

One-component, switchable ionic liquids derived from siloxylated amines

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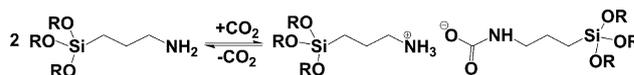
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A new class of one-component, thermally reversible, neutral to ionic liquid solvents derived from siloxylated amines is presented and characterized.

Smart solvents are those which undergo large step changes in properties when exposed to a stimulus (e.g. light or heat). The ability to change a solvent's properties significantly is advantageous for chemical processes involving multiple steps (e.g. reactions, extractions, and/or separations) each of which requires different solvent characteristics. For this reason, the design of switchable smart solvents is valuable. There are a few switchable solvents that have been reported.^{1–3} This report will focus on the creation of a new class of switchable ionic liquids. Many reports highlight the use of ionic liquids in catalysis and as green reaction media; however, few address the issue of separation. Switchable ionic liquids can increase the utility of their earlier generations by including a facile, built-in separation. Recently, we described two-component, reversible ionic liquid systems based on amidines or guanidines with alcohols.⁴ In this communication, we present a new class of one-component, thermally reversible ionic liquids derived from siloxylated amines and carbon dioxide (see Scheme 1). While other groups have investigated the capture of carbon dioxide by reaction with amine groups on ionic liquids, their systems greatly differ from ours.^{5–7} In all of these cases, task-specific ionic liquids were converted to different ionic species. In contrast, we examine a switch from a neutral solvent to an ionic liquid. Our one-component systems are simple from a processing standpoint. Also, they incorporate silicon into their structure, which introduces weak Lewis acid functionality and subsequently alters the solvent's physical properties. In addition, we show how one-component, reversible ionic liquid solvents could be used in purifying crude oil.

Trimethoxy- and triethoxysilylpropylamine have been shown to react with carbon dioxide (CO₂) at room temperature and atmospheric pressure to form the corresponding ionic liquids: 3-(trimethoxysilyl)propylammonium 3-(trimethoxysilyl)propylcarbamate (TMSAC) and 3-(triethoxysilyl)propylammonium 3-(triethoxysilyl)propylcarbamate (TESAC). Ionic liquid formation was evidenced by a noticeable viscosity increase and exotherm. The products, TMSAC and TESAC, were characterized by ¹H NMR, ¹³C NMR, IR, and elemental



Scheme 1 Reversible reaction of alkoxyamine precursors with carbon dioxide where R = methyl or ethyl.

analysis. While these one-component ionic liquids would not operate well in high water-concentration environments, due to reactive alkoxy groups, modest structural variations could ameliorate this limitation.

TMSAC: Ammonium carbamate formation was confirmed by the appearance of the characteristic carbamate carbon peak in the ¹³C NMR spectra (162.6 ppm referenced to CDCl₃).⁸ All of the other carbon peaks were shifted from trimethoxysilylpropylamine (TMSA). ¹H NMR peaks were also shifted from TMSA along with the appearance of hydrogen peaks for the hydrogens attached to nitrogen.⁹ In addition, elemental analysis verified the complete conversion to products (Found: C, 38.34; H, 8.57; N, 6.95. Calc. for C₁₃H₃₄N₂O₈Si₂: C, 38.78; H, 8.51; N, 6.96%). Infrared spectra also validated product formation ($\nu_{\max}/\text{cm}^{-1}$ 3400–2400 br (–NH₃⁺ stretch) 1570 and 1471 (–CO₂[–] asymmetric and symmetric stretch), 1071 (Si–OR stretch), and 2940 and 2839 (C–H stretch)).

