Enhanced Gravimetric CO_2 Capacity and Viscosity for Ionic Liquids with Cyanopyrrolide Anion

Paul Brown, Burcu E. Gurkan, and T. Alan Hatton
Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

DOI 10.1002/aic.14819

Ionic Liquids (ILs) are considered as alternative solvents for the separation of CO_2 from flue gas due mainly to their CO_2 affinity and thermal stability. The cation architecture in a matrix of ammonium and mostly phosphonium-based ILs with 2-cyanopyrrolide as the anion to evaluate its impact on gravimetric CO_2 absorption capacity, viscosity, and thermal stability and the three fundamental properties vital for application realization are systematically investigated. Among the investigated ILs, [P2,2,2,8][2-CNpyr] demonstrated the lowest viscosity, 95 cP at 40°C, and highest CO_2 uptake, 114 mg CO_2 per g IL at 40°C. Combined effects of asymmetry and the optimized chain lengths also resulted in improved thermal stability for [P2,2,2,8][2-CNpyr], with a mass loss rate of 1.35×10^{-6} g h^{-1} (0.0067 mass % h^{-1}) at 80°C. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2280–2285, 2015
Keywords: CO_2 absorption, ionic liquids, thermal stability, viscosity

Introduction

There is consensus on the long-term need to suppress anthropogenic CO_2 emissions by eliminating fossil-fuel consumption and harvesting renewable energy sources. In the short term, however, a viable strategy for mitigating potential problems associated with the greenhouse gas effect is to capture and sequester CO_2 from existing fossil-fueled power plants. The most mature technology for postcombustion CO_2 capture from coal-fired power plants is a two-stage process in which CO_2 is absorbed selectively by an aqueous monoethanolamine (MEA) solvent and subsequently desorbed at an elevated temperature and compressed for geologic sequestration.[1] However, associated with this approach is a large enthalpy of reaction and a significant energy cost to release the CO_2, as well as heat lost to water vaporization (~85 kJ mol^{-1} at 40°C).[2] These amines are also fairly corrosive to the plant equipment.[3] To overcome these issues, solid adsorbents such as selective membranes,[4] polymeric materials,[5] and metal organic frameworks[6,7] are being developed. The challenges facing these materials are long-term structural integrity, heat transfer to the sorbent, and related practical implementations. A recent review by *Espinal et al. discussed* various CO_2 capture materials and their respective challenges in implementation.[8]

Among the alternative candidates for solvent-based CO_2 capture are chilled ammonia, advanced amine blends, and ionic liquids (ILs).[9] Although ILs suffer from high viscosities and high cost, they have been proposed specifically due to their low volatility,[10] high thermal stability,[11] and high CO_2 solubility,[12,13] relative to conventional solvents. ILs are low temperature molten salts (<100°C) with a multicomponent structure that makes them highly tunable; it is estimated that there are $\sim 10^9$ potential cation/anion combinations.[14] Several research groups have contributed to the optimization of ILs for the separation of CO_2 from flue gas.[15–22] To enhance CO_2 absorption at low pressures, for example, from flue gases, Bates et al. functionalized the imidazolium cation through attachment of an amine moiety,[23] designed to react with CO_2 in a 2:1 (IL:CO_2) molar stoichiometry to form the carbamate-ammonium ion pair. They reversed this reaction by increasing the temperature, bubbling with nitrogen, or applying a vacuum. Functionalization of the anion with the amine, in the case of amino acid-based ILs,[16] allowed a 1:1 stoichiometry to be attained.[24] Although these early-model CO_2-reactive ILs were effective in enhancing CO_2 absorption capacity, they also suffered from dramatic increases in viscosity on binding with the CO_2. Such increases potentially render the CO_2 absorption and desorption processes infeasible due to mass-transfer limitations and pumping costs. The viscosity increase upon complexation with CO_2 was shown computationally to be caused by increased hydrogen-bonding networks.[25] This theory was later confirmed experimentally[21] by the lack of viscosity increase upon CO_2 absorption by ILs with aprotic heterocyclic anions, where no proton was present to enable hydrogen-bonding. Moreover, their reaction enthalpies were found to be much smaller than those of the corresponding amino acid-based ILs and of MEA.[21] The most attractive of the reported ILs was trihexyl(tetradecyl)-phosphonium 2-cyanopyrrolide [P6,6,6,14][2-CNpyr] with an activation energy of about 11 kJ mol^{-1} and fast binding kinetics with CO_2 (Figure 1).[26] As a result of this low activation energy, the desorption reaction can be accomplished readily without the need for excessively elevated

---

Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to T. A. Hatton at tahatton@mit.edu.

