Chem. Mater. **2008,** *20,* 5337–5344

Carbon Dioxide and Molecular Nitrogen as Switches between Ionic and Uncharged Room-Temperature Liquids Comprised of Amidines and Chiral Amino Alcohols

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Received April 29, 2008. Revised Manuscript Received June 2, 2008

The properties of reversible, room-temperature, chiral, ionic liquids (L-A-C) are reported. They are easily prepared by passing CO_2 gas through equimolar mixtures of a simple amidine (L) and a chiral amino alcohol (A), L/A, derived from a naturally occurring amino acid, and they can be returned to their L/A states by passing a displacing gas, N_2, through the ionic liquid; the process of passing from uncharged to charged states can be repeated several times without discernible degradation of each phase. All of the 40 L/A combinations examined form room-temperature ionic liquids (most to ca. 50 °C under 1 atm of CO_2) and they remain liquids to at least −20 °C. The L-A-C phases are more viscous than their corresponding L/A phases, the conductivities are much higher in the L-A-C phases than in the L/A phases, and the solubility characteristics of the liquids can be modulated significantly by exposing them to either CO_2 or N_2 gas. The spectroscopic characteristics of the L/A and L-A-C phases have been compared also. Their reversibility, chirality, broad temperature ranges, tolerance to water, and ease of preparation should make the combination of L/A and L-A-C phases useful as solvents for several "green" applications.

Introduction

Their unique physical and chemical properties[1] make room-temperature ionic liquids (RTILs)[2] attractive solvents for a wide variety of applications.[3] Recently, examples of the use of task-specific, chiral, ionic liquids[4] for performing enantioselective reactions[5] and enantiomeric separations[6] have been reported. However, there are no general procedures of which we are aware that separate products (or catalysts) from their host ionic liquids in a manner that allows the liquids (and catalysts) to be reused.[7] Finding such procedures poses a serious challenge to expanded exploitation of these materials. A potential solution to this problem that others[8a,b,e,9] and we[8c,d] are exploring is the development of ionic liquids that can be transformed easily, rapidly, and reversibly into uncharged, low-polarity analogs by the selective addition of gases. In several respects, this approach is an example of the formation and use of "gas-expanded liquids".[10]

Here, we describe the properties of amidinium carbamates—reversible, room-temperature, chiral ionic liquids that are easily made from readily available amidines and chiral amino alcohols. Results from this work are compared with those from mixtures of amidines and alcohols[8a,9] and of amidines and achiral amines[8c] or chiral amino acid esters.[8d] Among their other attributes, the ionic liquids reported here persist

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(1) (a) Weingärtner, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 654–670. (b) Aki, S. N. V. K.; Brennecke, J. F.; Samanta, A. *Chem. Commum.* **2001**, *5*, 413–414. (c) Earle, M. J.; Esperança, J. M. S. S.; Manuela, A. G.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature* **2006**, *439*, 381–384.

(2) (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083. (b) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2003. (c) Rogers, R. D., Seddon, K. R., Eds. *Ionic Liquids: Industrial Applications to Green Chemistry*; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002. (d) Rogers, R. D., Seddon, K. R., Eds. *Ionic Liquids IIIA and IIIB: Fundamentals, Progress, Challenges, and Opportunitities*; ACS Symposium Series 901 and 902; American Chemical Society: Washington, DC, 2005. (e) Wasserscheid, P.; Kein, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773–3789.

(3) (a) Anderson, J. L.; Armstrong, D. W.; Wei, G. *Anal. Chem.* **2006**, *78*, 2892–2902. (b) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391–1398. (c) Sheldon, R. *Chem. Commun.* **2001**, *23*, 2399–2407. (d) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792–793. (e) Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, *37*, 123–150.

(4) (a) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A. C.; Plaquevent, J. C. *Tetrahedron Asymm.* **2003**, *14*, 3081–3093. (b) Wasserscheid, P.; Bosmann, A.; Bolm, C. *Chem. Commun.* **2002**, *3*, 200–201. (c) Nockemann, P.; Thijs, B.; Pittois, S.; Thoen, J.; Glorieux, C.; Van Hecke, K.; Van Meervelt, L.; Kirchner, B.; Binnemans, K. *J. Phys. Chem. B* **2006**, *110*, 20978–20992. (d) Yu, S.; Lindeman, S.; Tran, C. D. *J. Org. Chem.* **2008**, *73*, 2576–2591.

(5) (a) Solinas, M.; Pfaltz, A.; Cozzi, P. G.; Leitner, W. *J. Am. Chem. Soc.* **2004**, *126*, 16142–16147. (b) Doherty, S.; Goodrich, P.; Hardacre, C.; Luo, H.-K.; Roony, D. W.; Seddon, K. R.; Styring, P. *Green Chem.* **2004**, *6*, 63–67.

(6) (a) Han, X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, *40*, 1079–1086. (b) Ding, J.; Armstrong, D. W. *Chirality* **2005**, *17*, 281–292.

(7) (a) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459–2477. (b) Baudequin, C.; Bregeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J. C.; Gaumont, A. C. *Tetrahedron Asymm.* **2005**, *16*, 3921–3945. (c) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692. (d) Parvulescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, *107*, 2615–2665.

(8) (a) Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. *Nature* **2005**, *436*, 1102. (b) Liu, Y.; Jessop, P. G.; Cunningham, M.; Eckert, C. A.; Liotta, C. L. *Science* **2006**, *313*, 958–960. (c) Yamada, T.; Lukac, P. J.; George, M.; Weiss, R. G. *Chem. Mater.* **2007**, *19*, 967–969. (d) Yamada, T.; Lukac, P. J.; Yu, T.; Weiss, R. G. *Chem. Mater.* **2007**, *19*, 4761–4768. (e) Phan, L.; Andreatta, J. R.; Horvey, L. K.; Edie, C. F.; Luco, A.-L.; Mirchandani, A.; Darensbourg, D. J.; Jessop, P. G. *J. Org. Chem.* **2008**, *73*, 127–132.

(9) Phan, L.; Chiu, D.; Heldebrant, D. J.; Huttenhower, H.; John, E.; Li, X.; Pollet, P.; Wang, R.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *Ind. Eng. Chem. Res.* **2008**, *47*, 539–545.

(10) Jessop, P. G.; Subramaniam, B. *Chem. Rev.* **2007**, *107*, 2666–2694.

