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Single component, reversible ionic liquids for energy applications

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ABSTRACT

Single component, reversible ionic liquids have excellent potential as novel solvents for a variety of energy applications. Our energy industry is faced with many new challenges including increased energy consumption, depleting oil reserves, and increased environmental awareness. We report the use of reversible ionic liquids to solve two energy challenges: extraction of hydrocarbons from contaminated crude oil and carbon capture from power plant flue gas streams. Our reversible solvents are derived from silylated amine molecular liquids which react with carbon dioxide reversibly to form ionic liquids. Here we compare the properties of various silylated amine precursors and their corresponding ionic liquids. We show how the property changes are advantageous in the two aforementioned energy applications. In the case of hydrocarbon purification, we take advantage of the polarity switch between precursor and ionic liquid to enable separations. In carbon capture, our solvents act as dual physical and chemical capture agents for carbon dioxide. Finally, we show the potential economics of scale-up for both processes.

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1. Introduction

When activated, reversible solvents undergo vast solvent property transformations which can be exploited in a wide range of industrial applications. The ability of these solvents to combine multiple processing steps (*e.g.* coupling reactions and separations) and be recycled for reuse yields reductions in process waste, operating costs, and environmental impact. There have been several recent publications on the development and application of reversible solvents [1–5]. Towards this goal of developing sustainable technologies, our group has created reversible, single component, ionic liquids derived from silylated amines (see Scheme 1). Not only can these molecules switch between neutral and ionic forms, but they can also be tuned by varying their molecular architecture. This article focuses on two applications of these reversible ionic liquids in the energy industry: (1) extraction of hydrocarbons from crude oil and (2) carbon capture from post-combustion power plant flue gas streams.

Depletion of conventional oil reserves, increasing focus on energy independence, and rising oil prices may lead to the increased use of tar sands and oil shale as alternate fossil fuel resources. The United States has the world's largest oil shale deposits located in the Green River Formation which contains an estimated 800 billion barrels of recoverable oil [6]. Currently, the isolation of hydrocarbons from tar sands and oil shale is difficult mainly due to the physical properties of these materials, such as high viscosity and density [7,8]. Steam has been used to extract oil from these unconventional sources, but the process is energy-intensive and produces large quantities of contaminated waste water. Although oil-miscible organic solvents can cut the viscosity of these oils, the process is cumbersome and wasteful. The common method for organic solvent recovery, distillation, is energy-intensive and low-end carbon fractions from the oil will be distilled along with the solvent. Our reversible solvents solve this problem by utilizing a built-in, energy-efficient and environmentally benign solvent separation technique. First, mixing the molecular liquid with oil allows for simple filtration of the oil's contaminants. Second, a phase split is enacted between the oil and solvent phase upon the formation of the ionic liquid. And finally, the ionic liquid is reversed to its precursor and recycled.

Although conventional ionic liquids can separate CO_2 from mixed gas streams [9–13], our reversible solvents are superior by enabling a dual-capture mechanism. Specifically, they function not only as physical absorbents but also as chemical adsorbents for CO_2 capture. Two moles of solvent react with one mole of CO_2 to form the ionic liquid, which then acts as a solvent to absorb physically additional CO_2. The benefits of using reversible ionic liquids include the high selectivity of CO_2 over N_2 in dilute post-combustion flue gas streams, high capacity loadings of CO_2, and a drastic reduction in solvent quantity compared to conventional amine scrubbing processes. We have found that these solvents produce a clean CO_2 stream upon reversal. Also, we show that process variables, such as viscosity and capacity, can be tuned by structural

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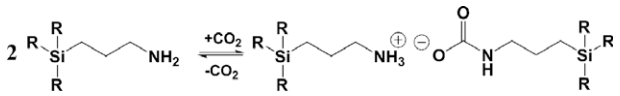

Scheme 1. Reaction of trialkylsilylamines with carbon dioxide to form reversible ionic liquids.

modifications. The ability of designing custom solvents enable us to meet the desired goals for CO_2 capture efficiency that will be capable for direct application to existing power plants.