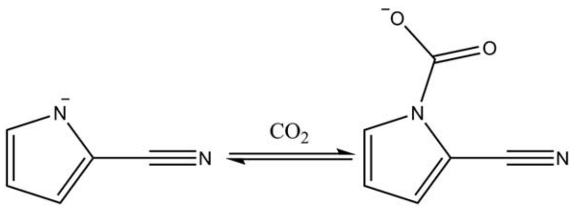

Figure 1. Reaction of [2-CNpyr] anion with CO_2.

temperatures while a high working capacity on a molar basis can still be maintained. However, the gravimetric CO_2 absorption capacity of this IL is reported to be 57.4 mg CO_2 per g IL at 40°C and 1 bar of CO_2. This is not quite half the CO_2 capacity of 30 wt % aqueous MEA under the same conditions, a difference that is due to the high molecular weight of the IL ([P6,6,6,14][2-CNpyr]: 574.96 g mol^{-1}).

In this article, we report ways in which the gravimetric uptake of ILs may be improved without the strong adverse changes in rheological behavior observed with earlier systems. To this end, we investigated a series of ILs in which we paired the [2-CNpyr] anion with different cations, namely tetraalkylammonium (TAA) and tetraalkylphosphonium, with varying chain length, asymmetry, and functionalization. As the reaction enthalpy depends mainly on the anion, the reaction energy with CO_2, and hence the working capacity of CO_2 on a molar basis, was expected to be unaffected (the working capacity is a relative property, determined by the difference in CO_2 uptake capacity at absorption and desorption temperatures and other experimental factors, such as the partial pressures in the feed and stripping gases; the magnitude of the uptake capacity is an independent thermodynamic property that is fixed under a given set of experimental conditions). A change in the cation can also have a great effect on the melting point, thermal decomposition, and viscosity of the IL, all of which are relevant physical properties for the CO_2 capture process. We provide a systematic investigation of the series of cations shown in Figure 2 and their effects on these properties using [P6,6,6,14][2-CNpyr] as a basis for comparison.

Tetraalkylphosphonium salts were considered in this study primarily because they are low in cost, exhibit much higher thermal stability than do their TAA analogs, and, unlike imidazolium cations, which have acidic carbons on the α-position, do not undergo irreversible reactions with CO_2. The CO_2 absorption capacity and the long-term thermal stability of the ILs were measured using a thermogravimetric analyzer (TGA). The long-term stability, in particular, was investigated here since an economically viable process requires the efficient cycling of the absorbent. Most of the published studies on ILs report decomposition temperatures based on fast temperature ramps as it is easier to screen different ILs using this method. However, results using the ramping method are misleading and overpredict the thermal decomposition temperatures; it has been shown that isothermal methods are more reliable.[27–29] This article advises caution in extolling the virtues of ILs for specific applications based on their supposed negligible vapor pressures and high thermal stabilities as we show here that not all ILs exhibit these traits.

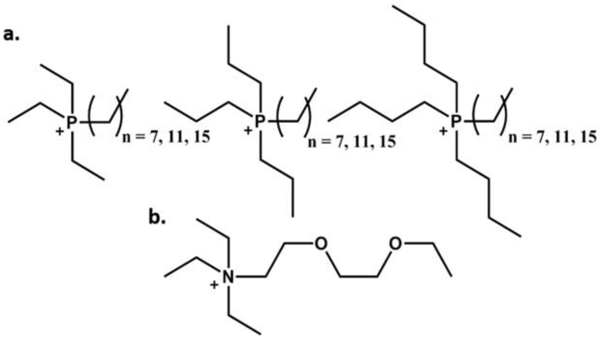

Figure 2. (a) Phosphonium cations studied and (b) cation with ethoxy groups present [N2,2,2,E8].

Experimental

Materials

Triethylphosphine (99%), tripropylphosphine (97%), tri-*n*-butylphosphine (99%), 1-bromooctane (99%), 1-bromododecane (≥99.5%), 1-chlorohexadecane (95%), and pyrrole-2-carbonitrile (96%) were purchased from Sigma Aldrich and used without purification. 2-(2-ethoxyethoxy) ethylbromide (98%, stabilized with potassium carbonate) was bought from Alfa Aesar and distilled before use.

Details of synthesis procedures

Triethyloctylphosphonium 2-cyanopyrrolide [P2,2,2,8][2-CNpyr] was synthesized by first generating the bromide precursor [P2,2,2,8]Br according to literature procedures,[30,31] whereby 1-bromooctane (6.944 mL, 37.8 mmol, 0.95 eq.) was added to triethylphosphine (5 g, 42.3 mmol, 1 eq.) in a nitrogen atmosphere in a flask equipped with a reflux condenser and magnetic stirrer. The solution was heated to 90°C in an oil bath and stirred for 18 h. The flask was then allowed to cool to room temperature and the small volume of supernatant decanted. The remaining IL was washed with ether. A white solid was obtained and recrystallized three times from ethyl acetate and 1-propanol. The solid was dried *in vacuo* at 40°C for more than 48 h.^{31}P-NMR (300 MHz, methanol-d_4, 23°C): δ 39.74 (s); ^{1}H-NMR (300 MHz, methanol-d_4, 23°C): δ 0.86–0.95 (t, 3H), δ 1.14–1.66 (m, 21H), δ 2.13–2.33 (m, 8H).