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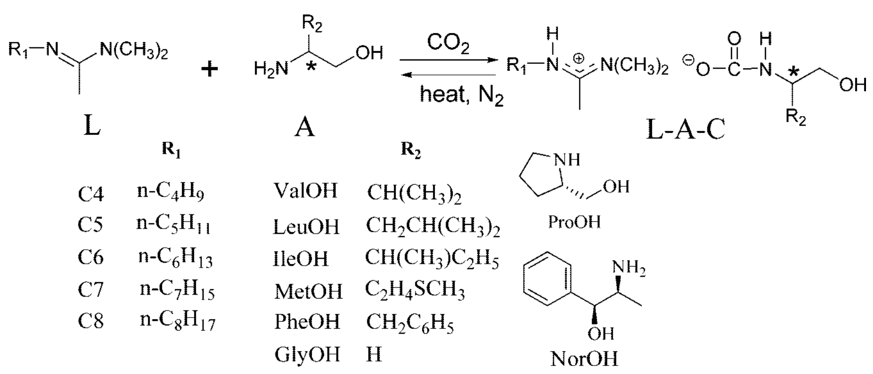
Scheme 1



over very wide temperature ranges, are much more tolerant to added water than analogous reversible ionic liquids made from amidines and alcohols (that must be kept dry to avoid the formation of solids[8b]),[8a,9] and lack chromophores absorbing in the visible and into the UV region. Although several RTILs employing amino acids and their derivatives are known,[11] none of which we are aware (except our own involving amino acid esters[8d]), including one which employs CO_2,[12] has switchable capability between nonionic and ionic states.

The ionic liquid phases are prepared by exposing a 1/1 (mol/mol) mixture of an easily synthesized amidine (*N*′-alkyl-*N*,*N*-dimethylacetamidine; L) and an amino alcohol (A), obtained in one step by reduction of a naturally occurring amino acid, to CO_2 gas (C) (Scheme 1); one commercially available amino alcohol with two chiral centers, (1*R*, 2*S*)-(−)-norephedrine, and one achiral amino alcohol, glycinol (i.e., 2-aminoethanol; GlyOH), have been employed as well. All of the possible 40 combinations from the L/A mixtures in Scheme 1 form room-temperature ionic liquids (L-A-C) in this way. They are stable indefinitely under an atmosphere of CO_2 and all of them remain liquids to −20 °C. The L-A-C can be reconverted to their nonionic (L/A) states after an inert gas (such as N_2) is bubbled through them at room temperature or, more rapidly, at slightly elevated temperatures.

Experimental Section

Materials. Unless stated otherwise, all reagents were used as received. L-Proline (Pro; 99%), L-leucine (Leu; 99%), L-isoleucine (Ile; 99%), L-methionine (Met; 98.5%), L-phenylalanine (Phe; 98.5%), and 4-dimethylamino benzaldehyde (98%) were from Acros; triethylamine (99.9%) and methyl amine (40% aqueous solution) were from Alfa Aesor; L-valine (Val; 98%), (1*R*, 2*S*)-(−)-norephedrine (Nor; 99%), ethanolamine (GlyOH; 99%), *n*-decane (99%), and lithium aluminum hydride ($LiAlH_4$, 95%) were from Aldrich; nitromethane (analytical grade) was from Fisher. Eosin Y (99%) was from Allied Chemical Co. Methanol (Aldrich, 99.8%) was dried by Vogel's method.[13] Toluene (Aldrich, 99.9%) and tetrahydrofuran (Acros, 99.9%) were refluxed over sodium metal for 5 h, followed by distillation. Carbon dioxide gas was generated by warming dry ice and dried by passing it through a tube filled with anhydrous $CaSO_4$ (Drierite).

Instrumentation. NMR spectra (referenced to internal tetramethylsilane (TMS) for ^1H and to $CDCl_3$ for ^{13}C) were recorded on a Varian 300 MHz spectrometer interfaced to a Sparc UNIX computer using Mercury software. IR spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer interfaced to a PC, using an attenuated total reflection accessory or NaCl plates. UV−vis spectra were recorded on a Varian CARY 300 Bio UV−visible spectrophotometer in Hellma quartz cells with 0.1 cm path lengths. Thermal gravimetric analysis (TGA) measurements were performed under a nitrogen atmosphere at a 5 °C/min heating rate on a TGA 2050 thermogravimetric analyzer (TA Instruments) interfaced to a computer. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with flame ionization detectors and a DB-5 (15 m × 0.25 mm) column (J & W Scientific). Optical rotations were recorded on a Rudolph Instruments DigiPal 781 automatic polarimeter at 589 nm in Hellma quartz cells with 0.1 mm path lengths. Conductivities were measured with a Yellow Spring Instrument Co. model 31 conductivity meter using Au electrodes. The conductivity values were calibrated using various concentrations of standard KCl solutions in water purified with a Millipore Co. Milli-Q system (resistance 18.3 mΩ·cm; conductivity 50 μS/cm).[14] It was sealed in a flask until use to prevent adventitious absorption of CO_2 from the atmosphere. Viscosities were measured on an AR2000 stress-controlled rheometer (TA Instruments, Newark, DE) at 25 °C using a cone and plate geometry (40 mm diameter, 2° cone angle). CD spectra were recorded on a Jasco-700 CD spectrometer at room temperature.

Syntheses. The general procedure for synthesis of the amino alcohols is presented in detail for L-leucinol (LeuOH); minor variations were adopted for the other amino alcohols.

Over a 30 min period, lithium aluminum hydride (4.0 g, 0.10 mol) was added to a cooled (ice bath) suspension of L-leucine (10.0 g, 0.076 mol) in 100 mL of THF under a nitrogen atmosphere. The ice bath was removed and the reaction mixture was warmed to room temperature, then refluxed for 24 h under a nitrogen atmosphere, and quenched by slow sequential addition of water (4.0 mL), aqueous 15% sodium hydroxide (4.0 mL), and water (12.0 mL). The mixture was stirred for 30 min and a white precipitate was separated by filtration. The filter cake was washed with dichloromethane and the combined organic layers were dried with sodium sulfate, concentrated under reduced pressure, and distilled at bp 90 °C (0.9 Torr) (lit[15] 64−65 °C (1.5 Torr)) to yield 5.3 g

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[11] (a) Tao, G.; He, L.; Liu, W.; Xu, L.; Xiong, W.; Wang, T.; Kou, Y. *Green Chem.* **2006**, *8*, 639–646. (b) Fukumoto, K.; Ohno, H. *Chem. Commun.* **2006**, *29*, 3081–3083.

[12] Zhang, J.; Zhang, S.; Dong, K.; Zhang, Y.; Shen, Y.; Lv, X. *Chem. Eur. J.* **2006**, *12*, 4021–4026.

[13] Vogel, A. I. *Textbook of practical organic chemistry, 5th ed.*; Longman Scientific & Technical: New York, 1989, pp 401−402.

[14] Ohno, H. *Electrochemical Aspects of Ionic Liquids*; Wiley-Interscience: New York, 2005.

[15] Itsuno, S.; Hirao, A.; Nakahara, S.; Yamazaki, N. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1673–1676.