2. Materials and methods

2.1. Raw materials

The following chemicals were stored in a nitrogen filled glove box until use: HPLC methanol (Sigma, 99+%), (3-aminopropyl)-trimethoxysilane (Fluka, 97%), (3-aminopropyl)-triethoxysilane (Aldrich, 98%), allylamine (Aldrich, 99+%), triethylsilane (Aldrich, 99%), tripropylsilane (Aldrich, 99%), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene ~2% (Aldrich). Carbon dioxide was SFC grade (Air gas, 99.999%) and further purified to remove trace water and other impurities via a Matheson gas purifier and filter cartridge (Model 450B, Type 451 filter). Crude oil was supplied from Prof. Phillip Jessop's laboratory at Queen's University in Ontario and used as received. The crude oil was analyzed by Chevron for sulphur content and hydrocarbon fractions. The sample contained 1.17 wt.% sulphur and is therefore a sour feedstock. The largest hydrocarbon cut was detected at 235 °C. The oil was medium grade as its density was 0.88 g/mL (API density of 28.7) which was determined using a 2 mL pycnometer. Bitumen was provided by ConocoPhillips and used as received having a density of 1.03 g/mL (API density of 5.9).

2.2. Ionic liquid formation

Molecular precursors (silylated amines) are reacted with CO_2 by bubbling through these liquids at room temperature until completion of the exothermic reaction. This reaction proceeds within minutes.

2.3. Hydrosilylation reactions

Hydrosilylations were run according to literature procedure [14]. Silane (1 equivalent), platinum(0) catalyst (100 ppm), and solvent (30 mL) were added to a round bottom flask in the glove box. Allyl amine (3 equivalents) was then added dropwise via an addition funnel to the mixture. The reaction was stirred with a magnetic stir bar and run at 110 °C for 5–24 h. Any vapor generated was condensed by a cooling water condenser. Following reaction, the mixture was rotovaped at room temperature to remove solvent and unreacted starting materials. To remove trace quantities of catalyst the sample was distillation purified. The sample was then analyzed by ^1H and ^{13}C NMR using $CDCl_3$ (NMRs were run at room temperature using a Varian-Mercury VX400 MHz spectrometer), elemental analysis (Atlantic Microlab Inc., Atlanta, GA), and ESI mass spectrometry (Georgia Institute of Technology, Mass Spec. Laboratory).

2.4. Viscosity tests

Viscosity measurements were made on a Anton Paar MCR 300 rheometer using a 0.97 mL coquette geometry sample holder with Peltier temperature control. Shear rates increased from 0 to 100 s^{-1} and then decreased from 100 to 0 s^{-1}, with the reported values being the average of all data points from 10 to 100 s^{-1}.

2.5. Nile red polarity tests

UV–vis spectra were collected using a HP 8453 UV–vis spectrophotometer and a quartz cuvette. Nile red was added to the liquids at a concentration that kept the UV absorbance lower than a value of 1.5, thereby ensuring that there was no saturation of the detector. The wavelength of maximum absorption was then determined and the average of three repeats was taken as the Nile red λ_{max}. For the viscous ionic liquid samples, Nile red was added to the molecular liquids which were then converted to the ionic liquids by bubbling CO_2 through the cuvette. This procedure eased the dissolution of Nile red into the liquids. Note that the results presented in this paper for (3-aminopropyl)-triethoxysilane (TESA) and (3-aminopropyl)-trimethoxysilane (TMSA) differ slightly from those previously reported [5], because of a more accurate method for calculating the maximum absorbance of the dye. Previous reports fit the data to a polynomial and obtained the maximum by setting the polynomial curve's derivative to zero. Here we take the actual highest absorbance value for the maximum absorbance to avoid issues with curve fitting.

2.6. Differential scanning calorimetry (DSC)

DSC was run from 20 °C to 300 °C or 400 °C (for higher boiling point precursors) at 20 °C/min or 30 °C/min on a Q20 TA Instruments machine. Nitrogen flow was set at 50 mL/min. The reversal temperature, or first endotherm from the thermogram, was taken as the average of three repeats.

2.7. Crude oil purification proof of principle recycles using TESA

Crude oil was added at 50 wt.% to TESA producing a single-phase system. At this stage filtration may be needed to remove inorganic salts, sand, or other contaminants, but for our oil sample this was not necessary. After bubbling CO_2 until completion of the exothermic reaction, the single phase became more viscous indicating ionic liquid formation. 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 densities between the crude oil and the ionic liquid. Each phase was sampled to determine impurity via ^1H NMR integration. The top phase was decanted and the bottom phase was heated at 120 °C for 2 h to reverse. The cycle was then repeated three times by reintroducing oil. This recycle experiment was repeated three times and the average of the three runs was reported as the separation efficiency. Bitumen tests were run using the same procedure with a mixture of 20 wt.% bitumen to molecular liquid precursor. This mixture was then filtered under aspirator vacuum.