[P2,2,2,8]Br was then stirred overnight in a Dowex Monosphere 550A UPW suspension in 50:50 (v/v) methanol/water. After filtration of the ion exchange resin, 1 eq. pyrrole-2-carbonitrile was added to the solution which was stirred for 30 min. The brown product [P2,2,2,8][2-CNpyr] was then obtained by removing the solvent at reduced pressure and drying *in vacuo*. Karl Fisher coulometric titration (Metrohm) was used to measure the residual water content of the ILs. Analyses were conducted as a function of time over 3 days, under ambient atmospheric conditions, until water levels fell below 1000 ppm.^{31}P-NMR (300 MHz, methanol-d_4, 23°C): δ 39.66 (s); ^{1}H-NMR (300 MHz, methanol-d_4 23°C): δ 0.84–0.97 (t, 3H), δ 1.14–1.65 (m, 21H), δ 2.09–2.27 (m, 8H), δ 6.13–6.18 (dd, 1H), δ 6.74–.79 (dd, 1H), δ 6.94–6.99 (dd, 1H). Water content = 322 ppm.

This general synthetic procedure was repeated for all compounds by substitution of the phosphine and haloalkane precursors. The reactions were conducted successfully either under reflux conditions in acetonitrile or under solvent-free conditions at temperatures of ∼120°C. Most compounds with alkyl groups bulkier than that in [P2,2,2,8]Br yielded

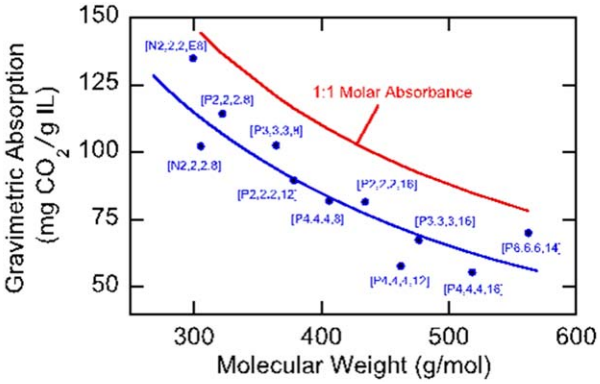

Figure 3. Measured CO_2 absorption capacity as a function of molecular weight (Mw) at 40°C.

The blue curve indicates that the trends shown by the experimental data are similar to those calculated for complete chemisorption of one molar equivalent of CO_2, given by the red curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

clear viscous liquids as product. All ^{1}H-NMR and ^{31}P-NMR results can be found in Supporting Information.

Viscosity measurements

An AR-G2 Rheometer (TA Instruments), fitted with a cone and plate (2°/40 mm), was used to determine viscosities between 22 and 60°C. First, viscosity was measured as a function of shear stress (10–1000 Pa) at 22°C to ensure the materials gave linear responses with no shear history. Measurements were then repeated at 25, 30, 40, 50, and 60°C. Once Newtonian behavior was verified, the viscosities were recorded as a function of temperature under constant shear stress (4.3 Pa; Supporting Information).

Thermogravimetric analysis

The IL decomposition profiles were determined between 25 and 500 ± 0.05°C by thermogravimetry on a TGA-Q50 (TA Instruments, DE) with a ramp rate of 10°C min^{-1}, and a nitrogen flow rate of 60 mL min^{-1}; a platinum pan was used to hold the IL. Long-term thermal stability studies were performed isothermally at 80 ± 0.05°C for 1000 min. In the CO_2 absorption studies, the temperature was held at 40 ± 0.05°C with a CO_2 (bone dry—$[H_2O] < 2$ ppm, 1 bar, Airgas) flow rate over the sample of 60 mL min^{-1}. A typical sample mass was approximately 20 mg. It is important to note that sample mass affected the kinetics of both CO_2 absorption and the rate of decomposition for the long scans. In addition, sample viscosity and surface tension also played a key role in controlling the spreading of the IL on the TGA pan, and thereby determining the available surface area for interfacial mass transfer. These effects could not be factored into the analysis.

Results and Discussion

The synthesis of the new ILs was facile and purification was fairly simple with ^{31}P-NMR and ^{1}H-NMR showing no significant impurities in the samples (See Supporting Information Figures S1 and S2). All of the absorption and decomposition measurements were performed after excess water content had been reduced to levels less than 500 ppm in the IL.

