488 ± 19	656 ± 21	434 ± 6	417 ± 9	493 ± 77	334 ± 5	685 ± 35	417 ± 32
1,3-butadiene	1077 ± 76	1370 ± 170	1653 ± 141	1843 ± 20	1550 ± 60	2096 ± 97	1269 ± 15	1947 ± 415	1179 ± 34
1-butene	461 ± 34	471 ± 78	846 ± 30	576 ± 13	563 ± 32	849 ± 97	424 ± 9	1156 ± 100	499 ± 39
Butane	264 ± 61	435 ± 10	715 ± 46	342 ± 12	356 ± 24	NA	NA	795 ± 59	371 ± 17
	Selectivity								
CO_2/N_2	21	20	15	NA	14	9.4	15	11	20
CO_2/CH_4	13	9.2	7.6	11	8.4	5.5	7.6	4.5	9.8
1,3-butadiene/butane	4.1	3.2	2.3	5.4	4.4	NA	NA	2.5	3.2
1-butene/butane	1.8	1.1	1.2	1.7	1.6	NA	NA	1.5	1.4

NA = not available.

tivities for the ammonium-based RTILs are between those reported for the imidazolium-based RTILs [1] and phosphonium-based RTILs [2] (imidazolium > ammonium > phosphonium). This trend is consistent with the trend predicted by Camper et al. [10], as the molar volume increases the selectivity decreases.

For alkene/alkane separations the imidazolium-based RTILs appear to have an advantage over the phosphonium-RTILs report in our work. The 1-butene/butane selectivities for the ammonium-based RTILs are less than the imidazolium values reported by Camper et al. [11] with average values of 1.44 versus 1.96. Likewise, the butadiene/butane selectivities for the ammonium-based RTILs are less than the imidazolium values reported by Camper et al. [11] with average values of 3.56 versus 5.28.

3.2. *Gas solubilities*

With the exceptions of the alkane solubilities and the $[N_{(1)444}{}^{+}][Tf_2N^{-}]$ data, we previously published the CO_2 and the alkene gas solubilities in ammonium-based RTILs discussed below in Kilaru et al. [12]; however, for the reader's convenience they also appear in Tables 3 and 4. Tables 3 and 4 contain the experimental solubilities and Henry's law data, respectively, for ammonium-based RTILs at 30 °C. The gas solubilities (in mol/L atm) of the ammonium-based RTILs are of the same magnitude as gas solubilities for the previous tested RTILs as reported by Morgan et al. [1] and Ferguson and Scovazzo [2]. The Henry's law constant of ammonium-based RTILs, however, are approximately twice the respective values for phosphonium-based RTILs reported by Ferguson and Scovazzo [2] and half the respective values for imidazolium-based RTILs reported by Camper et al. [11]. The difference in Henry's Law reflects the general difference in molar volumes between the classes of RTILs and does not indicate any order of magnitude difference in the capacity of different classes of RTILs to dissolve gases as indicated by the gas solubilities in Table 3 reported on a volume basis. We observed, one more time, that the exception to this discussion is CO_2, which have similar Henry's law constants for imidazolium, phosphonium, and ammonium RTILs.

Hydrocarbon solubility in ammonium-based RTILs follows the same trend followed in imidazolium-based [1] and phosphonium-based RTILs, [2] the solubility increases as the number of solute carbons increases. Hydrocarbon solubility also increases as the number of carbon double bonds increases in hydrocarbon solutes with the same number of carbons. Based on mol/L atm, the hydrocarbon solubility trend in ammonium-based RTILs is between the imidazolium-based and phosphonium-based RTILs previously tested (phosphonium > ammonium > imidazolium). Based on mol/mol, the hydrocarbon solubility trend in ammonium-based RTILs is also between the imidazolium-based and phosphonium-based RTILs previously tested (phosphonium > ammonium > imidazolium).

3.3. *Gas diffusivities*

Table 5 contains the experimental gas diffusivities at 30 °C for the ammonium-based RTILs. The majority of the data is of the same order of magnitude (10^{-6} cm^2/s) as imidazolium-based and phosphonium-based RTILs. The RTIL gas diffusivities in all three classes of RTILs are generally an order of magnitude slower than in conventional solvents such as water, short chain alcohols, and low molecular weight hydrocarbons [1].