Table 1. Appearances of 1/1 (mol/mol) Amidine/Amino Alcohol Mixtures at Room Temperature and at −20 °C (in Parentheses) before (*B*) and after (*A*) Exposure to CO_2[a]

	amino alcohol															
	Glycinol		Prolinol		Leucinol		Isoleucinol[b]		Valinol[b]		Methioninol[b]		Phenylalaninol[b]		Norephedrine	
amidine	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*
C_4	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	L^c (L)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)
C_5	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	L^c (L)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)
C_6	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	L^c (L)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)
C_7	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	L^c (L)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)
C_8	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	L^c (L)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)	*L*(*L*)
none	*L*	*L*	*L*	*L*	*L*	*S*	*S*	*S*	*S*	*S*	*S*	*S*	*S*	*S*	*S*	*S*

[a] *L* and *S* indicate liquid and solid, respectively, at room temperature. [b] Samples were heated slightly above 50 °C until amino alcohols were dissolved before CO_2 bubbling. [c] Samples were initially a milky white mixture that became a totally clear liquid upon further exposure to CO_2.

(60%) of a colorless liquid (98% pure by GC). ^{1}H NMR: δ 3.56 (d-d, 1H, J_{HH} 10.5 Hz, 3.9 Hz, CH_2−OH); 3.23 (d-d, 1H, J_{HH} 10.5 Hz, 5.1 Hz, CH_2−OH); 2.87 (m, 1H, H_2N−C*H); 1.8−2.4 (br, 3H, NH_2 and OH); 1.68 (m, 1H, CH_2−CH(CH_3)$_2$); 1.21 (t, 2H, J_{HH} 10.5 Hz, C*H−CH_2−CH); 0.89−0.94 (m, 6H, CH(CH_3)$_2$). ^{13}C NMR: δ 67.12, 50.83, 43.68, 24.89, 23.58, 22.38.

L-Prolinol (ProOH). Yield: 48% of a yellowish clear liquid; 99% pure (GC); bp 46−47 °C (0.2 Torr) (lit[16] 89 °C (6 Torr)). ^{1}H NMR: δ 3.22−3.58 (m, 5H, −NH−C*H−CH_2−OH); 2.90 (t, 2H, J_{HH} 6.8 Hz, −CH_2−CH_2−NH−); 1.65−1.88 and 1.34−1.46 (m, 4H, CH_2−CH_2−C*H). ^{13}C NMR: δ 64.90, 59.92, 46.50, 27.65, 26.01.

L-Valinol (ValOH). Yield: 50.2% of a colorless solid (98% pure by GC); mp 31.3−33.6 °C (lit[12] 32 °C); bp 38−39 °C (0.15 Torr) (lit[12] 55−57 °C (2 Torr)). ^{1}H NMR: δ 3.64 (d-d, 1H, J_{HH} 13.5 Hz, 3.9 Hz, CH_2−OH); 3.28 (d-d, 1H, J_{HH} 13.5 Hz, 8.7 Hz, CH_2−OH); 2.56 (m, 1H, H_2N−C*H); 1.7−2.2 (br, 3H, NH_2 and OH); 1.57 (m, 1H, C*H−CH(CH_3)$_2$); 0.92 (m, 6H, CH(CH_3)$_2$). ^{13}C NMR: δ 64.89, 58.64, 31.71, 19.48, 18.56.

L-Isoleucinol (IleOH). Yield: 54% of a colorless solid (98% pure by GC); mp 32.5−37.3 °C (lit[17] mp 38−40 °C); bp 61 °C (0.5 Torr) (lit[13] 100−101 °C (5 Torr)). ^{1}H NMR: δ 3.64 (d-d, 1H, J_{HH} 10.5 Hz, 3.9 Hz, CH_2−OH); 3.28 (d-d, 1H, J_{HH} 10.5 Hz, 9.0 Hz, CH_2−OH); 2.64 (m, 1H, H_2N−C*H); 1.48−1.57 (m, 1H, C*H−CH−); 1.12−1.39 (m, 2H, CH−CH_2−CH_3); 1.87 (br, 3H, NH_2 and OH), 0.87−1.12 (m, 6H, CH(CH_3)−CH_2CH_3). ^{13}C NMR: δ 64.52, 57.19, 38.79, 25.50, 15.29, 11.48.

L-Methioninol (MetOH). Yield: 83.5% of a yellowish solid (99% pure by GC); mp 33.1−34.6 °C. (lit[12] 34−35 °C). ^{1}H NMR: δ 3.60 (d-d, 1H, J_{HH} 10.5 Hz, 3.9 Hz, CH_2−OH); 3.34 (d-d, 1H, J_{HH} 10.5 Hz, 7.5 Hz, CH_2−OH); 2.95 (m, 1H, H_2N−C*H); 2.62 (m, 2H, CH_2−S−CH_3); 2.11(s, 3H, CH_2−S−CH_3); 2.0−2.3 (br, 3H, NH_2 and OH); 1.73 and 1.54 (m, 2H, CH_2− CH_2−S−CH_3). ^{13}C NMR: δ 66.92, 52.16, 33.83, 31.26, 15.83.

L-Phenylalaninol (PheOH). Yield: 62% of a colorless solid (99% pure by GC); mp 92.5−94.4 °C (lit[18] 91−93 °C). ^{1}H NMR: δ 7.18−7.34 (m, 5H, Ph−H); 3.64 (d-d, 1H, J_{HH} 13.5 Hz, 3.9 Hz, CH_2−OH); 3.36 (d-d, 1H, J_{HH} 13.5 Hz, 7.5 Hz, CH_2−OH); 3.12, (m, 1H, H_2N−C*H); 2.80 (d-d, 1H, J_{HH} 10.5 Hz, 5.1 Hz, CH_2−Ph); 2.53 (d-d, 1H, J_{HH} 10.5 Hz, 8.5 Hz, CH_2−Ph); 1.64 (br, 3H, NH_2 and OH). ^{13}C NMR: δ138.95, 129.47, 128.85, 126.69, 66.64, 54.43, 41.22.

The acyclic amidines and 1-(*para*-dimethylaminophenyl)-2-nitroethylene (DAPNE) were available from previous investigations.[8c] Their preparation methods and purities are collected in the Supporting Information file. Methods for the preparation of the ionic liquids, their reversion to their nonionic states, the preparation of samples for NMR investigations, the measurement and calculation of optical rotations, and the measurement of CO_2 uptake as a function of time have been reported previously.[8c,d]

Results and Discussion

Preparation of RTILs. The appearances of the phase of the L/A combinations at room temperature and at −20 °C, both before and after bubbling CO_2, are collected in Table 1. All the L/A combinations formed clear, nearly colorless ionic liquids after exposure to CO_2 at room temperature and remained so to −20 °C. By comparison, exposure of mixtures of the same amidines and either a simple amine or simple esters of the amino acids from which the amino alcohols were derived led to liquids in many cases, but to solids in others, even at room temperature.[8c,d] As expected, the L/A mixtures were qualitatively less viscous than the corresponding L-A-C ionic liquids (with their added electrostatic interactions), and those with the phenyl-substituted amino alcohols, PheOH and NorOH, were more viscous than the ionic liquids with alkyl-substituted amino alcohols. The ionic liquids are stable indefinitely at room temperature under 1 atm of CO_2 pressure and some are stable for very long periods in the air. TGA measurements indicate that the loss of CO_2 occurs very rapidly at ca. 50 °C in air.