CO_2 absorption

The absorption capacities of the synthesized ILs at 1 bar CO_2 at 40°C are shown in Figure 3. The molar uptake at 40°C is lower than the 1:1 molar absorbance predicted at 25°C (indicated by the red line), reflecting the finite, temperature-dependent reversibility of the reaction. The CO_2 absorbance decreased with increasing molecular weight of the IL; the scatter about the line may be accounted for by typical limitations of TGA analysis (c.f. experimental) as well as differences in physical CO_2 solubility in the ILs. For example, ILs containing longer alkyl chains should exhibit enhanced CO_2 solubility.[32] With a maximum loading of ~112 mg CO_2 per g IL, [P2,2,2,8] exhibited the highest gravimetric CO_2 absorption of all phosphonium-based ILs, about 62% higher than observed with the benchmark [P6,6,6,14] (~70 mg CO_2 per g IL, Figure 3). It is interesting to note that [P2,2,2,8] had a higher capacity than did its ammonium analog [N2,2,2,8] (Supporting Information). This was probably due to increased physical absorption.[33] When a nitrogen atom is exchanged for a heavier element such as phosphorous, more "free space" is available for physical absorption.[13,31] With this in mind, we synthesized ILs with heavier elements built into the alkyl chain.[34] As can be seen in Figure 3, when ethoxy groups were added to one of the alkyl chains in [N2,2,2,E8] (triethyl,2-(2-ethoxyethoxy)ethylammonium), dramatic increases in CO_2 absorption were obtained (~135 mg CO_2 per g IL, Supporting Information). Unfortunately, the corresponding phosphonium salt could not be generated (Supporting Information). Depending on the application, especially for low-temperature processes, [N2,2,2,E8] may be a promising candidate as a CO_2 absorbent.

Rheology

Most ILs can be classified as Newtonian fluids as their viscosities remain constant with increasing shear rate.[35] This behavior was observed for all the compounds considered in this work, within the studied shear rate range ($0.2 < \sigma$ (Pa) < 12.0, Supporting Information). The measured viscosities at 25°C ranged from 160 to 454 mPa s, falling to between 25 and 73 mPa·s at 60°C (Figure 4 and Table 2). Here, [P2,2,2,8] exhibited a 38% decrease in viscosity

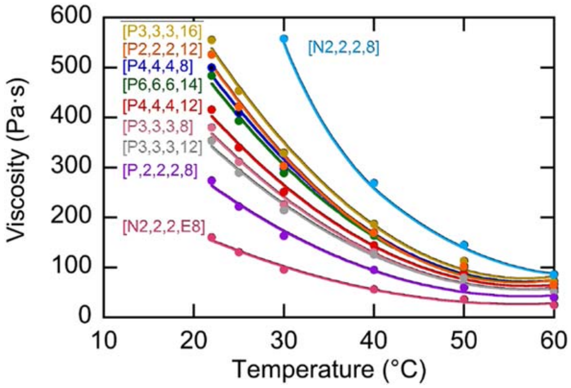

Figure 4. Effect of the cation on the viscosity of the IL with the [2-CNpyr] anion.

The lines show the Arrhenius behavior. Semilogarithmic Arrhenius-like plots are found in Supporting Information Figure S5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. Viscosities and Fitted Arrhenius Parameters of ILs with the [2-CNpyr] Anion at 25 and 60°C

Cation	η at 25°C (mPa s)	η at 60°C (mPa s)	E_a (kJ mol^{-1})
[N2,2,2,E8]	160.0	25.1	38.6
[N2,2,2,8]	841.4	86.17	54.9
[P2,2,2,8]	221.9	39.9	41.4
[P3,3,3,8]	311.3	52.83	42.4
[P2,2,2,12]	421.6	66.34	44.6
[P4,4,4,8]	409.3	66.77	43.4
[P3,3,3,12]	289.7	51.91	41.2
[P4,4,4,12]	340.4	58.64	42.2
[P3,3,3,16]	453.5	73.08	43.7
[P4,4,4,16]	393.4	66.33	42.8
[P6,6,6,14][a]	360	64	–

[a]Data from Gurkan et al.[21]; [P2,2,2,16] was solid at room temperature.

relative to the viscosity of the benchmark [P6,6,6,14] cation at all temperatures (Ahrennius-like plots may be found in Supporting Information). Generally, increases in the alkyl chain length of ILs result in increases in viscosity due to increased van der Waals interactions. However, this general rule was not expected to apply directly to the compounds studied here owing to the simultaneous changes in the asymmetry of the cation with changing alkyl tail length. In this case, increases in the degrees of freedom may compensate for any extra van der Waals interaction effects. However, owing to the added effect of the relatively large bulky anion, such predictions become more complex. The phosphonium-based IL [P2,2,2,8] showed a reduction in dynamic viscosity of almost 75% when compared with its ammonium analog [N2,2,2,8] (Figure 4 and Table 1). This observation is in good agreement with the results reported by Tsunashima and Sugiya for the same cations with different anions, with the central atom still having a large impact on physicochemical properties despite being surrounded by large alkyl chains.[36]

The substitution of other large electronegative elements is also known to lower the dynamic viscosity of ILs.[31] Therefore, to further reduce viscosity, we attempted to introduce heavier elements into the cation architecture (structures in Supporting Information). To this end, triethyl,2-(2-ethoxyethoxy)ethylammonium bromide [N2,2,2,E8]Br and triethyl,2-(2-ethoxyethoxy)ethylphosphonium bromide [P2,2,2,E8]Br were prepared.

