Applications and Properties of Ionic Liquid-Based Gels and Soft Solid Composites

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Abstract

Voss, Bret Alan McGinness (Ph.D., Chemical Engineering) Department of Chemical and Biological Engineering, University of Colorado Applications and Properties of Ionic Liquid-Based Gels and Soft Solid Composites Thesis directed by Profs. Richard D. Noble & Douglas L. Gin

Solid-liquid composites (gels) have a combination of properties that afford new material applications in which high solute diffusion is desirable. These composites have a soft-solid mechanical integrity and will not flow under gravity, but entrain a liquid matrix (i.e. 60-98 mass %) which allows for high diffusion and high reactivity. Room temperature ionic liquid (RTILs) are molten organic salts with a melting point below room temperature and negligible vapor pressure. If the RTILs are used as the liquid component of a gel, then the gel matrix will not evaporate (unlike other organic solvents) and may be used for long term applications. This thesis research applies RTIL gels for two new applications; carbon dioxide/nitrogen separation and chemical warfare agent (CWA) barrier and decontamination.

Separating CO₂ from the flue gas of coal and gas fired power-plants is an increasingly economically and environmentally important gas separation. In this first study, RTIL gels are cast in a supported membrane and gas permeability and ideal selectivity are measured. The RTIL matrix has an inherent affinity for CO₂ and provides a high diffusion, hence high permeability (i.e. 500-700 barrer). The solidifying component is a low molecular-weight organic gelator (LMOG) which through physical

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bonding interactions (i.e. hydrogen bonding, π - π stacking and van der Walls forces) forms an entangled network which provides mechanical stability (i.e. increase transmembrane pressure required to expel selective material from the support). In these studies two LMOGs and five RTILs are used to make supported gel membranes and determine gas permeability and temperature dependent trends.

The second application for RTIL gels is a decontaminating barrier for CWAs and toxic industrial compounds (TICs). In these studies a layer of RTIL gel is applied on top of a substrate contaminated with a CWA simulant (i.e. chloroethylethylsulfide, CEES). The gel performs well as a barrier, preventing CEES vapor from penetrating the gel. Simultaneously, the RTIL gel actively decontaminated the substrate by reacting CEES with a sacrificial amine. The RTIL gel barrier was able to decontaminate up to 98% of the CEES applied to a painted steel substrate. Two gel barriers are tested: 1) RTIL gel with a LMOG solidifying agent, and 2) RTIL gel with a polymeric cross-linked network solidifying agent. The polymer gel provided a more mechanically robust barrier, however, the LMOG gel decontaminated at a faster rate.

These new applications are but two of many possible applications for RTIL gels. Their negligible vapor pressure affords long term application in ambient conditions and their unique chemistry allows them to be tailored for specific applications.

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Chapter 1

Introduction and Objectives

1.1 Overview of Composite Materials

Composite materials are increasingly being used for a greater number and wider range of applications, a trend that started when the first man-made composite of mud and straw was used to create bricks¹. Composites are made from two or more components with significantly different properties that remain physically distinct in the final material². Ideally, the new material has a combination of the desirable properties from each component and none of their disadvantages.

For example, solid materials have mechanical stability and will not flow under shear stress. They are also relatively easy to manipulate, process, and are non-volatile. Liquids, on the other hand, have a high diffusivity of solute molecules, which enables a high rate of adsorption and a high rate of reactivity. A high-diffusivity soft solid (i.e., a gel) is created by combining these two phases of materials^{3,4}. Gels are commonly used in biological applications (e.g., agarose gels for electrophoresis, PEO hydrogels for tissue scaffolding) and non-biological applications (e.g., ballistic gels for shock absorption, gel electrolyte for batteries and solar-cells, and deodorant gels for personal hygiene)^{5,6,7,8}. Each of these gel systems has a combination of solid-like and liquid-like properties to afford functionality not possible solely through the use of each individual component.

The most common type of gel is a polymer gel, in which long polymer chains are cross-linked with chemical bonds to entrain a liquid⁹. These polymer networks will not dissolve nor spread under shear stress and thus can only be cast once. Another less common type of gel is a physical gel network^{10,11}. In this latter type of gel, a gelator agent non-covalently bonds via van der Waals interactions, hydrogen bonding, and/or pi-pi stacking to form a physically cross-linked network. These physical gels can be dissolved at higher temperatures, will spread with sufficient shear stress, and can be recast multiple times.