Consistent with our observations on analogous systems employing an amidine and either a simple amine or an amino acid ester,[8c,d] the L/A and L-A-C retain their general phase characteristics when as much as 10% of water is added; the addition of water to an L/A mixture did not impede the formation of L-A-C upon bubbling CO_2 and no precipitate or cloudiness was observed. To ensure quantitative reproducibility, all experiments reported here were conducted under dry conditions unless stated otherwise.

Characterization of RTILs. The existence of amidinium carbamates was confirmed by the quantitative determination of %CO_2 uptake by the L/A systems as a function of time using a mercury burette apparatus[19] and, independently, by FT-IR, TGA, and ^{1}H and ^{13}C NMR measurements before and after samples were exposed to CO_2. The examples in Figure 1 show that the rates of CO_2 uptake during the first 10 min are fast and reached plateau values after approximately 50 min. For C8/LeuOH and C8/ValOH mixtures, the theoretical amount is absorbed after ca. 30 min and another ca. 10% is absorbed thereafter. These results indicate

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(16) Doyle, F. P.; Mehta, M. D.; Sach, G. S.; Pearson, J. L. *J. Chem. Soc.* **1958**, 4458–4466.

(17) McKennon, M. J.; Meyeres, A. *J. Org. Chem.* **1993**, *58*, 3568–3571.

(18) Atwood, D. A.; Gabbai, F. P.; Lu, J.; Remington, M. P.; Rutherford, D.; Sibi, M. P. *Organometallics* **1996**, *15*, 2308–2313.

(19) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 2.

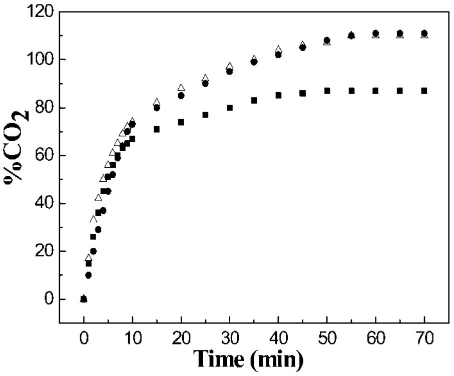

Figure 1. Percentage uptake of CO_2 (%CO_2; based upon a presumed 1/1 stoichiometry for CO_2 and amino alcohol) by 1/1 (mol/mol) C8/ProOH (■), C8/LeuOH (Δ), and C8/ValOH (●) as a function of time upon their exposure to 1 atm pressure of dry CO_2 gas at room temperature. Samples were stirred to increase the rate of molecular exchange at the gas−liquid interfaces.

that both chemically fixed and physically adsorbed CO_2 are present.[20] The initial absorption is probably the result of the conversion of L/A to L-A-C phases, and the ca. 10% excess is the physically adsorbed part. Only 87% uptake of CO_2 was observed in the C8/ProOH system; the fractions that are chemically and physically absorbed are not known. It is known that the efficiency of CO_2 uptake by secondary amines, such as ProOH, is much less than that of primary amines.[8d] Because hydroxyl groups are also capable of reacting with CO_2 and then with an amidine,[8a,9,10,21] the %CO_2 uptake by 2/1 C8/LeuOH and C8/ValOH systems was examined to determine whether 2 molecules of gas can react per 1 molecule of amino alcohol when ample amidine is present (Tables S4 and S5 of the Supporting Information). In both cases, ca. 1.5 equiv of CO_2 were absorbed, indicating that conversion of the hydroxyl groups to carbonates was not complete.

Figure 2 shows the FT-IR spectra of a C8/ValOH sample before and after bubbling CO_2 through it. After bubbling, the typical N=C stretching band of the C8 component at 1629 cm^{-1} [22] is replaced by bands at 1646 and 1575 cm^{-1} which can be assigned, respectively, to protonated amidine and carbamate stretching modes. In addition, a broad band, centered at 3380 cm^{-1}, from amidinium and carbamate N−H stretching modes, is found after bubbling.

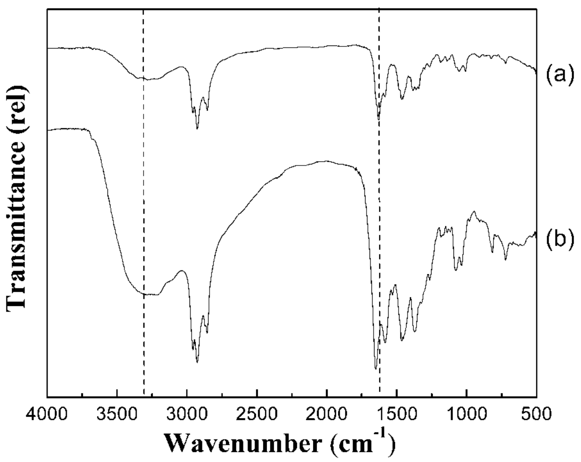

Figure 2. FT-IR spectra of C8/ValOH (a) and C8-ValOH-CO_2 (b).

Table 2. Specific Rotations[a] of Amino Alcohols and of Amino Alcohol/Amidine Mixtures before and after Exposure to 1 atm CO_2 Gas at 25 °C[b]

sample	$[\alpha]_{total}$	$[\alpha]_{opt}$	sample	$[\alpha]_{total}$	$[\alpha]_{opt}$
ProOH	36.7		LeuOH	4.8	
C6/ProOH	10.9	27.4	C6/LeuOH	2.7	3.8
C6-ProOH-CO_2	−20.1	−20.5	C6-LeuOH-CO_2	−21.5	−23.7

[a] $[\alpha]_{total}$ = specific optical rotation of neat samples and mixtures; $[\alpha]_{opt}$ = specific optical rotation of the amino alcohol component in mixtures. [b] The measured rotations, α, are collected in the Supporting Information. [α] values are ±0.1°.