However, when the halide salt was converted to the functionalized IL, the phosphonium ion degraded, as evidenced by ^{1}H-NMR and ^{31}P-NMR. This occurred even at temperatures below 35°C, and was most probably due to a weakening of cation-anion electrostatics and a freeing up of the [2-CNpyr] anion to act as a nucleophile.[37] Conversely, [N2,2,2E8][2-CNpyr] exhibited the lowest viscosity of all the ILs investigated with a dynamic viscosity of around 25 mPa·s at 60°C. While this performance is rather impressive when considered alongside its high gravimetric CO_2 capacity, we shall see later that its thermal stability is still an issue and may preclude its use in certain applications.

The activation energies for viscous flow (E_a) of the ILs were estimated by a fitting of the measured viscosities to the Arrhenius expression $\eta = \eta_\infty \exp(-E_a/RT)$, which was considered more appropriate than the comparative Vogel–Fulcher–Tammann equation due to the asymmetry and bulk of the anions (Supporting Information Figure S5; Table 1). In this equation, η_∞ is the apparent viscosity at infinite temperature, and E_a is the viscosity activation energy. The magnitude of E_a is an indication of the difficulty with which molecules can transfer through the liquid matrix. The value of E_a for the studied phosphonium ILs ranged between 41 and 44 kJ mol^{-1}. The calculated activation energy for molecular transfer in the phosphonium ILs was much larger than that for typical molecular solvents (c.f. H_2O (20°C) = 17.0 kJ mol^{-1}, benzene = 10.4 kJ mol^{-1}, and acetone = 7.1 kJ mol^{-1})[38] and many common imidazolium-based ILs (c.f. [bmim][PF_6] = 34.1 kJ mol^{-1}),[39] but smaller than some surfactant (dioctyl sodium sulfosuccinate, AOT) based ILs (c.f. [bmim][AOT] = 49.46 kJ mol^{-1}).[40] The value of E_a for triethyloctylammonium 2-cyanopyrrolide, [N2,2,2,8][2-CNpyr] was almost 25% higher than that for the triethyloctylphosphonium 2-cyanopyrrolide, [P2,2,2,8][2-CNpyr] (54.9 and 41.4 kJ mol^{-1}, respectively), consistent with the smaller central atom providing stronger interionic interactions arising from a smaller ionic volume.

Thermal decomposition

The most common measure of thermal decomposition temperatures is the onset temperature, T_{onset}, obtained from the intersection of the weight baseline and the tangential line at the inflection point, as demonstrated in Figure 5. The thermograph was obtained at a heating rate of 10°C min^{-1}. For [P2,2,2,8][2-CNpyr], T_{onset} was determined to be 284°C. However, this is clearly an overestimation, as the actual degradation begins at much lower temperatures[41]; recently, Stevens and coworkers[28] reviewed such thermal decomposition measurements. Here, we report $T_{0.01}$, which is the temperature at which a 1 wt % loss is observed under the assumption that there is no water uptake during the measurements, although this assumption is unlikely to be valid for samples with large surface area to volume ratios. As is highlighted in Figure 3, there can be a 150°C difference in the decomposition temperatures determined by the two indicators T_{onset} and $T_{0.01}$, both of which are listed in Table 2. Clearly, when any potential long-term application of ILs is considered for CO_2 absorption this fundamental issue needs to be addressed; for removal of CO_2 from a flue gas, $T_{0.01}$ is the more relevant measure as the IL is cycled continuously over a long-time period through a high-temperature desorber.

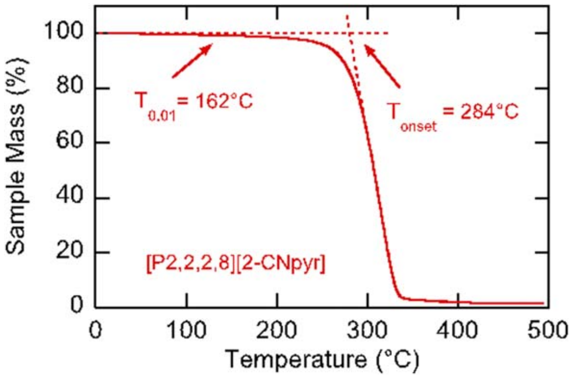

Figure 5. Thermogravimetric analysis of decomposition of [P2,2,2,8][2-CNpyr] as a function of temperature.