Fig. 2 contains a log–log plot of the measured diffusivities versus viscosities of the imidazolium-based, phosphonium-based, and ammonium-based RTILs. The viscosity range of the tested ammonium-based RTILs is between the previously tested imidazolium-based and phosphonium-based RTILs (imidazolium < ammonium < phosphonium). Ammonium-based RTILs

Table 3

Solubilities of several gases in ammonium ionic liquids at 30 °C (from Kilaru et al. [12] unless footnoted). The listed uncertainties are the standard errors resulting from averaging three or more experimental runs.

Gas	Solubility (mol/L atm)								
	$[N_{(4)111}{}^{+}]$ $[Tf_2N^{-}]$	$[N_{(6)111}{}^{+}]$ $[Tf_2N^{-}]$	$[N_{(10)111}{}^{+}]$ $[Tf_2N^{-}]$	$[N_{(4)113}{}^{+}]$ $[Tf_2N^{-}]$	$[N_{(6)113}{}^{+}]$ $[Tf_2N^{-}]$	$[N_{(10)113}{}^{+}]$ $[Tf_2N^{-}]$	$[N_{(1)444}{}^{+}]$ $[Tf_2N^{-}]$[a]	$[N_{(1)888}{}^{+}]$ $[Tf_2N^{-}]$	$[N_{(6)222}{}^{+}]$ $[Tf_2N^{-}]$
Oxygen[a]	ND	NQ	NQ	ND	ND	NQ	0.012 ± 0.004	NQ	ND
Nitrogen[a]	ND	ND	ND	N/A	ND	ND	0.014 ± 0.005	ND	ND
Carbon dioxide	0.058	0.073 ± 0.004[a]	0.059	0.051	0.057	0.057	0.053 ± 0.005	0.062	0.048
Methane[a]	NQ	NQ	0.014 ± 0.004	NQ	0.023 ± 0.008	NQ	0.020 ± 0.006	ND	NQ
Ethylene	0.032	0.032	0.036	0.031	NQ	0.034	N/A	0.046	0.042
Propylene	0.077	0.120	0.094	0.074	0.089	0.099	0.130 ± 0.002	0.148	0.091
1,3-Butadiene	0.188	0.218	0.214	0.29	0.25	0.346	0.380 ± 0.010	0.28	0.27
1-Butene	0.114	0.114	0.173	0.15	0.14	0.19	0.230 ± 0.006	0.29	0.17
Butane[a]	0.077 ± 0.004	0.145 ± 0.010	0.185 ± 0.023	0.110 ± 0.012	0.120 ± 0.017	N/A	N/A	0.270 ± 0.021	0.146 ± 0.021

[a] Data from this work. ND = non-detectable, NQ = non-quantifiable, NA = not available.

Table 4
Henry's law constants for several gases in ammonium ionic liquids at 30 °C, calculated from Kilaru et al. [12] unless footnoted. The listed uncertainties are the standard errors resulting from averaging three or more experimental runs.

	Henry's law constant (atm)								
Gas	$[N_{(4)111}^+]$ $[Tf_2N^-]$	$[N_{(6)111}^+]$ $[Tf_2N^-]$	$[N_{(10)111}^+]$ $[Tf_2N^-]$	$[N_{(4)113}^+]$ $[Tf_2N^-]$	$[N_{(6)113}^+]$ $[Tf_2N^-]$	$[N_{(10)113}^+]$ $[Tf_2N^-]$	$[N_{(1)444}^+]$ $[Tf_2N^-]$[a]	$[N_{(1)888}^+]$ $[Tf_2N^-]$	$[N_{(6)222}^+]$ $[Tf_2N^-]$
Oxygen[a]	ND	NQ	NQ	ND	ND	NQ	218 ± 72	NQ	ND
Nitrogen[a]	ND	ND	ND	N/A	ND	ND	187 ± 70	ND	ND
Carbon dioxide	60	43 ± 2[a]	44	63	51	42	50 ± 5	28	58
Methane[a]	NQ	NQ	180 ± 50	NQ	125 ± 50	NQ	131 ± 38	ND	NQ
Ethylene	108	99	73	104	NQ	70	N/A	37	65
Propylene	46	27	28	44	33	25	21 ± 0.2	12	31
1,3-Butadiene	19	15	13	12	12	7.8	7.9 ± 0.2	6.9	11
1-Butene	31	28	16	22	21	13	12 ± 0.3	6.8	17
Butane[a]	46 ± 2	22 ± 1	15 ± 2	30 ± 3	25 ± 3	N/A	N/A	7.2 ± 0.5	20 ± 3

[a] Data from this work. ND = non-detectable, NQ = non-quantifiable, NA = not available.