Because each of the A components is optically active, the changes of the specific optical rotations ([α]) upon changing from L/A to L-A-C phases could be investigated (Table 2). The specific rotations of the molecular mixtures, $[\alpha]_{total}$, changed sign and magnitude during the L/A to L-A-C transformations. Furthermore, the specific rotations of the A components of the L/A mixtures, $[\alpha]_{opt}$, were lower than the [α] values of the corresponding neat amino alcohols. These results are consistent with our observations on systems with amidines and amino acid esters,[8d] and can be attributed to the interactions between amino alcohols and amidines even before CO_2 is added to form the ionic liquids. A manifestation of those interactions is the qualitatively higher viscosity of the L/A mixtures than of either of the components alone. We conjecture that the protons of the amino and hydroxyl groups of the A become strongly associated with the basic amidine functionalities. Such interactions can alter the conformations of the amino alcohols and lead to the observed changes of optical rotations.[23a] Although additional experimentation will be required to determine whether and to what extent the alkyl chains of amidinium cations associate in microheterogeneous domains within the L-A-C ionic liquids,[23b,c] we suspect that they do and that such associations will lead to additional changes of the optical rotations. The self-association of surfactants in other ionic liquids has been demonstrated.[24]

However, attempts to observe solvent-induced dichroism in guest dye molecules[25] have been unsuccessful thus far. For example, addition of the uncharged dye, 1-(*para*-dimethylaminophenyl)-2-nitroethylene (DAPNE) or the anionic dye, 2′,4′,5′,7′-tetrabromofluorescein (Eosin Y), to an L/C and the corresponding L-A-C did not result in discernible

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(20) Previously, we found that 1:1 amidine:alkylamine[8c] and 1:1 amidine: amino acid esters[8d] take up more than 1 equiv of CO_2 as well. Both of those amines lack a hydroxyl group (capable of forming a carbonate upon reaction with a second molecule of CO_2). Also, simple electrostatic arguments disfavor the production of proximal carbamate and carbonate groups on one amino alcohol. If the ionic state is a mixture of two different compounds, the second (an amidinium carbonate) must be a very small amount with respect to the first (an amidinium carbamate)

(21) (a) Hori, Y.; Nagano, Y.; Nakao, J.; Taniguchi, H. *Chem. Express* **1986**, *1*, 173–176. (b) Hori, Y.; Nagano, Y.; Nakao, J.; Fukuhara, T.; Taniguchi, T. *Chem. Express* **1986**, *1*, 224–227.

(22) Corset, C.; Froment, F. *J. Phys. Chem.* **1990**, *94*, 6908–6911.

(23) (a) Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. *Organic Structural Analysis*; Macmillan: New York, 1976; Part Three, Chapter 3. (b) Wang, Y.; Jiang, W.; Yan, T.; Voth, G. A. *Acc. Chem. Res.* **2007**, *40*, 1193–1199. (c) Wang, Y.; Voth, G. A. *J. Phys. Chem. B* **2006**, *110*, 18601–18608.

(24) Anderson, J. L.; Pino, V.; Hagberg, E. C.; Sheares, V. V.; Armstrong, D. W. *Chem. Commun.* **2003**, *19*, 2444–2445.

(25) See, for example (a) Franke, D.; Vos, M.; Antonietti, M.; Sommerdijk, N. A. J. M.; Faul, C. F. J. *Chem. Mater.* **2006**, *18*, 1839–1847. (b) Kodaka, M. *J. Phys. Chem.* **1991**, *95*, 2110–2112.

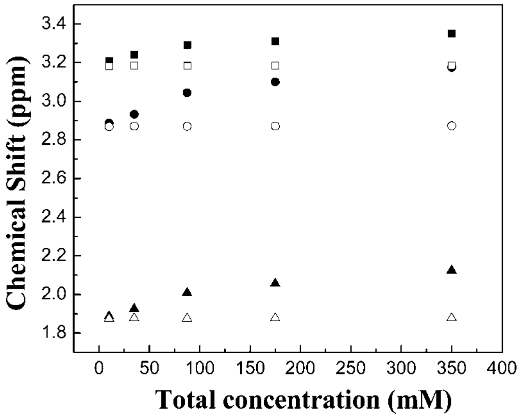

Figure 3. Chemical shifts of protons in equimolar mixtures of C6 and IleOH (open symbols) and the corresponding amidinium carbamate (closed symbols) that are most sensitive to concentration in $CDCl_3$ solutions: $\mathrm{C}\mathit{H}_2\mathrm{N{=}C{-}N}$ (□, ■: 3.20− 3.35 ppm), $\mathrm{N{=}C{-}N(C}\mathit{H}_3)_2$ (○, ●: 2.89−3.18 ppm), $\mathrm{N{=}C(C}\mathit{H}_3)\mathrm{{-}N}$ (Δ, ▲: 1.89−2.12 ppm).

CD signals in the region where the dyes absorb (Figures S6 and S7 of the Supporting Information). These results indicate that to effect strong interactions between a guest and one of the host molecules, it will be necessary to increase the specificity of the interactions.

The concentration dependence of the NMR chemical shifts of selected ^{1}H and ^{13}C resonances in chloroform-*d* solutions of the L-A-C (but not the L/A mixtures) provides evidence that is consistent with the aggregation of amidinium−carbamate ionic pairs[8d] and microdomains of amidinium alkyl chains.[23] As an example, the concentration dependence of the resonances from C6/IleOH and C6-IleOH-CO_2 in $CDCl_3$ at room temperature are shown in Figure 3 and Table S8 in the Supporting Information. The L-A-C protons that are closest to ionic centers (N.B., the *N*-dimethyl groups ($\mathrm{N{=}C{-}N\ (C}\mathit{H}_3)_2$), the C-methyl protons ($\mathrm{N{=}C\ (C}\mathit{H}_3)\mathrm{{-}N}$), and the α-methylene protons ($\mathrm{{-}C}\mathit{H}_2\mathrm{N{=}C{-}N}$)) exhibited slight, but reproducible, downfield shifts as concentration was increased to 350 mM.

Reversibility Studies. An interesting and potentially very useful attribute of these L/A ⇔ L-A-C systems is their ease of reversibility. The L-A-C ionic liquids were reconverted slowly to their nonionic L/A phases by bubbling N_2 through them at room temperature or, more rapidly, by bubbling at slightly elevated temperatures. Clearly, other inert gases should be able to effect the L-A-C → L/A phase transformations.

A demonstration of this reversibility for the C6/ProOH system is shown by the NMR data in Figure 4. The amidinium carbamate was formed as a deuteriochloroform solution upon exposure to CO_2 and the nonionic components, C6 and ProOH, were reformed by bubbling N_2 through the chloroform solution at 50 °C for 3 min. The chemical shift data indicate little or no discernible changes to the amidinium carbamate or the uncharged precursors upon repeated cycling. The FT-IR spectra in Figure 5, recorded during two bubbling cycles, provide additional evidence for the reversibility of the C6/ProOH system in the absence of chloroform as a diluent. The N=C stretch at 1629 cm^{-1} was replaced by peaks attributable to amidinium and carbamate at 1646 and 1575 cm^{-1} after exposure to CO_2; see Figure 2 and associated text for band attributions.