Labels indicate two methods of estimating decomposition temperature: $T_{0.01}$ and T_{onset}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

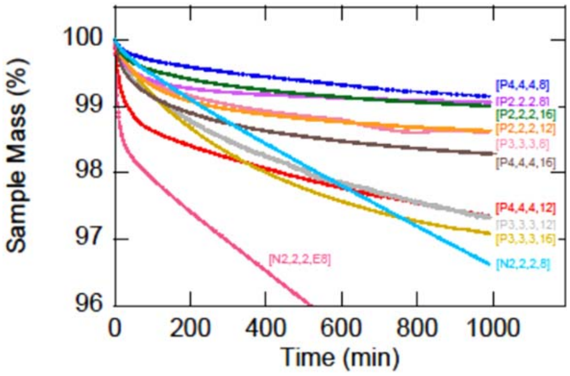

Figure 6. Long-term (1000 min) thermal stability studies of ILs at 80°C using thermogravimetric analysis.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

From the data shown in Table 2, it appears that there is no correlation between degradation temperature and either total hydrocarbon bulk or asymmetry. The degree of asymmetry and resulting change in polarization effects depended on where on the cation the extra carbons were added. In contrast to the case with simple inorganic salts, it is not possible to estimate these effects computationally for such large ion pairs. For imidazolium salts, a change in cation structure did not have as significant an effect on the properties as did modifications to the anion; alkylation of the cation resulted in only a minimal increase in thermal stability.[35,42] It has been reported that, for a matrix of 22 isomeric TAA salts each containing 20 carbon atoms, there was no correlation between the position of the carbon addition and the melting point.[43] As is typical with ILs, the nitrogen analogs exhibited lower thermal stability than did the corresponding phosphonium salts.

A more compelling demonstration of long-term stability was achieved by running the TGA experiments at 80°C for 1000 min (Figure 6 and Table 2). This temperature was not selected arbitrarily: 80°C is the typical desorption temperature to achieve an effective working CO_2 capacity and a minimal energy cost associated with the reaction enthalpy. It was assumed that the initial mass loss was due to dissolved gases, absorbed water, impurities from the starting material, and residual amounts of cyanopyrrole. [P2,2,2,8] had the lowest rate of mass loss at 1.47×10^{-6} g h^{-1} (0.0067% h^{-1}) after 1000 min. The NMR spectra of [P2,2,2,8][2-CNpyr] before and after 1000 min at 80°C were identical indicating degradation using nuclear magnetic resonance (NMR) was not quantifiable. Either a purely evaporative process occurred or the degradation products desorbed rapidly from the sample. To address this issue, we placed approximately 0.25 g [P2,2,2,8][2-CNpyr] in a sealed 7-mL vial for 5 days at 85°C; the resulting NMR spectrum was also unchanged from that of the starting material. The rate of mass loss of [P2,2,2,8] over 10,000 min was reduced even further by more than three-fold to around 0.0021% h^{-1} indicating improved thermal stability compared with other ILs investigated. It is important to note that the mass loss rate is expected to be reduced even further once the sample volumes are scaled up and the corresponding surface area to volume ratio is reduced.

Conclusions

The CO_2 gravimetric capacity, viscosity, and degradation temperatures of a matrix of tetraalkylphosphonium 2-cyanopyrrolide ILs show no direct correlation with cation architecture. The complexity afforded by variations in cation asymmetry and in the interplay between the anion-cation pairs does not allow for simple predictions of the physical properties of these ILs. It is clear, however, that smaller cations with shorter chain lengths and conserved asymmetry, such as [P2,2,2,8], result in lower viscosities (up to 60% lower) than those of previously reported functionalized ILs for CO_2 absorption.[21] Our thermal analysis highlights the importance of experimental procedure and analysis in the selection of an IL for a specific application with degradation temperatures occurring far below those initially considered.[21,41] Additionally, we show that while there is a clear difference in the thermal stability of phosphonium and ammonium ILs (phosphoniums having higher stability), the cation molecular weight did not influence the thermal decomposition temperatures significantly. Importantly, [P2,2,2,8][2-CNpyr] proved to have one of the higher onset temperatures ($T_{0.01} = 162$°C) and exhibited the best long-term stability at 80°C with a mass loss rate of only 1.35×10^{-6} g h^{-1}. [P2,2,2,8][2-CNpyr] also had the greatest CO_2 absorption capacity of all phosphonium ILs at 40 C and 1 bar of CO_2 at around 114 mg CO_2 per g IL; again more than 60% greater than that of other reactiveILs.[21] The data

Table 2. T_{onset} and $T_{0.01}$ Temperatures for the Selected ILs with [2-CNpyr] Anion[a]

Cation	C Atoms	T_{onset} (Tangent) (°C)	$T_{0.01}$ (1 wt % Loss) (°C)	Difference Between Methods (°C)	Mass Loss (%) 1000 min	Mass Loss (%)/h	Mass Loss (%)/ h (Final Hour)
[N2,2,2,E8]	12	168	107	61	6.163	0.370	0.355
[N2,2,2,8]	14	178	101	77	3.625	0.218	0.179
[P2,2,2,8]	14	284	162	122	0.933	0.056	0.006
[P3,3,3,8]	17	287	144	143	1.546	0.093	0.052
[P2,2,2,12]	18	278	182	96	1.366	0.082	0.017
[P4,4,4,8]	20	290	158	132	0.853	0.051	0.024
[P3,3,3,12]	21	292	157	135	2.671	0.160	0.070
[P2,2,2,16]	22	257	139	118	0.992	0.060	0.017
[P4,4,4,12]	24	290	125	165	2.644	0.159	0.057
[P3,3,3,16]	25	291	143	148	2.913	0.175	0.050
[P4,4,4,16]	28	294	170	124	1.714	0.103	0.021

[a] Mass loss percentages are indicative of the long term thermal stabilities of these ILs at the measured temperature of 80°C. Mass loss is reported as both that averaged over 1000 min and as the rate of mass loss during the final hour of the experiment. For reference, pyrrole-2-carbonitrile loses around 65.2 wt % h^{-1} at 80°C.

suggest that the new benchmark for CO_2 reactive ILs may be set by [P2,2,2,8][2-CNpyr].