This Ph.D. project focuses on the development of new gelled, room-temperature ionic liquid (RTIL) materials for two chemical transport applications: (1) carbon dioxide separation from flue gas via supported gel RTIL membranes, and (2) containment and decontamination of highly toxic chemical warfare agents (CWAs) on CWA-contacted substrate materials. Both physically cross-linked gelator-based RTIL gels and chemically cross-linked polymer-based RTIL gels are used in these transport applications. The importance of each application area is described in the following sections, as well as the importance of the composite properties of the gel RTIL materials for each application.

1.2 Importance of Carbon Dioxide Separation from Other Light Gases

 CO_2 separation from other light gases is required in many industrial applications (e.g., natural gas sweetening, respiratory gas enrichment for life-support systems, and CO_2 scrubbing of power plant combustion exhaust)^{12,13,14}. Natural gas obtained from the well often contains a high concentration of CO_2 that needs to be removed before it

can be combined with gases in the main pipeline¹⁵. Sealed vehicle environments, such as submarines and space craft, must recycle air by scrubbing out the CO_2 to prevent hypercapnia (elevated levels of CO_2 in the blood stream resulting in unconsciousness or death)¹⁶. Coal and natural gas power plants will need to capture CO_2 to prevent anthropogenic climate change and reduce operational costs in a carbon credit economy^{17,18}. Thus, CO_2 separation from other light gases is essential and functional component of many systems¹⁹.

There are three current methods for separating CO_2 from mixed gases: (1) aqueous amine solutions, (2) cryogenic distillation, and (3) pressure swing adsorption. Carbon dioxide can covalently bind to amines and the reaction can be reversed with elevated temperature and reduced pressure¹⁵. Industry currently uses aqueous solutions of amines, such as monoethanolamine (MEA) and diethanolamine (DEA), in a thermal cycle to capture CO₂ from combustion power plant exhaust and natural gas reservoirs²⁰. This technology is based on the ability of organic amines to reversibly react with CO₂ to form carbamate salts (Figure 1.1) and is limited by using water as a solvent in the reactive capture process. The thermal cycle to release CO₂ post-capture is highly energy-intensive because of the high heat capacity of water as the solvent. Also, the CO₂ can react with water to form carbonic acid, which corrodes piping, increases operating costs, and limits the type of materials that can be used in this application. Another method for separating CO₂ is cryogenic distillation, which involves lowering the temperature until CO₂ deposition occurs while the other gases remain fluid. This process requires even more energy than aqueous amine separation and is only viable for separating gaseous mixtures with high concentrations of CO₂. Finally,

pressure swing adsorption involves adsorbing CO_2 onto a selective adsorbent and then lowering the pressure to desorb the CO_2 . This requires a large mass of adsorbent and can frequently be poisoned by acidic gases in the flue stream.



Figure 1-1: Reaction mechanism of traditional aqueous amine-based CO₂ scrubbing

Membranes offer a fourth method to separate CO_2 that may offer significant operating cost reductions versus the three previously described methods^{21,22}. A membrane is a thin film that preferentially passes one chemical through the membrane more than another chemical, thereby enabling a separation²³. For gas separation membranes, a mixed gas stream is fed across one side of the membrane. Then dynamic vacuum is pulled on the other side of the membrane, causing a pressure differential, which will drive the gas through the membrane. Because membranes use a thin (0.1–1 µm) film for separation, they require less active component than aqueous amine scrubbers or pressure swing adsorption systems. Consequently, membranes have reduced capital costs¹². Additionally, the operational costs for membrane-based separation systems are relatively inexpensive because dynamic vacuum is cheaper than cryogenic cooling or heating aqueous amine solutions. The gas flux of a membrane scales with exposed surface area, so generally membranes are bundled into coated hollow fibers or spiral wound sheets to achieve a large surface area in a minimal volume.



Figure 1-2: Schematic of a CO₂-selective membrane.