TESAC: Ammonium carbamate formation was confirmed by the appearance of the carbamate carbon peak in the neat ¹³C NMR spectra (162.5 ppm referenced externally to a CDCl₃ capillary). All of the other carbon peaks were shifted upfield from the precursor triethoxysilylpropylamine (TESA). Neat ¹H NMR peaks were also shifted from TESA. Hydrogen peaks appeared for the hydrogen atoms attached to the nitrogens.¹⁰ In addition, elemental analysis verified the complete conversion to products (Found: C, 46.66; H, 9.49; N, 5.77. Calc. for C₁₉H₄₆N₂O₈Si₂: C, 46.88; H, 9.53; N, 5.76%). Infrared spectra also validated product formation ($\nu_{\max}/\text{cm}^{-1}$ 3400–2400 br (–NH₃⁺ stretch) 1570 and 1481 (–CO₂[–] asymmetric and symmetric stretch), 1070 (Si–OR stretch), and 2972 and 2882 (C–H stretch)).

These ionic liquids can be reversed thermally at moderate temperatures to their molecular precursors. Reversibility of the ionic liquids was demonstrated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and NMR. TGA indicated a mass loss of 13% by 88 °C and 9% by 125 °C corresponding to CO₂, in TMSAC and TESAC, respectively. Both TESAC and TMSAC show two endotherms in their DSC thermograms. For TESAC, the DSC plot showed loss of CO₂ starting at 50 °C and finishing at 150 °C, which is then followed by decomposition of the amine precursor at 200 °C. For TMSAC, the DSC showed the loss of CO₂ starting at 75 °C and ending by 175 °C followed by precursor

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decomposition at 260 °C.¹¹ A ¹³C NMR study of the formation and reversal of TESAC is shown in Fig. 1. Fig. 1 presents the ¹³C NMR for the precursor, TESA, (spectrum A), the ionic liquid, TESAC, (spectrum B), and TESAC after heating at 120 °C for 2 hours to reverse it back to TESA (spectrum C). The carbamate peak appears upon ionic liquid formation (spectrum B) and then disappears after reversal (spectrum C). Therefore, these one-component systems offer simple processing opportunities for industrial applications upon addition and removal of CO₂ alone.

In order to better understand, and thus to tune, the chemical and physical properties of these switchable solvents, polarity and viscosity measurements were also carried out. The solvatochromic dye Nile Red was used as a measure of polarity to

estimate the solvent's polarity change upon formation of the ionic species. The Nile Red wavelength of maximum absorbance, λ_{max} , directly correlates with solvent polarity and has previously been used as a polarity probe with ionic liquids.¹² TMSA showed a 9.0 nm λ_{max} increase (from 528.1 nm to 537.1 nm) when reacting to form TMSAC, where TESA showed a 11.4 nm increase (from 522.6 to 534.0 nm) when forming TESAC. TMSA is more polar than TESA, but undergoes less of a polarity change. In general, these solvents change from a polarity value similar to benzene (525.4 nm) to one similar to chloroform (537.6 nm).¹³ These results also illustrate that by applying structure–property relationships one can tune the properties of the solvent for a desired application. Viscosity was also shown to vary with structure: TMSAC has a viscosity of 2160 cP whereas TESAC has a viscosity of 930 cP.¹⁴ These values match visual observations that TMSAC is gel-like whereas TESAC is a viscous liquid.

As an example, one potential application of reversible solvent systems would take advantage of the switchability of TESAC in the recovery of alkanes from heavy crude oil. It is known that recovery of valuable products from crude oil is becoming more challenging as oil feedstocks are becoming non-conventional and contaminated (*e.g.* bitumen). TESAC has shown to be the better choice for this application due to its lower viscosity, lower reversal temperature, and larger polarity switch. Therefore, the following experiments were performed exclusively with this solvent as a proof of principle for heavy crude oil purification.