Literature Cited

1. Abu-Zahra MRM, Abbas Z, Singh P, Feron P. Carbon Dioxide Post-Combustion Capture: Solvent Technologies Overview, Status and Future Directions, in "Materials and processes for energy: communicating current research and technological developments", Editor: Mendez-Vilas A, Fromatex Research Center, Spain 2013:923–934.
2. Kim I, Svendsen HF. Heat of absorption of carbon dioxide (CO_2) in monoethanolamine (MEA) and 2-(aminoethyl)ethanolamine (AEEA) solutions. *Ind Eng Chem Res.* 2007;46:5803–5809.
3. Kittel J, Gonzalez S. Corrosion in CO_2 post-combustion capture with alkanolamines—a review. *Oil Gas Sci Technol–Rev d'IFP Energies nouvelles.* 2013;69:915–929.
4. Powell CE, Qiao GG. Polymeric CO_2/N_2 gas separation membranes for the capture of carbon dioxide from power plant flue gases. *J Membr Sci.* 2006;279:1–49.
5. Pevida C, Snape CE, Drage TC. Templated polymeric materials as adsorbents for the postcombustion capture of CO_2. *Energy Procedia.* 2009;1:869–874.
6. Nugent P, Belmabkhout Y, Burd SD, Cairns AJ, Luebke R, Forrest K, Pham T, Ma S, Space B, Wojtas L, Eddaoudi M, Zaworotko MJ. Porous materials with optimal adsorption thermodynamics and kinetics for CO_2 separation. *Nature.* 2013;495:80–84.
7. Sumida K, Rogow DL, Mason JA, McDonald TM, Bloch ED, Herm ZR, Bae TH, Long JR. Carbon dioxide capture in metal-organic frameworks. *Chem Rev.* 2011;112:724–781.
8. Espinal L, Poster DL, Wong-Ng W, Allen AJ, Green AL. Measurement standards, and data needs for CO_2 capture materials: a critical review. *Environ Sci Technol.* 2013;47:11960–11975.
9. Pellegrini G, Strube R, Manfrida G. Comparative study of chemical absorbents in postcombustion CO_2 capture. *Energy.* 2010;35:851–857.
10. Wilkes JS. A short history of ionic liquids – from molten salts to neoteric solvents. *Green Chem.* 2002;4:73–80.
11. Fredlake CP, Crosthwaite JM, Hert DG, Aki SNVK, Brennecke JF. Thermophysical properties of imidazolium-based ionic liquids. *J Chem Eng Data.* 2004;49:954–964.
12. Cadena C, Anthony JL, Shah JK, Morrow TI, Brennecke JF, Maginn EJ. Why is CO_2 so soluble in imidazolium-based ionic liquids? *J Am Chem Soc.* 2004;126:5300–5308.
13. Huang JH, Ruther T. Why are ionic liquids attractive for CO_2 absorption? An overview. *Aust J Chem.* 2009;62:298–308.
14. Earle MJ, Seddon KR. Ionic liquids. Green solvents for the future. *Pure Appl Chem.* 2000;72:1391–1398.
15. Davis JH. Task-specific ionic liquids. *Chem Lett.* 2004;33:1072–1077.
16. Fukumoto K, Yoshizawa M, Ohno H. Room temperature ionic liquids from 20 natural amino acids. *J Am Chem Soc.* 2005;127:2398–2399.
17. Muldoon MJ, Aki SNVK, Anderson JL, Dixon JK, Brennecke JF. Improving carbon dioxide solubility in ionic liquids. *J Phys Chem B.* 2007;111:9001–9009.
18. Jiang YY, Wang GN, Zhou Z, Wu YT, Geng J, Zhang ZB. Tetraalkylammonium amino acids as functionalized ionic liquids of low viscosity. *Chem Commun.* 2010;505–507.
19. Mindrup EM, Schenider WF. Computational comparison of tethering strategies for amine funtionalized ionic liquids. In: Seddon K, Rogers R, Plechkova N, editors. ACS Symposium Series. Washington D.C.: ACS, 2009.
20. Zhang Y, Zhang S, Lu X, Zhou Q, Fan W, Zhang X. Dual amino-functionalised phosphonium ionic liquids for CO_2 capture. *Chem Eur J.* 2009;15:3003–3011.
21. Gurkan B, Goodrich BF, Mindrup EM, Ficke LE, Massel M, Seo S, Senftle TP, Wu H, Glaser MF, Shah JK, Maginn EJ, Brennecke JF, Schneider WF. Molecular design of high capacity, low viscosity, chemically tunable ionic liquids for CO_2 capture. *J Phys Chem Lett.* 2010;1:3494–3499.