2.8. Carbon capture capacity

A Specac, Ltd. heated "Golden Gate" attenuated total reflectance (ATR) accessory with diamond crystal and ZnSe focusing lenses was used in combination with a custom-made high pressure reactor. The Fourier transform infrared (FT-IR) absorbance measurements were collected with a Shimadzu IRPrestige21 using a DLATGS detector, with 32 scans and a resolution of 1 cm^{-1}. The ionic liquids were prepared *ex situ* and transferred to the reaction chamber, which was heated to 35 °C. The CO_2 was introduced via an ISCO syringe pump at a pressure of 61.5 bar, and the ATR FT-IR spectra were recorded after the system had reached equilibrium. The CO_2 sorption and swelling were calculated following

procedures outlined by Kazarian and coworkers [15,16], with two minor changes in technique:

(1) a CO_2/methanol system was used to determine the relationship between absorbance of the ν_3 band of CO_2 (*ca.* 2335 cm^{-1}) and CO_2 concentration by comparing our ATR FT-IR results to experimental values reported in literature [17] (thereby assuming a negligible change in penetration depth of the evanescent wave in methanol and ionic liquid samples),
(2) the C–H stretching vibrations (located <3000 cm^{-1}) were used to determine swelling as we observed many peaks overlapping with the $\delta(CH_3)$ band in our samples.

The ionic liquid sample densities were measured using a 2.0 mL pycnometer and a total of three samples were averaged. This information was used to calculate the CO_2 absorption capacity from the ATR FT-IR experimental data on a CO_2-free basis of amine solvent. The CO_2 reaction capacities were calculated from the stoichiometric ratio of 1:2 (mole CO_2:mole amine), again reported on a CO_2-free basis.

2.9. Stability tests

Liquids were set under various atmospheres and/or concentrations of H_2O (either 0 vol.% or 10 vol.%). Samples were drawn weekly and analyzed via ^1H NMR to determine degradation, if any. This was continued over a period of approximately two months.

2.10. Scale-up simulations

A simulation for the removal of hydrocarbons from tar sands was created using Aspen HYSYS version 2006.5 and the extended NRTL fluid package. Tar sand was mixed with the molecular liquid, TESA, and sand was filtered off. The composition of tar sand was assumed to be 80 wt.% sand and the remainder hydrocarbons. A perfect separation of the sand from the oil was assumed during filtration. The TESA to hydrocarbon mixture entering the first conversion reactor was in a 50:50 mass ratio. Carbon dioxide was added stoichiometrically to the reactor to initiate the forward reaction. The forward reaction is exothermic and the exiting streams leave at 42 °C. Emulating experimental results, the forward conversion was set to 100% completion. Four mol.% (solubility of the ionic liquid in the oil phase as determined from experiments) of the ionic liquid was taken off in a decantation step along with the hydrocarbon product (using a splitter); the remaining ionic liquid (which was assumed to be free of hydrocarbons) was sent to a second conversion reactor. Here, the reverse reaction took place at 110 °C, which was the reversal temperature as determined from experimental results. Carbon dioxide leaves in this step and TESA was recycled back to the tar sand/precursor mixer and reused. Solvent losses were not considered in this simulation. For comparison, a simulation was made for processing the same quantity of tar sands by steam explosion. Tar sands and water (50:50 mass ratio) were preheated to 100 °C and mixed in a tank. The exiting vapor stream, comprised of oil and water, was cooled and oil was decanted from water.

3. Results and discussion

3.1. Property switches

The four silylated amine precursors examined were TESA, TMSA, (3-aminopropyl)-triethylsilane (TEtSA), and (3-aminopropyl)-tripropylsilane (TPSA). Their corresponding ionic liquids are termed TESAC, TMSAC, TEtSAC, and TPSAC, respectively. Viscosity, polarity, and reversal temperature were investigated for each solvent to determine how these properties trended with structural modifications.

Table 1 shows the measured viscosities for all ionic liquids discussed in this paper. The viscosity of TEtSAC was determined at 35 °C due to the difficulty of obtaining an accurate measurement at 25 °C. The viscosity of these materials decreases as the side chain unit is increased due to a disrupted packing efficiency. Specifically, the addition of a single methylene group to each silicon sidechain cut the viscosity in half. In addition, the siloxylated precursors are less viscous than the silylated precursors of the same chain length. This viscosity decrease is due to oxygen drawing electron density from the silicon center and allowing for electronic interactions. The viscosity of all precursor molecules was less than 5 cP.