As proof of principle for such a process we carried out three cycles (See Fig. 2). Crude oil was added at 50 wt% to TESA producing a single-phase system. After bubbling CO₂ until completion of the exothermic reaction, the single phase became more viscous. This solution was centrifuged to speed the separation between the non-polar hydrocarbon phase and the polar ionic liquid phase. The need to centrifuge is attributed to the high viscosity of the system and to similar

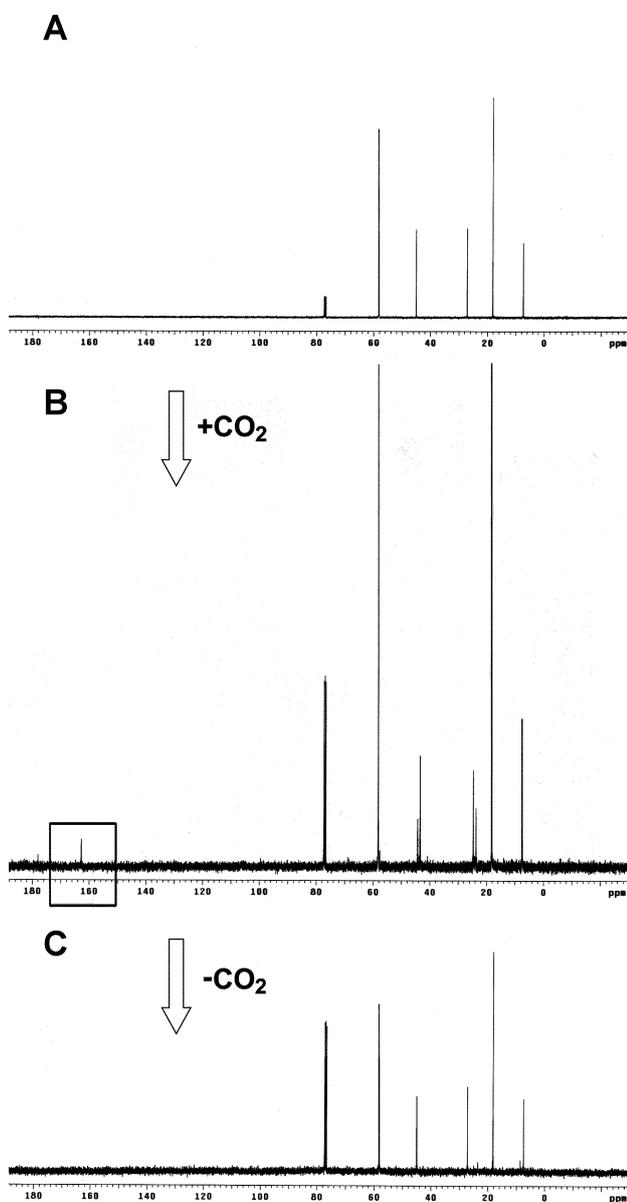


Fig. 1 ¹³C NMR of (A) TESA (B) TESAC (C) TESAC heated for 2 hours at 120 °C.

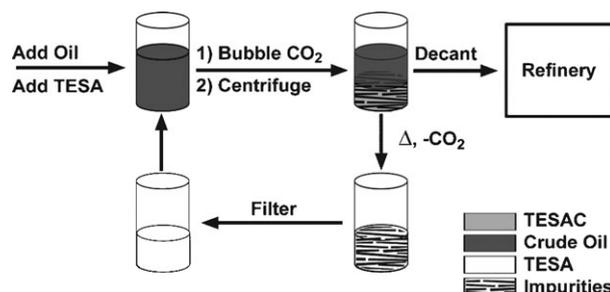


Fig. 2 Recyclable process diagram for hydrocarbon extraction from crude oil with TESAC.

Table 1 mol% TESAC impurity in the product phase after three cycles

Cycle	Hydrocarbon phase/ mol% TESAC
1	4.8
2	3.5
3	2.7

densities between the crude oil and the ionic liquid. The ionic liquid has a density of 1.06 g mL^{-1} compared to the crude oil, which has a density of 1.03 g mL^{-1} as determined using a pycnometer. After separating the phases, the top phase was decanted and the bottom phase was heated at $120 \text{ }^\circ\text{C}$ for 2 hours to reverse. After reversal, filtration may be needed to remove inorganic salts or other contaminants, but for our oil sample this was not necessary. The cycle can then be repeated by reintroducing oil. Table 1 shows the impurity of the product phase, as determined by ^1H NMR over the course of the three recycles. The hydrocarbon phase has only small amounts of TESAC dissolved. These results also demonstrate that the separation has not changed considerably over the course of three recycles. We expect the separation to improve on a larger scale. Also, the TESAC phase has a substantial amount of dissolved hydrocarbon, but this phase will be saturated after the first cycle and recycled. The TESAC phase is expected to contain other impurities such as sulfur, water, and heavy metals like arsenic that are common to crude oil.