22. Wang C, Luo X, Zhu X, Cui G, Jiang D, Deng D, Li H, Dai S. Strategies for improving carbon dioxide chemisorption by functionalized ionic liquids. *RSC Adv.* 2013;3:15518–15527.
23. Bates ED, Mayton RD, Ntai I, Davis JH. CO_2 Capture by a task-specific ionic liquid. *J Am Chem Soc.* 2002;124:926–927.
24. Gurkan BE, de la Fuente JC, Mindrup EM, Ficke LE, Goodrich BF, Price EA, Schneider WF, Brennecke JF. Equimolar CO_2 absorption by anion-functionalized ionic liquids. *J Am Chem Soc.* 2010;132:2116–2117.
25. Gutowski KE, Maginn EJ. Amine-functionalized task-specific ionic liquids: a mechanistic explanation for the dramatic increase in viscosity upon complexation with CO_2 from molecular simulation. *J Am Chem Soc.* 2008;130:14690–14704.
26. Gurkan BE, Gohndrone TR, McCready MJ, Brennecke JF. Reaction kinetics of CO_2 absorption in to phosphonium based anion-functionalized ionic liquids. *Phys Chem Chem Phys.* 2013;15:7796–7811.
27. Clough MT, Geyer K, Hunt PA, Mertes J, Welton T. Thermal decomposition of carboxylate ionic liquids:trends and mechanisms. *Phys Chem Chem Phys.* 2013;15:20480–20495.
28. Maton C, De Vos N, Stevens CV. Ionic liquid thermal stabilities: decomposition mechanisms and analysis tools. *Chem Soc Rev.* 2013;42:5963–5977.
29. Wooster TJ, Johanson KM, Fraser KJ, MacFarlane DR, Scott JL. Thermal degradation of cyano containing ionic liquids. *Green Chem.* 2006;8:691–696.
30. Desset SL, Reader SW, Cole-Hamilton DJ. Aqueous-biphasic hydroformylation of alkenes promoted by "weak" surfactants. *Green Chem.* 2009;11:630–637.
31. Shirota H, Fukazawa H, Fujisawa T, Wishart JF. Heavy atom substitution effects in non-aromatic ionic liquids: ultrafast dynamics and physical properties. *J Phys Chem B.* 2010;114:9400–9412.
32. Torralba-Calleja E, Skinner J, Gutiérrez-Tauste D. CO_2 capture in ionic liquids: a review of solubilities and experimental methods. *J Chem.* 2013, Article ID 473584.
33. Shariati A, Gutkowski K, Peters CJ. Comparison of the phase behavior of some selected binary systems with ionic liquids. *AIChE J.* 2005;51:1532−1540.
34. Muldoon MJ, Aki SNVK, Anderson JL, Dixon JK, Brennecke JF. Improving carbon dioxide solubility in ionic liquids. *J Phys Chem B.* 2007;111:9001–9009.
35. Huddleston JG, Visser AE, Reichert WM, Willauer HD, Broker GA, Rogers RD. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* 2001;3:156–164.
36. Tsunashima K, Sugiya M. Physical and electrochemical properties of low-viscosity phosphonium ionic liquids as potential electroytes. *Electrochem Commun.* 2007;9:2353–2358.
37. Tang S, Baker GA, Zhao H. Ether- and alcohol-functionalized task-specific ionic liquids: attractive properties and applications, *Chem Soc Rev.* 2012;41:4030–4066.
38. Wazer JRV, Lyons JW, Kim KY, Colwell RE. *Viscosity and Flow Measurement.* New York: Wiley, 1963:406.
39. Jacquemin J, Husson P, Padua AAH, Majer V. Density and viscosity of several pure and water-saturated ionic liquids. *Green Chem.* 2006;8:172–180.
40. Brown P, Butts CP, Eastoe J, Fermin D, Grillo I, Lee H, Parker D, Plana D, Richardson RM. Anionic surfactant ionic liquids with 1-butyl-3-methyl-imidazolium cations:characterization and application. *Langmuir.* 2012;28:2502–2509.
41. Baranyai KJ, Deacon GB, MacFarlane DR, Pringle JM, Scott JL. Thermal degradation of ionic liquids at elevated temperatures. *Aust J Chem.* 2004;57:145–147.
42. Ngo HL, LeCompte K, Hargens L, McEwen AB. Thermal properties of imidazolium ionic liquids. *Thermochim Acta.* 2000;357:97–102.
43. Wassersheid P, Welton T. *Ionic Liquids in Synthesis.* New York: Wiley, 2008:66.

Manuscript received Jan. 8, 2015, and revision received Feb. 20, 2015.