Nile red was used as a polarity probe to determine the relative polarity of each solvent. As expected, solvent polarity increased upon formation of the ionic liquids from their corresponding molecular liquid precursors. The polarity jump for all four solvents was approximately a 10 nm red shift of the absorbance maximum of Nile red indicator. For comparison, the polarity switch upon conversion to ionic liquid was similar to changing solvents from a polarity similar to benzene (525.4 nm) to one similar to chloroform (537.6 nm) [18]. Trends can be seen in Fig. 1. The longer alkyl side groups show less of a polarity switch when going from molecular to ionic liquids due to their overall more organic and therefore non-polar nature. Along the same line, the compounds with longer alkyl chains are less polar in both molecular and ionic forms. Siloxylated liquids are more polar than silylated liquids due to the increased electrophilicity of oxygen when compared to carbon.

Ionic liquid reversal temperature is the largest contributor to process cost. The reversal temperatures as determined from DSC of the ionic liquids investigated were: 110 °C for TESAC, 145 °C for TMSAC, 150 °C for TPSAC, and 146 °C for TEtSAC.

3.2. Proof of principle: extraction of hydrocarbons from crude oil

The polarity jump upon formation of the ionic liquid from the molecular liquid enables a phase change from a homogeneous mixture of precursor and hydrocarbon to a heterogeneous system. In the same way, this separation occurred with crude oil. A proof of principle experiment was run using crude oil and TESA with three

Table 1
Viscosity (cP) of reversible ionic liquids at 25 °C.

Ionic liquid	TMSAC	TESAC	TEtSAC	TPSAC
Viscosity (cP)	2160	930	1690[a]	4210

[a] Temperature was 35 °C.

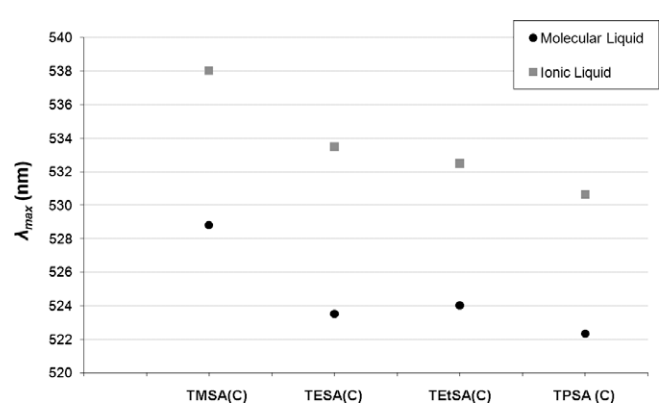

Fig. 1. Nile red λ_{max} values for four molecular liquid precursors and their corresponding ionic liquids.

recycles to quantify the separation ability of the proposed process. Tar sands or oil shale were not used for preliminary experiments; however, the results from our model study should directly transfer since the only difference in processing these feedstocks is a filtration step before the cycle begins.

The results for the product phase contamination with TESAC are shown after each of the three recycles in Table 2. The product hydrocarbon phase is relatively pure with less than 4 mol.% ionic liquid contamination. Furthermore, the separation efficiency is not altered over each cycle.

Bitumen was used as a more contaminated crude oil feedstock to verify separation potential. Bitumen and molecular precursor were filtered before the cycle was started to remove solid impurities. Again after converting the molecular liquid to the ionic liquid a phase separation was seen. The fractions collected (two liquid phases and one solid phase) are currently under investigation.

3.3. Carbon capture capacity

The measured ionic liquid densities, swelling, and CO_2 capture capacities for both physical absorption and chemical reaction at 35 °C and 62.5 bar are shown in Table 3.

Since the stoichiometric ratio of 1:2 (mole CO_2:mole amine) was used to determine the reaction capacities, the capacity decreases with increasing solvent molecular weight. However, the data indicate that the trends in ionic liquid density, swelling, and CO_2 physically absorbed all follow the same trend as observed with the viscosity. Specifically, as the alkyl side groups become longer, it is expected that the steric effects between the ionic pairs is also increased. Subsequently, the ordering of the ionic pairs in 3-D space is disrupted, which results in a decrease in density. This, in turn, results in more void volume between ionic species which allows for higher concentrations of CO_2 to be absorbed, which is directly related to the swelling percentages reported. The last column in Table 3 shows the total amount of CO_2 capacity in terms of both reaction and absorption, highlighting the dual-capture mechanism of the reversible ionic liquids.