Gas separation membranes are typically based on dense polymers, supported liquids, and nanoporous materials²³. Nanoporous materials with uniform size pores (e.g., zeolites and metal-organic framework (MOF) compounds) use molecular size-exclusion to separate different gaseous species^{24,25}. Dense polymers and supported liquids separate different gases and vapors via the solution-diffusion (S-D) mechanism²⁶. The S-D mechanism assumes all gas species absorb into the membrane from the feed side, diffuse through the membrane and desorb from the membrane on the permeate side. The difference in both diffusivity (D) and solubility (S) of different

gases in the membrane matrix causes a difference in flux across the membrane, consequently concentrating one gas species in the permeate²⁶. The permeability (P) of a membrane is determined by normalizing flux for membrane thickness and transmembrane pressure, or by the product of diffusivity and solubility (Equation 1-1).

$$P = S \cdot D = \frac{Q}{\Delta p/l}$$

Equation 1-1: Permeability (*P*) of a gas as a function of solubility (*S*) and diffusivity (*D*) and as a function of flux (*Q*), membrane thickness (*I*), and transmembrane pressure difference (Δp).

In addition to permeability, the selectivity of a membrane is an important characteristic. Ideal separation selectivity (α) is expressed as the ratio of the permeability of two gases as measured from single-gas experiments (Equation 1-2). Generally, the selectivity of mixed gas systems is lower than the ideal selectivity. The separation selectivity can be further broken down to the product of solubility selectivity and diffusivity selectivity.

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \frac{D_i}{D_j}$$

Equation 1-2: Permeability selectivity (α) of two gases (*i* and *j*) as a function of their respective solubility (*S*) and diffusivity (*D*).

The overall separation performance of a new membrane can be compared to other types of membranes using a "Robeson plot", which tracks permeability vs. selectivity on a log-log scale.²⁷ The resulting plot has an empirical upper-bound for dense polymer membranes, illustrating a well-established flux-selectivity trade-off. ²⁸ Any material at or above this upper bound line (i.e., in the upper right quadrant) is considered to have very good transport properties (i.e., high permeability <u>and</u> high selectivity) and is more attractive for industrial applications.



CO₂ Permeability (barrers)



The "upper bound" is defined by low-permeability, glassy (more dense) polymer membranes and high-permeability, rubbery (less dense) polymer membranes. The high-permeability membranes (1000–100,000 barrers) generally have large interstitial gaps and low selectivity, mostly from *diffusion* selectivity (e.g., siloxane polymers)²⁹. The low-permeability membranes (0.1–100 barrers) generally have polar functional groups that have lower void volume between the polymer chains, with a high selectivity mostly from *solubility* selectivity (e.g., polyamines and phosphazenes)²⁷. There are two general approaches to designing a better performing dense membrane that operates via the S-D mechanism: (1) add functional groups to a high permeability membrane that increase solubility selectivity, and (2) increase the diffusivity (i.e., increase the void volume) of a high solubility-selective membrane^{30,31}. Room-temperature ionic liquid (RTIL)-based materials represent a relatively new materials platform for designing new dense membrane that allow for this level of control.

1.3 Room-temperature lonic Liquids (RTILs)

Room-temperature ionic liquids (RTILs) are organic salts that are liquid at or below room temperature and 1 atm pressure; they are usually comprised of an anion and/or cation with delocalized charge.³² RTILs generally have negligible vapor pressure because of the strong attractive Coulombic interactions between the charged constituents. So unlike typical uncharged organic solvents (even high boiling point solvents), once applied, RTILs will remain resistant to evaporative loss almost indefinitely³³. RTILs are also very thermally stable and provide an unusual ionic solvent environment for enhancing many chemical reactions that involve charged or polar intermediates of transition states^{34,35}.



Figure 1-4: Some common organic ations and anions that compose RTILs.

The most popular RTIL cation, imidazolium, is prepared from imidazole, a readily available and inexpensive natural product, and can be synthesized in large batches³⁶. The two N atoms on the ring can be independently functionalized, and the anion can also be varied in order to vary the properties of the RTIL. In particular, when the imidazolium cation is combined with the bis(trifluoromethylsulfonyl)imide anion, it forms an RTIL that is immiscible with water³⁷. This tailorable chemistry of the imidazolium cation allows the resulting RTIL to be tuned to selectively adsorb certain molecules over others³⁸. Since RTILs have negligible vapor pressure, tunable chemistry, and a unique ionic environment, they are excellent candidates for new materials for transport applications (i.e., chemical separation membranes or barrier films).