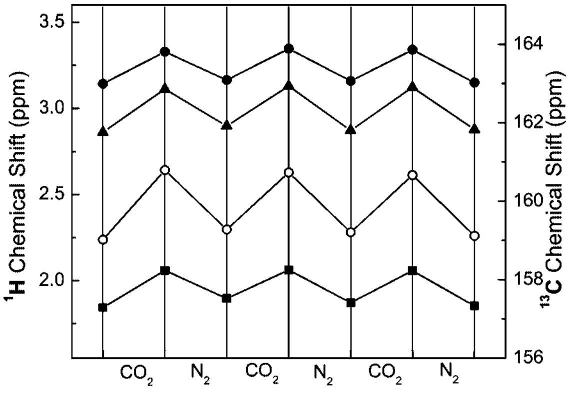

Figure 4. Chemical shifts of the protons and carbon atoms of 350 mM C6/ProOH in $CDCl_3$ by alternating the bubbling of CO_2 and N_2 over three cycles. (a) $\mathrm{{-}C}\mathit{H}_2\mathrm{N{=}C{-}N}$ (●), (b) $\mathrm{N{=}C{-}N(C}\mathit{H}_3)_2$ (▲), (c) $\mathrm{N{=}C(C}\mathit{H}_3)\mathrm{{-}N}$ (■), and $\mathit{N}{=}^{13}\mathit{C}\mathrm{{-}N}$ (○). The scale on the left is for the filled symbols; the scale on the right is for the open circles.

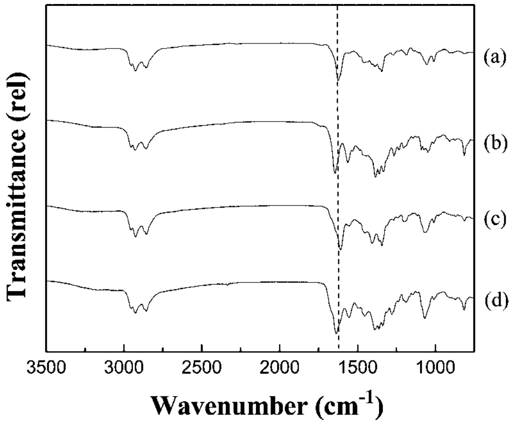

Figure 5. Vertically offset FT-IR spectra recorded sequentially for neat C6/ProOH (a), after bubbling CO_2 (i.e., C6-ProOH-CO_2) (b), the compound in (b) after bubbling with N_2 (c) at 50 °C, and the compound in (c) after bubbling with CO_2 (d).

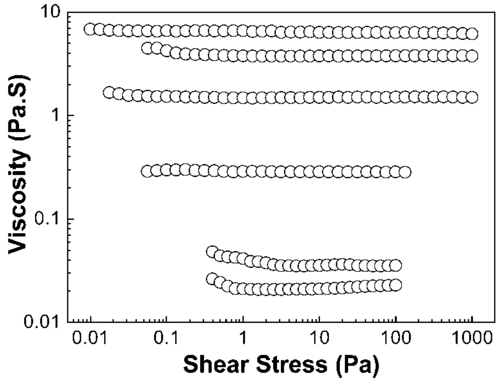

Figure 6. Viscosities (Pa•S) at 25 °C of C8-IleOH-CO_2, C8-LeuOH-CO_2, C4-IleOH-CO_2, C4-LeuOH-CO_2, C8/IleOH, and C8/LeuOH (from top to bottom) as a function of shear stress (Pa).

Viscosity Measurements. As shown in Figure 6, the viscosities of the L/A and L-A-C are virtually independent of shear rate; they exhibit Newtonian behavior; shear rate versus shear stress plots are shown in Figure S5 of the Supporting Information. The average viscosities over the ranges of shear stress for the L/A mixtures, C8/LeuOH and C8/IleOH, are 0.020 and 0.036 Pa•S, respectively. After exposure to CO_2, the viscosities of these samples increase by orders of magnitude to 3.78 Pa•S (C8-LeuOH-CO_2) and

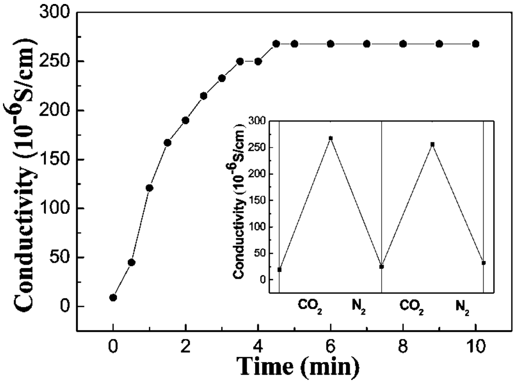

Figure 7. Conductivity at 25 °C of 50 wt % C8/IleOH in $CHCl_3$ as a function of time of bubbling CO_2. The inset shows maximum conductivities at 25 °C when CO_2 (at 25 °C) and N_2 (at 50 °C) were bubbled through sequentially. The N_2 bubbling was conducted at 50 °C to accelerate the loss of CO_2.

6.50 Pa•S (C8-IleOH-CO_2). With the shorter chained amidine, C4, the L-A-C viscosities are somewhat lower—0.28 Pa•S for C4-LeuOH-CO_2 and 1.51 Pa•S for C4-IleOH-CO_2—but both are higher than the viscosities of the more common ionic liquids.[1]

Conductivity Measurements. We have also measured the electronic conductivity (σ) of chloroform solutions of some mixtures that were cycled between their L/A and L-A-C forms by bubbling with CO_2 and N_2. Chloroform was added to reduce the viscosity, thereby allowing more rapid flow of ions and decreasing of the amount of aggregation among the ions.[8d,26]

The conductivity of the neat chloroform employed remained <0.1 μS/cm after bubbling CO_2 through it for 30 min. As expected, addition of an uncharged L/A mixture, C8/IleOH (Figure 7), did not increase the conductivity to a high level. However, the conductivity increased rapidly as CO_2 was bubbled through the solution and the ionic C8-IleOH-CO_2 formed; at the C8/IleOH concentration employed, the conductivity reached a plateau value of 268 μS/cm. When N_2 was passed subsequently through the solution, the conductivity decreased to 25 μS/cm, a value nearly identical to the conductivity of the original C8/IleOH solution. The inset in Figure 7 shows the conductivity changes during two bubbling cycles. We attribute the small decrease after the second CO_2 bubbling to evaporation of some of the chloroform (and resultant increase in viscosity and ion aggregation) that occurs during the bubbling procedures.

The conductivity values at room temperature of three neat C8 amidine and amino alcohol combinations, before and after their exposure to CO_2 for 30 min, are shown in Table 3. The conductivity values of the L-A-C phases are similar to those of related ionic liquids,[9] but are less than those of imidazolium-based ionic liquids.[14] The mobilities of the ions in the L-A-C phases are attenuated by the relatively high viscosities as well as the aforementioned ion aggregation.[23]

To explore further the influences of viscosity and ion pairing on conductivity of the L-A-C, various dilutions of C8/IleOH and C8-IleOH-CO_2 were prepared in chloroform and water and their conductivities were measured at room temperature (Figure 8). As expected, the conductivities of the C8/IleOH remained low at all concentrations in chloroform but increased significantly with increasing water content, to a plateau value of ca. 2.1 mS/cm.