Although the reversible ionic liquids exhibit high CO_2 absorption capacities through physical absorption and selective capture of CO_2 through reaction, the real benefit of their application to CO_2 capture can be visualized when considering their use for the treatment of dilute feed streams, namely flue gas from coal fired power plants. Consider a 350 MW pulverized coal power plant that produces roughly 6000 tons of CO_2 a day. Conventional amine scrubbing processes use a reactant, like diethanolamine (DEA), and require an additional solvent (typically water) as the product formed from the reaction with CO_2 is a solid. With reversible ionic liquids the reactant is the solvent. Although TEtSA does have a higher molecular weight than DEA, for DEA in solution with 70 wt.% water the capacity in terms of mass solvent required is twice that for TEtSA without even considering the physical absorption of CO_2 in the reversible ionic liquid. The result is a substantial energy savings in terms of solvent regeneration, which dominates the operating cost of amine scrubbing processes.

Table 2
Post-cycle TESAC in product phase.

Cycle number	mol.% TESAC
1	3.6
2	3.3
3	2.6

Table 3
Carbon capture results at 35 °C and 62.5 bar.

Ionic liquid	Density (g/cm^3)	Swelling (%)	CO_2 absorption capacity (mole CO_2/kg amine)	CO_2 reaction capacity (mole CO_2/kg amine)	Total CO_2 capacity (mole CO_2/kg amine)
TMSA	1.151	17	10.9	2.79	13.69
TESA	1.060	23	12.5	2.26	14.76
TEtSA	0.945	16	12.3	2.88	15.15
TPSA	0.907	31	17.9	2.32	20.2

3.4. Amine stability

TESA and TEtSA were chosen as model precursors to examine their comparative stabilities in either an argon atmosphere, a standard atmosphere, and in the presence of water. Over the course of the experiments, both liquids were stable under dry and inert conditions. In fact, TEtSA was stable under all conditions for the duration of the examination. Therefore, it can be inferred that alkylsilyl amines are stable molecules under common atmospheres. As hypothesized, the alkoxy groups on TESA reacted immediately with the added water. In addition, the TESA sample which was put under a standard atmosphere showed small signs of reaction with atmospheric moisture by week three. This reaction increased throughout the following weeks so that by the end of the tests there was a considerable amount of precursor degradation. These results indicate that when applying these solvents to applications which contain water (including the applications presented here), alkylsilyl amines will remain stable whereas the alkoxysilyl amines are susceptible to degradation.

3.5. Scale-up simulations

The simulation of hydrocarbon extraction from tar sands, assuming ideal separation of the sand from oil and oil from ionic liquid, using our reversible ionic liquid, TESAC, produced 58 million barrels of crude oil per year which is typical of a large capacity refinery. It was assumed that the process runs 80% of the year in order to account for maintenance downtime. The main processing cost arises from the energy requirements of the ionic liquid reversal step. Currently, electricity costs $0.07/kWh (industrial scale price averaged over the USA) [19]. The total energy cost to run the reversal step, 42 million dollars per year, is currently much less than the sale of the oil at $58.73/barrel thereby generating an annual profit of $3.4 billion [20]. Our solvent process costs about 70 cents per barrel of oil manufactured. For comparison, the current steam explosion technology was simulated using the same tar sand quantity as used in our solvent process. While still profitable, this process has an estimated $25.12 per barrel energy cost and generates a smaller quantity of refined oil (40 million barrels per year). Therefore, our solvent technology can be significantly less costly than the steam explosion route.

4. Conclusions

We have demonstrated a new class of reversible ionic liquids which have significant potential in energy applications. The properties of these solvents, such as viscosity, density, and polarity can be tuned by making structural modifications. The alkylsilyl amines were stable after two months in all of the atmospheres tested including in the presence of water. Siloxylated amines were immediately reactive with water, but otherwise stable over time in a dry and inert atmosphere. A proof of principle for using these solvents to extract hydrocarbons from tar sands/oil shale was demonstrated with crude oil and TESA producing a product stream with less than 4 mol.% contamination. Scale-up simulation of this process shows a large profit to be made and a drastic improvement over current technology. Our reversible ionic liquids were also

shown to have high capacities for carbon dioxide due to a dual-capture mechanism. The reduction in solvent required promises a substantial decrease in the regeneration energy requirement for our solvent system over competitive technologies.

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