1.4 Polymeric and Low Molecular-weight Organic Gelators

The solidifying component of gel system can be either a low molecular-weight organic gelator (LMOG), or a more traditional cross-linked polymer network. In the former case, physical gels are formed by LMOGs. LMOGs are small organic molecules that can form soft-solid composites with a solvent at low concentrations.³⁹ A small amount of LMOG (0.1-5 wt%) can be typically dissolved in a solvent at elevated temperatures to form a homogeneous solution. When the temperature is lowered, the LMOG will begin to precipitate out of the solution. However, unlike traditional recrystallizations, the LMOG will aggregate into one-dimensional strands via hydrogen bonding, van der Walls interactions, and/or π - π bond stacking.⁴⁰ These strands elongate, entangle, and aggregate to form a three-dimensional network that entrains the solvent and forms a soft-solid composite.⁴¹ The microscopic structure of the gel is highly dependent on the molecular structure of the LMOG, the structure of the aggregate strands they form, and the thermal profile of the system during gel formation. Usually, LMOGs form one-dimensional strands, but some have been known to form intersecting planes or connected spheres.⁴² When rapidly cooled, an LMOG-based physical gel will contain a fine network of small LMOG strands, which will form a more rigid network with lower diffusivity.⁴³,⁴⁴ Conversely, when slowly cooled, this gel will form thicker strands with more space between strands; this network is softer with higher diffusivity.

In the second case in which a cross-linked polymer is the solidifying agent, a chemical gel is formed. In this situation, the solidifying agent (polymer) has similar

properties, but instead forming of a physically linked three-dimensional network as in the LMOG case, the polymer serves as a covalently linked, three-dimensional network.⁴⁵ Often, a condensation polymer is employed, which can be composed of bifunctional monomer that forms linear macro-molecules or it can be composed of multifunctional cross-linker units that create interconnects between the linear polymer chains.⁴⁶ The diffusivity of the soft-solid composite is like-wise determined by the microscopic structure of the network. There are three main parameters of a polymeric gel that can be altered to affect diffusion: (1) the volume fraction of included liquid, (2) the inter-nodal chain length, and (3) the cross-link density.⁴⁷ When the volume fraction of free liquid in the polymer network is increased, the diffusivity increases as well, and the sample becomes more liquid-like. If the inter-nodal chain length is increased, the polymer network becomes more flexible and rubbery, allowing a higher diffusion rate of solute.⁴⁸ Finally, if the cross-link density is increased, the diffusivity in the gel will decrease as the polymer becomes more solid-like and less mobile.

A composite made of RTILs and a solidifying agent (i.e., a polymer or an LMOG gelator) will have both liquid-like and solid-like properties. The RTIL can introduce the liquid properties of high diffusivity, solubility selectivity and high adsorption, at the same time, the RTIL will have negligible vapor pressure, unlike other common solvents. The polymer or gelator network will provide mechanical stability and easier processing. This composite will have the 'best of both worlds' so to speak; liquid-like diffusion and solid-like mechanical stability. The high-diffusivity soft-solid composite can be used in a supported membrane format for light gas separation. Current supported liquid membranes are limited to low trans-membrane pressures (approximately 1 bar),

otherwise the liquid will blowout (i.e., expelled out of the porous support). The gel supported membrane would have increased stability from the solid matrix and be able to withstand higher trans-membrane pressures before blowout. The liquid matrix of the RTIL will have an intrinsically high solubility-selectivity for CO₂/N₂ due to the polar nature of the solvent and as a liquid it will have higher diffusivity than a solid polymer. Carbon dioxide has a high affinity for polar environments, and readily adsorbs into materials with Lewis-base, polar or ionic groups. This affinity is partially explained by the positive interaction between the CO₂ guadrupole and the dipole generated by these functional groups⁴⁹. Imidazolium-based RTILs have a polar environment and generally have excellent solubility and solubility-selectivity for CO₂ over N₂.^{50,51} The high solubility-selectivity and high diffusivity would allow a supported gel membrane to have high permeability and high permeability-selectivity (equations 1.1 and 1.2), leading to a gas transport performance that is near the industrially attractive region of the Robeson plot. The advantages of this composite will need to be balanced by the disadvantages of the individual components. The gel can be made more mechanically stable with a higher loading of the solidifying agent; however, this would reduce the diffusivity of the entrained liquid and lower permeability. There is a direct trade off between the range of mechanical stability, moving between shearable liquid to hard solid, and the range of permeability, moving between pure liquid diffusion to a solid barrier. The end result of this composite system would be a porous membrane support filled with a soft-solid composite of RTIL entrained by gelator, which has high CO₂ permeability, high CO₂/light gas permeability-selectivity and a mechanical stability between supported liquid membranes and dense polymer membranes.