Table 3. Conductivities of Three C8 and Amino Alcohol Combinations before and after Their Exposure to CO_2 for 30 min at Room Temperature

	conductivity (μS/cm)	
amino alcohol	L/A	L-A-C
ProOH	22	85
MetOH	15	66
IleOH	14	58

In contrast, the conductivity of C8-IleOH-CO_2 increased dramatically when small amounts of *either* chloroform *or* water were added; a maximum of 319 μS/cm, about 5.5 times higher than the conductivity of neat C8-IleOH-CO_2, was reached at 80 wt % of $CHCl_3$, and the maximum conductivity, at 70 wt % water, was 7.1 mS/cm. Clearly, the net effect of adding chloroform or water is a convolution of two factors that increase conductivity—higher ion mobilities and less ion pairing—and one that decreases it—lower ion concentrations. Separation of these factors and quantification of each are not trivial.[23,27] Furthermore, the very large conductivities when water is added to C8-IleOH-CO_2 must be due in part to reaction of water and CO_2 to form carbonates.[28]

Miscibility and Polarity. Knowledge of the degree of miscibility of ionic liquids with other solvents is important for several applications, including their use in liquid–liquid extraction processes.[29] As with many other types of RTILs, our L-A-C phases are miscible with highly polar solvents, such as water, DMSO, and ethanol (Table 4). Although the polarity of most ionic liquids depends on the length of the alkyl chains on (what is usually) the cationic portion,[30] the length of the amidine alkyl chain does not appear to influence strongly the miscibility of the L-A-C phases we have investigated. Instead, the structural differences among the carbamates derived from the amino alcohols seem to be the most important determinant of L-A-C polarity. When the L-A-C are mixed with lower polarity solvents, such as hexane, toluene, and diethyl ether, two phases, whose volumes were similar to the amounts of each added, were observed. The L-A-C RTILs prepared from the phenyl-substituted amino alcohols, NorOH and PheOH, were immiscible or only partially miscible with dichloromethane and ethyl acetate, and C6-NorOH-CO_2 was also only partially miscible with chloroform. The other L-A-C RTILs investigated here were completely miscible with dichloromethane, ethyl acetate, and chloroform.

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(26) (a) Fraser, K. J.; Izgorodina, E. I.; Forsyth, M.; Scott, J. L.; MacFarlane, D. R. *Chem. Commun.* **2007**, *37*, 3817–3819. (b) Xu, W.; Cooper, E. I.; Angell, C. A. *J. Phys. Chem. B* **2003**, *107*, 6170–6178. (c) Salanne, M.; Simon, C.; Turq, P.; Madden, P. A. *J. Phys. Chem. B* **2007**, *111*, 4678–4684.

(27) (a) Jarosik, A.; Krajewski, S.; Lewandowski, A.; Radzimski, P. J. *Mol. Liq.* **2006**, *123*, 43–50. (b) Vila, J.; Gines, P.; Rilo, E.; Cabeza, O.; Varela, L. M. *Fluid Phase Equilib.* **2006**, *247*, 32–39.

(28) Hori, Y.; Nagano, Y.; Miyake, S.; Teramoto, S.; Taniguchi, T. *Chem. Express* **1986**, *1*, 311–314.

(29) (a) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2004**, *108*, 5113–5119. (b) Domanska, U.; Casas, L. M. *J. Phys. Chem. B* **2007**, *111*, 4109–4115.

(30) (a) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156–164. (b) Wakai, C.; Oleinikova, A.; Ott, M.; Weingärtner, H. *J. Phys. Chem. B* **2005**, *109*, 17028–17030.

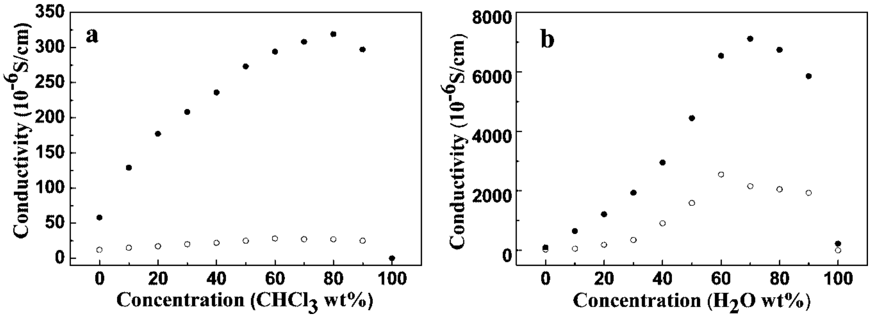

Figure 8. Conductivity of C8/IleOH as a function of $CHCl_3$ (a) and H_2O (b) concentrations before (○) and after (●) bubbling CO_2 through their solutions at room temperature.

Table 4. Miscibility Behavior of Various 1/1 (v/v) L-A-C/Organic Solvent Mixtures at Room Temperature.[a]

ionic liquid: solvent	C4-IleOH -CO_2	C5-IleOH -CO_2	C6-ProOH -CO_2	C6-NorOH -CO_2	C8-PheOH -CO_2	C8-ProOH -CO_2	C8-ValOH -CO_2
hexane	*I*	*I*	*I*	*I*	*I*	*I*	*I*
toluene	*I*	*I*	*I*	*I*	*I*	*I*	*I*
diethyl ether	*I*	*I*	*I*	*I*	*I*	*I*	*I*
dichloromethane	*M*	*M*	*M*	*I*	*I*	*M*	*M*
ethyl acetate	*M*	*M*	*M*	*I*	*P*	*M*	*M*
chloroform	*M*	*M*	*M*	*P*	*M*	*M*	*M*
ethanol	*M*	*M*	*M*	*M*	*M*	*M*	*M*
DMSO	*M*	*M*	*M*	*M*	*M*	*M*	*M*
water	*M*	*M*	*M*	*M*	*M*	*M*	*M*

[a] *I* = immiscible, *M* = miscible, *P* = partially miscible (i.e., only part of this solid amino alcohol was dissolved; most of the amino alcohols are liquids at room temperature).

The L/A and L-A-C are potentially interesting hosts for optical spectroscopic studies. Neat 1.0 mm path length samples of both with A molecules containing acyclic, saturated side groups are almost completely transparent above 300 nm (Supporting Information Figure S4a), and others are transparent at >400 nm (Supporting Information Figure S4b). As a demonstration of this utility, the changes in solvent polarity induced by bubbling CO_2 through an L/A sample or N_2 through an L-A-C sample were investigated using an uncharged solvatochromic dye,[31] DAPNE.[32]

The λ_{max} of this dye in C8/ValOH, 424 nm, indicates a polarity like that of toluene (425 nm) (Supporting Information Table S9). Upon exposure to CO_2, the λ_{max} value was shifted bathochromically to 443 nm, indicating an environment whose polarity is between that of acetone ($\lambda_{max} = 433$ nm) and DMF ($\lambda_{max} = 446$ nm).[32] In general, the L/A and L-A-C polarities reported by DAPNE are somewhat higher than and similar to, respectively, those found for mixtures of L-A-C in which the A component is an amino acid ester.[8d] The difference between the polarities of the two sets of L/A can be attributed to the polar hydroxyl groups in the amino alcohols. Regardless, the L-A-C appear to be less polar than imidazolium-based RTILs; for example, the spectroscopically determined polarities of 1-butyl-3-methyl imidazolium ionic liquids are like those of methanol and ethanol.[33,34]

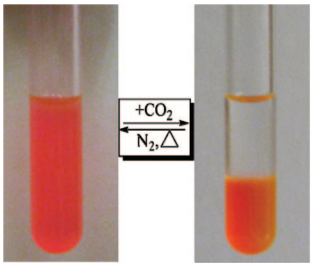

Figure 9. Photographs of a 1/1 (v/v) *n*-decane/(C6/ProOH) solution containing 0.3 μM Eosin Y (left) and after CO_2 bubbling for 1 min and centrifugation for 3 min (right). The two-phase system became one phase again by bubbling through N_2 for 5 min at 50 °C.