Table 5
Diffusivities of several gases in phosphonium ionic liquids at 30 °C. The listed uncertainties are the standard errors resulting from averaging three or more experimental runs.

	Diffusivity $(cm^2/s) \times 10^6$								
Gas	$[N_{(4)111}^+]$ $[Tf_2N^-]$	$[N_{(6)111}^+]$ $[Tf_2N^-]$	$[N_{(10)111}^+]$ $[Tf_2N^-]$	$[N_{(4)113}^+]$ $[Tf_2N^-]$	$[N_{(6)113}^+]$ $[Tf_2N^-]$	$[N_{(10)113}^+][Tf_2N^-]$	$[N_{(1)444}^+]$ $[Tf_2N^-]$	$[N_{(1)888}^+]$ $[Tf_2N^-]$	$[N_{(6)222}^+]$ $[Tf_2N^-]$
Oxygen	NQ	NQ	NQ	NQ	NQ	NQ	2.29 ± 0.72	NQ	NQ
Nitrogen	NQ	NQ	NQ	NQ	NQ	NQ	0.90 ± 0.22	NQ	NQ
Carbon dioxide	4.87 ± 0.48	4.38 ± 0.26	4.60 ± 0.31	4.83 ± 0.23	3.72 ± 0.12	3.78 ± 0.33	3.41 ± 0.31	3.43 ± 0.38	4.68 ± 1.10
Methane	NQ	NQ	2.64 ± 0.65	NQ	1.22 ± 0.47	ND	1.21 ± 0.29	ND	NQ
Ethylene	2.29 ± 0.26	3.19 ± 0.32	3.07 ± 0.24	2.67 ± 0.22	NQ	3.44 ± 1.40	N/A	2.70 ± 0.22	1.90 ± 0.45
Propylene	1.73 ± 0.15	1.39 ± 0.13	2.37 ± 0.17	2.02 ± 0.35	1.59 ± 0.07	1.73 ± 0.28	0.90 ± 0.008	1.58 ± 0.05	1.56 ± 0.10
1,3-Butadiene	1.95 ± 0.09	2.14 ± 0.08	2.63 ± 0.10	2.13 ± 0.09	2.12 ± 0.10	2.06 ± 0.06	1.13 ± 0.04	2.33 ± 0.13	1.46 ± 0.05
1-Butene	1.37 ± 0.07	1.39 ± 0.08	1.67 ± 0.08	1.33 ± 0.07	1.33 ± 0.05	1.59 ± 0.48	0.62 ± 0.01	1.37 ± 0.08	1.02 ± 0.06
Butane	1.16 ± 0.06	1.02 ± 0.08	1.32 ± 0.09	1.09 ± 0.16	1.02 ± 0.11	N/A	N/A	1.01 ± 0.14	0.88 ± 0.11

NQ = non-quantifiable, NA = not available.

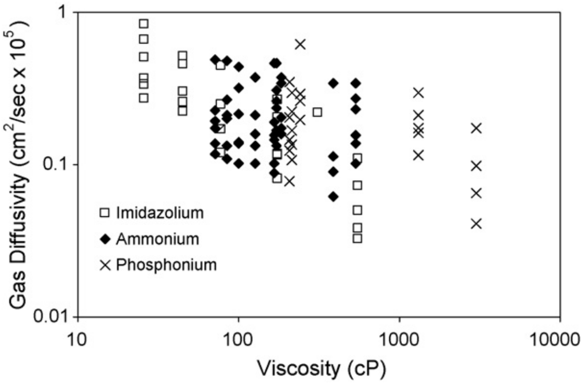

Fig. 2. Diffusivity versus ionic liquid viscosity for imidazolium, phosphonium, and ammonium ionic liquids. The tested ammonium-based RTILs viscosity range is between the imidazolium-based and phosphonium-based RTILs previously tested. For RTILs, diffusivity appears to vary inversely with viscosity.