1.5 Blocking and Decontamination of Toxic Chemical Warfare Agent Vapors

In addition to having benefits in membrane-based CO₂/light gas separation applications, RTIL-based gel materials could also be applied to the blocking and chemical degradation of substrate materials that have been contacted by chemical warfare agents. The combined properties of RTILs with those inherent in a gel system have distinct benefits for blocking and decontamination of certain toxic compounds in vapor and liquid form.

1.5.1 Chemical Warfare Agents

Chemical warfare agents (CWAs) are defined as highly toxic chemical compounds that are applied over large areas in vapor or aerosol form to inflict damage on or to kill enemy combatants. Simple CWAs have been in use for thousands of years; modern chemical warfare began in World War I with the use of chlorine gas⁵². In quick succession, phosgene and sulfur mustard were weaponized as well. In World War II, the G-series agents (e.g., tabun and sarin) and V-series agents (e.g. VX) were developed and weaponized⁵³. CWAs are categorized into two general classes depending on their toxicity mechanism: (1) nerve agents (i.e. G-series and V-series) and (2) blister agents (i.e., mustard agents)⁵⁴.



Figure 1-5: Chemical Structures of common blister agents and nerve agents

Nerve agents are usually reactive organophosphate esters that block acetylcholinesterase, a neural enzyme that degrades the neurotransmitter acetylcholine. When acetylcholinesterase is blocked, the acetylcholine concentration increases causing muscles to spasm and tighten⁵⁵. Frequently, victims of nerve agents die of suffocation because they are unable to relax their diaphragm. Blister agents are 2chloroether moieties attached to a central atom of sulfur or, less commonly, nitrogen. Blister agents act as powerful vesicants and cause painful blisters and swelling of mucus membranes (e.g., throat and lungs)⁵⁶. They are also strongly mutagenic and carcinogenic due to their intrinsic ability to alkylate and cross-link with guanine in DNA⁵⁷. It may take 2–24 hours to feel the effects of blister agents after exposure to mustard gas; however recovery can take weeks or months⁵⁶.

1.5.2 Chemical Warfare Agent Protection

An area contaminated with these highly toxic and persistent CWAs presents a threat to military personnel, first-responders, and civilian populations both immediately after exposure and over a multi-day period as the CWAs slowly decompose^{58,59,60}. Many methods have been developed to mitigate and decontaminate CWA-contacted or infused materials and personnel^{61,62,63,64}. Traditional decontamination methods for vehicles and buildings involve washing with reactive solutions that chemically degrade the CWAs, absorbed into a powder or evaporating the CWAs out with heated forced air.

CWA decontamination solutions are typically based on aqueous oxidizing agents or strong bases (e.g., bleach, sodium hydroxide)^{65,66}. These solutions may be a heterogeneous emulsion and also contain surfactants to help solubilize oily CWAs⁶⁷. The aqueous washing is cheap and effective for decontaminating CWAs on the surface of equipment but requires a designated staging area for contaminated run-off, and cannot be used to remove CWAs that have soaked-in (i.e. absorbed into porous or swellable materials such as wood or rubber)^{68,69}. Absorbent powders (e.g., talcum powder and flour) and reactive powders (e.g., chlorinated lime or magnesium oxide) wick up, contain and/or decontaminate the CWA in the powder for easier disposal^{70,71,72}. These powders are good for large pools of CWAs but are ineffective against soaked-in CWAs as well as application on crevices and vertical surfaces. After the contaminant has been absorbed the powder must then be collected and disposed. The final catch-all measure for removing CWAs is applying heated forced air, where large fans with heating coils are blown into and across the contaminated materials or zone⁶³. Heated

forced air simply speeds up the natural evaporation rate of the CWA by flushing the area with a flow of air and increases the natural decomposition rate by heating the reaction. This method is effective for all forms of CWAs and types of contaminated zones; however, it creates a hazardous 'down-wind' zone and may take days to reduce the concentration to non-hazardous levels. Consequently, there is a need for an easily applied, portable decontamination system for military personnel and first-responders to effectively and rapidly contain and decontaminate CWA-contacted field equipment, materials, and structures.