Ionic—Uncharged Phase Reversibility. The ability of the L/A and L-A-C to interconvert without adding liquid or solid reagents opens the possibility for these RTILs to be used to solubilize and precipitate/phase-separate added species selectively. Figure 9 shows an example of how such a system can be employed. After exposure to CO_2 for 1 min followed by centrifugation for 3 min, an initial solution of *n*-decane and C6/ProOH (containing a very low concentration of Eosin Y, a polar dye, as an indicator) separated into two phases, with *n*-decane on top and much more polar C6-ProOH-CO_2 (with the dye) on the bottom. When N_2 was bubbled through the two-phase system (at room or slightly elevated temperature) to displace the CO_2, the one-phase (low-polarity) solution was reformed.

Conclusions

A series of easily prepared, chiral, room-temperature ionic liquids has been made and characterized. A very important attribute of these liquids is their ability to be transformed from high-polarity, ionic states to low-polarity, uncharged phases by exposure to an inert gas such as N_2 and to

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(31) (a) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319–2358. (b) Reichardt, C. *Chem. Soc. Rev.* **1992**, *21*, 147–153.

(32) Richter-Egger, D. L.; Tesfal, A.; Flamm, S. J.; Tucker, S. A. *J. Chem. Educ.* **2001**, *78*, 1375–1378.

(33) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591–595.

(34) It should be recognized, however, that the heterogeneous nature of ILs makes determinations of their polarity by solvatochromic probes less reliable than those in "normal" liquids. (a) Jin, H.; Baker, G. A.; Arzhantsev, S.; Dong, J.; Maroncelli, M. *J. Phys. Chem. B* **2007**, *111*, 7291–7302. (b) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247–14254.

reconvert the low-polarity phases to their high-polarity phases by adding CO_2 gas. It was somewhat surprising, but gratifying, that all of the combinations of amidines and amino alcohols examined form room-temperature ionic liquids when exposed to CO_2. They appear to remain liquids with larger structural variations and over wider temperature ranges—generally from below −20 °C to ca. 50 °C under 1 atm of CO_2—than the amidine-alkylamine[8c] and amidine-amino acid ester[8d] systems examined previously. The L-A-C phases are more viscous than their corresponding L/A phases, the conductivities increase dramatically between the L/A and L-A-C phases, and the solubility characteristics of the liquids can be modulated significantly by the gas to which they are exposed.

Also, the amino alcohols provide a chiral center and a potentially useful hydroxyl functionality for future applications (i.e., as task-specific RTILs). In addition, the L-A-C system is much less sensitive to water than other reversible RTILs that have been reported.[8a,9] Thus, experiments need not be performed under scrupulously dry conditions. Additionally, the components of these RTILs are biodegradable[35] and have low toxicity.[36] Their reversibility, chirality, broad temperature ranges, tolerance to water, and ease of preparation should make the combination of L/A and L-A-C phases useful as solvents for several "green" applications.

In that regard, the addition of a second chiral center, as in (1*R*, 2*S*)-(−)-norephedrine, may improve the affinity of an amino alcohol for CO_2 and the ability of its L-A-C phases to act as chiral inductors for guest reactions, separations, etc.[37] The reversibility of these liquids is especially promising for the easy separation of components of reactions in which the products are soluble in low-polarity media and their formation depends on contact with a metal catalyst soluble only in high-polarity media; the catalyst should be easily recoverable if it precipitates when N_2 is bubbled through the L-A-C phase in which the reaction was conducted. Future work will focus on such applications, on their use as hosts for optical spectroscopic studies (because they lack chromophores absorbing in the visible and into the UV region), and on increasing their upper temperature limits. Possible strategies for accomplishing the latter are to place the ionic liquids under several atmospheres of CO_2 pressure[38] or to use CS_2 in place of CO_2 (yielding more thermally stable dithiocarbamates[39]) as a means to convert the L/A into ionic liquids.

Acknowledgment. We are grateful to the National Science Foundation for its financial support of this research. We thank Prof. Judith (Faye) Rubinson for helpful discussions about conductivity measurements and Mr. Paul Joseph Lukac for performing some preliminary experiments. We also acknowledge Mr. Rakesh Kumar and Prof. Srinivasa Raghavan of the Department of Chemical & Biomolecular Engineering, University of Maryland, for help in obtaining the viscosity data.

Supporting Information Available: Physical properties and purities of amidines and DAPNE, %CO_2 uptake as a function of time by L/A samples, measurements of densities of liquids, optical rotations of L/A and amino alcohol samples, plots of TGA for some L/A and L-A-C, concentration dependence of chemical shifts of selected protons of an amidine and amino alcohol in $CDCl_3$, a plot of shear rate vs shear stress for 4 L-A-C, UV−vis spectra of an L/A and L-A-C pair, λ_{max} values (UV−vis) of DAPNE in various solvents, and CD spectra of DAPNE and Eosin Y in an L/A and L-A-C (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) (a) Fukumoto, K.; Yoshizawa, M.; Ohno, H. *J. Am. Chem. Soc.* **2005**, *127*, 2398–2399. (b) Ohno, H.; Fukumoto, K. *Acc. Chem. Res.* **2007**, *40*, 1122–1129. (c) Bao, W.; Wang, Z.; Li, Y. *J. Org. Chem.* **2003**, *68*, 591–593.

(36) (a) Gathergood, N.; Garcia, M. T.; Scammells, P. J. *Green Chem.* **2004**, *6*, 166–175. (b) Garcia, M. T.; Gathergood, N.; Scammells, P. J. *Green Chem.* **2005**, *7*, 9–14. (c) Docherty, K. M.; Kulpa, C. F. *Green Chem.* **2005**, *7*, 185–189.

(37) Ding, J.; Welton, T.; Armstrong, D. W. *Anal. Chem.* **2004**, *76*, 6819–6822.

(38) Rayner, C. M. *Org. Proc. Res. Dev.* **2007**, *11*, 121–132.

(39) George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 1017–1025.