In conclusion, we have developed a new class of one-component, reversible, ionic liquid solvents. These solvents have advantageous properties that can be tuned by varying their chemical structure. As presented here, TESAC has been successfully used to remove hydrocarbons from contaminated crude oil with a built-in separation technique. We are currently looking at this class of solvents for CO_2 capture from flue gas streams. These molecules can act as both physical and chemical adsorption agents for selective carbon capture. In addition, their properties, such as reversal energy requirements, can be tuned to improve process economics. Further, we are developing one-component ionic liquids able to operate better in the presence of water.

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- NMR spectra were run at room temperature using a Varian-Mercury VX400 MHz spectrometer. Neat NMR spectra were run using a capillary tube inside the NMR tube.
- ^{13}C NMR for TMSAC δ_{ppm} : 50.0 (OCH_3), 43.9 (CH_2N), 42.8 (CH_2N), 23.8 (CH_2), 23.2 (CH_2), 5.8 (CH_2Si); for TMSA δ_{ppm} : 49.7 (OCH_3), 45.0 (CH_2N), 27.1 (CH_2), 6.1 (CH_2Si). ^1H NMR for TMSAC δ_{ppm} : 6.0 (3H, br, NH_3^+), 4.5 (1H, br, NH), 3.5 (18H, br, OCH_3), 3.0 (2H, br, CH_2N), 2.6 (2H, br, CH_2N), 1.6 (2H, br, CH_2), 1.5 (2H, br, CH_2), 0.6 (4H, br, CH_2Si); for TMSA δ_{ppm} : 3.9 (9H, s, OCH_3), 2.9 (2H, t, CH_2N), 1.8 (2H, m, CH_2), 0.9 (2H, t, CH_2Si).
- ^{13}C NMR for TESAC δ_{ppm} : 57.7 (OCH_2), 44.1 (CH_2NH), 41.5 (CH_2NH), 23.7 (CH_2), 21.3 (CH_2), 17.9 (CH_3), 7.6 (CH_2Si), 7.4 (CH_2Si); for TESA δ_{ppm} : 58.1 (OCH_2), 45.3 (CH_2NH_2), 27.6 (CH_2), 18.3 (CH_3), 7.8 (CH_2Si). ^1H NMR for TESAC δ_{ppm} : 9.6 (3H, br, NH_3^+), 6.0 (1H, br, NH), 4.0 (12H, br, OCH_2), 3.2 (2H, br, CH_2NH), 3.0 (2H, br, CH_2NH), 1.9 (2H, br, CH_2), 1.7 (2H, br, CH_2), 1.4 (18H, br, CH_3), 0.8 (4H, br, CH_2Si); for TESA δ_{ppm} : 4.1 (6H, m, OCH_2), 2.9 (2H, t, CH_2NH_2), 1.8 (2H, m, CH_2), 1.5 (9H, t, CH_3), 0.9 (2H, t, CH_2Si).
- TGA on the ionic liquids was run from 20 to $500 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C min}^{-1}$ on a Q50 TA Instruments machine. Residual mass left at the end of the run ($\sim 10 \text{ wt}\%$) is due to decomposition products. Nitrogen flow was at 40 mL min^{-1} . DSC was run from 20 to $300 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C min}^{-1}$ on a Q20 TA Instruments machine. Nitrogen flow was at 50 mL min^{-1} .
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- Viscosity measurements were made on a 1 mL cup and bob Anton Paar MCR 300 viscometer with the temperature controlled at $25 \text{ }^\circ\text{C}$. Shear rates increased from 0 to 500 s^{-1} and then decreased from 500 to 0 s^{-1} . The solvents are both Newtonian fluids and no shear thinning is evident.