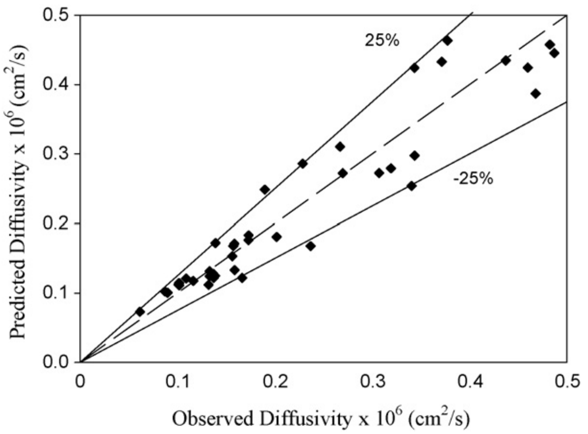

Fig. 4. Predicted diffusivity from Eq. (2) versus observed diffusivity.

viscosity range is, however, smaller compared to the previous RTILs-classes tested. This smaller range gives us a lower confidence in correlating the diffusivity versus viscosity for ammonium-based RTILs compared to imidazolium-based and phosphonium-based RTILs. That said, however, Fig. 2 indicates that the trend followed by ammonium-based RTILs appears to be similar to previously reported viscosity trends.

Fig. 3 contains a log–log plot of the measured diffusivities versus solute (gas) molar volumes at their normal boiling point. The molar volumes were calculated using the Tyn and Calus method [13]. Fig. 3 shows that the diffusivity appears to be inversely proportional to solute molar volume to the power of approximately 1.27. As with imidazolium-based and phosphonium-based RTILs this differs from the Stokes–Einstein model power of 0.33 due to being a small solute in an environment of large solvent molecules [1,2].

1,3-butadiene diffuses faster than molecules of similar size such as, 1-butene (53% faster) and butane (86% faster). This phenomenon was already observed in phosphonium-based RTILs [2] and, in hindsight, was also observable to a lesser extent in imidazolium-based RTILs [1]. We offer the following hypothesis as a potential explanation for this phenomenon. The conjugated double bonds in 1,3-butadiene may allow a resonance stabilization of a weak complexation with the positively charged RTIL cation. If a weak association or complexation occurs with the cation, then the observed phenomenon indicates facilitated transport for conjugated dienes in RTILs and the observed “effective” diffusivity would be higher than that predicted for uncomplexed solutes in RTILs [14]. The greater de-localization of the positive charge in the ring structure of the imidazolium may explain why the phenomenon is smaller for 1,3-butadiene diffusion in imidazolium-based RTILs. The other alkenes in our studies only have one double bond, therefore, they may not as easily form a complex with the cation relative to the formation allowed by the chemistry of conjugated dienes.

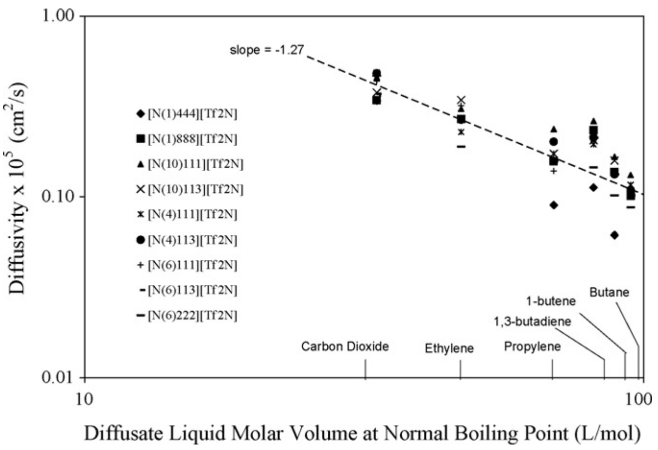

Fig. 3. Diffusivity versus solute molar volume. For the ionic liquids of this study, diffusivity varies inversely with the molar volume of the solute gas. Note, the line with a slope of −1.27 is provided as a reference and is not fitted to the data.

3.4. Gas diffusivity correlations

The previous paper by Morgan et al. [1] shows some conventional correlations for gas diffusivity in liquids. Multivariable linear regression was used in the previous two studies, [1,2] and it was again used here to determine the diffusivity correlation for ammonium-based RTILs. We eliminated the 1,3-butadiene data from the diffusivity correlation because they do not follow the solute trend displayed by other gases (see the previous discussion and Fig. 3). Nitrogen, oxygen, and methane data were eliminated from the diffusivity correlation because the results were too close to the method detection limits and, therefore, had unacceptable percent errors in the reported diffusivities. The variables initially chosen for the diffusivity regression were RTIL viscosities, molecular weights of the gases, molecular weights of the RTILs, molar volume of the gases, and molar volume of the RTILs. Upon doing the regression both molecular weights were found statistically insignificant predictors of diffusivity. However, all other variables were found to be statistically significant. The resulting diffusivity correlation for gases in ammonium-based RTILs at 30 °C was:

$$D_{1,\mathrm{RTIL}} = 6.69\times 10^{-7}\,\frac{V_{\mathrm{RTIL}}^{1.57\pm0.30}}{\mu_{\mathrm{RTIL}}^{0.59\pm0.10}V_{1}^{1.27\pm0.06}} \qquad (2)$$

with molar volumes (V) in cm^3/mol, viscosity (μ_{RTIL}) in cP, diffusivity ($D_{1,\mathrm{RTIL}}$) in cm^2/s. The coefficient of multiple determination (r^2) for this correlation was 0.92. Fig. 4 shows that when Eq. (2) is used to predict the diffusivity values of ammonium-based RTILs, the values are within 25% of the observed values for diffusivity in ammonium-based RTILs.

The powers of μ_{RTIL} and V_1 in Eq. (2) are consistent with the theory discussed by Morgan et al. [1] for modeling diffusion in RTILs as a small gas (solute) molecule diffusing through an environment of large RTIL solvent molecules. While Stokes–Einstein predicts a viscosity, μ, power of −1, Stokes–Einstein also assumes that the diffusing solute molecule is much larger than the solvent molecules. Other models, such as Arnold discussed by Morgan et al. [1], do not make this large solute molecule assumption and predict a viscosity correlation power of −0.5. All three classes of RTILs tested by our group have correlated diffusivity on viscosity dependencies consistent with the Arnold model with the following published correlation powers; imidazolium [1], −0.66, phosphonium [2], −0.47, and ammonium −0.59, [this study].

Similarly, Stokes–Einstein predicts a power on the molar volume of the diffusing solute, V_1, to be −1/3. The Scheibel model, also discussed in Morgan et al. [1], predicts that as the volume of the solvent molecule increases, the power on the solute molar volume in the diffusion correlation should approach −1. This again is what we have reported for all three classes of RTILs tested by our group with the following published correlation powers on V_1; imidazolium [1], −1.04, phosphonium [2], −1.26, and ammonium −1.27, [this study].

Imidazolium-based RTILs with $R \leq 4$ showed no significant diffusivity correlation with the RTIL molar volume [1]; however, Eq. (2) does show a correlation for ammonium-based RTILs. The appearance of a correlation dependency on the RTIL molar volume for ammonium-based as well as phosphonium-based RTILs [2] may suggest that the amount of free volume in the ionic liquid is an indicator for diffusivity. To quote the observation of Ferguson and Scovazzo [2], cations with flexible aliphatic chains could produce an alternative micro-environment for solute diffusion, "...in ionic liquids the microviscosity experienced by solutes (gases) is significantly lower than the macroviscosity of the medium, because the latter depends on movement of the entire solvent molecule whereas the former only requires movement of segments of solvent molecules and is affected by the amount of free volume in the ionic liquid [15]."

Even though there are similarities in the three published diffusivity correlations, particularly in the correlation powers for viscosity, μ, and solute molar volume, V_1, we do not at this time recommend a "universal" correlation encompassing all classes of RTILs. However, we do note that these trends can be used "universally" to qualitatively judge the potential effects on diffusivity in RTILs. Specifically that diffusivity scales inversely with the square-root of viscosity, μ, and diffusivity, also, scales inversely to the solute molar volume to the power of 1–1.3. This means that diffusivity is less dependent on viscosity, and more dependent on solute size than predicted by the conventional Stokes–Einstein model.

4. Conclusions

The ammonium-based RTILs gas permeabilities have similar magnitudes as the previously tested imidazolium-based and phosphonium-based RTILs. The permeabilities of CO_2 in ammonium-based RTILs are an exception; they are similar than the permeability values for phosphonium-based RTILs; and approximately 36% less than the permeabilities for imidazolium-based RTILs. The CO_2/N_2 and CO_2/CH_4 selectivities for the ammonium-based RTILs range between imidazolium RTILs and phosphonium RTILs (imidazolium > ammonium > phosphonium). The 1-butene/butane selectivity values are less than the 1,3-butadiene/butane selectivity values for the ammonium-based RTILs. The gas solubilities of the ammonium-based RTILs are of the same magnitude as gas solubilities for the previous tested RTILs. The Henry's law constants of ammonium-based RTILs are double the respective values for phosphonium-based RTILs; and half the respective values for imidazolium-based RTILs. We observed one more time that the exception is CO_2, which have similar Henry's law constants for imidazolium-based, phosphonium-based, and ammonium-based RTILs. The viscosity trend followed by ammonium-based RTILs appears to be similar to previously reported viscosity trends, as viscosity increases diffusivity decreases.

The diffusivity correlation powers of μ_{RTIL} and V_1 are consistent with the theory discussed by Morgan et al. [1], a mode of a small gas molecule diffusing through large RTIL molecule solvents. Diffusivity correlation dependency on RTIL molar volumes for the classes of RTILs with cations having long flexible alkyl chains ($R \geq 4$) may show that void space is an indicator for diffusivity in RTILs. While a correlation covering all classes of RTILs is not recommended, certain "universal" trends can be used to qualitatively judge potential changes to diffusivity in RTILs. Specifically, diffusivity scales inversely with the square-root of viscosity, μ, and diffusivity, also, scales inversely to the solute molar volume to the power of 1–1.3. This means that diffusivity, in RTILs, is less dependent on viscosity, and more dependent on solute size than predicted by the conventional Stokes–Einstein model.

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References

[1] D. Morgan, L. Ferguson, P. Scovazzo, Diffusivities of gases in room-temperature ionic liquids: data and correlations obtained using a lag-time technique, Ind. Eng. Chem. Res. 44 (2005) 4815–4823.

[2] L. Ferguson, P. Scovazzo, Solubility, diffusivity, and permeability of gases in phosphonium-based room temperature ionic liquids: data and correlations, Ind. Eng. Chem. Res. 46 (2007) 1369–1374.

[3] P.-Y. Chen, Ch. Hussey, Electrodeposition of cesium at mercury electrodes in the tri-1-butylammonium bis((trifluoromethyl)sulfonyl)imide room-temperature ionic liquid, Electrochem. Acta 49 (2004) 5125–5138.

[4] Y. Hou, R. Baltus, Experimental measurement of the solubility and diffusivity of CO_2 in room-temperature ionic liquids using a transient thin-liquid-film method, Ind. Eng. Chem. Res. 46 (24) (2007) 8166–8175.

[5] D. Camper, C. Becker, C. Koval, R. Noble, Diffusion and solubility measurements in room temperature ionic liquids, Ind. Eng. Chem. Res. 45 (2006) 445–450.

[6] M.B. Shiflett, M.A. Harmer, C.R. Junk, A. Yokozeki, Solubility and diffusivity of 1,1,1,2-tetrafluoroethane in room-temperature ionic liquids, Fluid Phase Eq. 242 (2) (2006) 220–232.

[7] P. Kilaru, G. Baker, P. Scovazzo, Density and surface tension measurements of imidazolium-, phosphonium-, and ammonium-based room temperature ionic liquids: data and correlations, J. Chem. Eng. Data 52 (2007) 2306–2314.

[8] P. Kilaru, G. Baker, P. Scovazzo, Corrections, density and surface tension measurements of imidazolium-, phosphonium-, and ammonium-based room temperature ionic liquids: data and correlations, J. Chem. Eng. Data 53 (2008) 613.

[9] P. Kilaru, R. Condemarin, P. Scovazzo, Correlations of low-pressure carbon dioxide and hydrocarbon solubilities in imidazolium-, phosphonium-, and ammonium-based room temperature ionic liquids. Part 2. Using activation energy of viscosity, Ind. Eng. Chem. Res. 47 (2008) 910–919.

[10] D. Camper, J. Bara, C. Koval, R. Noble, Bulk-fluid solubility and membrane feasibility of Rmim-based room temperature ionic liquids, Ind. Eng. Chem. Res. 45 (2006) 6279–6283.

[11] D. Camper, C. Becker, C. Koval, R. Noble, Low pressure hydrocarbon solubility in room temperature ionic liquids containing imidazolium rings interpreted using regular solution theory, Ind. Eng. Chem. Res. 44 (2005) 1928–1933.

[12] P. Kilaru, R. Condemarin, P. Scovazzo, Correlations of low-pressure carbon dioxide and hydrocarbon solubilities in imidazolium-, phosphonium-, and ammonium-based room temperature ionic liquids. Part 1. Using surface tension, Ind. Eng. Chem. Res. 47 (2008) 900–909.

[13] M.T. Tyn, W.F. Calus, Estimating liquid molar volume, Processing 21 (4) (1975) 16.

[14] M. Mulder, Basic Principles of Membrane Technology, 2nd ed., Kluwer Academic Publishers, The Netherlands, 1996.

[15] J.F. Wishart, P. Neta, Spectrum and reactivity of the solvated electron in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide, J. Phys. Chem. B 107 (2003) 7261–7267.