1.5 Thesis Scope

The focus of this thesis work is the development of gelled RTIL systems as (1) a new type of membrane material for CO₂ separation from flue gas, and (2) a new type of blister agent containment and decontamination barrier material that can be used on a wide range of CWA-contaminated substrates. In these two transport-related applications, research will capitalize on the dual liquid-like and solid-like properties of these RTIL gel systems to provide benefits not possible in either a pure liquid or pure solid RTIL material alone. Systematic design and development of these gel RTILL materials are presented to illustrate the wide range of other possible target gas species for separation and other target CWAs and toxic industrial compounds (TICs) for decontaminating barriers. The following is a synopsis of each chapter after the introduction in Chapter 1.

Chapter 2 presents the first proof-of-concept use of a RTIL gel-based membrane for CO₂ light gas separations. An RTIL physically gelled by addition of a small amount of 12-hydroxystearic acid, a low molecular-weight organic gelator (LMOG), is used in a supported membrane configuration for enhanced CO₂ /light gas separation trials. The RTIL gel is a stable at room temperature, will not flow under gravity and is composed of 1.5 wt% LMOG and 98.5 wt% RTIL. The high RTIL liquid loading imparts liquid-like diffusion of gas solutes through the soft-solid composite membrane. The supported gel membrane has permeability slightly lower than the neat ionic liquid: probably due to the gel entrainment of the RTIL. As expected, the gel membrane shows the same permeability selectivity at the neat RTIL since the majority component is the same RTIL. The gel component increases the membrane stability by two-fold; it takes twice as much trans-membrane pressure to blow-out (i.e., expel) the active gel out of the porous support as compared to the supported neat RTIL. This membrane demonstrates high permeability from the liquid diffusion, high selectivity from the RTIL, and more mechanical stability than a pure liquid membrane.

Chapter 3 expands upon the initial proof-of-concept gel RTIL membrane for CO_2 gas separations with a more capable LMOG. This aspartame-derived LMOG is able to gel more types of RTILs than the initial proof-of-concept LMOG for RTILs used on Chapter 2. Also, while the other gelator was limited to 1.5 wt% loading due to phase separation in the sol phase, the aspartame-based LMOG has no such limitation. As such, the gel transition temperature (T_g) of the RTIL gel can be adjusted. This work is part of a collaboration with Los Alamos National Laboratories to develop a thin membrane on a support.

Chapter 4 focuses on the development of a gel RTIL-based decontaminating barrier film for use on dense and porous substrate materials contaminated with blister agent CWAs. This new reactive RTIL gel material is made of three components: (1) a liquid matrix based on RTILs, (2) an organic gelator to act as a solidifying agent, and (3) a polyamine that acts as a reactive agent to chemically degrade and help draw out the adsorbed blister agent. The gel material is easily applied over test coupons (glass, wood, rubber, painted steel) contaminated with 2-chloroethyl ethyl sulfide (CEES), a sulfur mustard simulant. This new type of coating material is shown to be an effective and immediate barrier to prevent CEES vapor, and simultaneously the material will decontaminate and draw out soaked-in CEES from the coupon.

Chapter 5 explores an alternate approach to the initial RTIL gel material for blister agent containment and mitigation by using chemically cross-linked RTIL-based gels rather than physical gels. This approach was investigated using a two part system of RTIL-based liquid mixtures that, when combined, react to form a RTIL gel polymerized matrix that prevents the passage of CWA vapor and also contains reactive groups to help draw out and degrade soaked-in blister agent. The first part (of the two part system) is comprised of 4 components: (1) a diol-functionalized imidazolium RTIL which acts as a bi-functional monomer in a step-growth (i.e., condensation) polymerization, (2) an alkyl-imidazolium RTIL that imparts liquid-like diffusion properties, (3) a polyamine which functions as a step-growth polymerization cross-linker and a reactive agent for blister agent capture/degradation, and (4) a tertiary amine catalyst to speed up the polymerization reaction. The second part (of the two part system) only has two components: (1) a di-isocyanate which is the other bi-functional monomer in the step-growth polymerization, and (2) the same alkyl imidazolium RTIL that adds solubility compatibility between the two monomers (isocyanates and alcohols). When the two solutions (parts one and two) are combined they react to form a homogeneous liquid matrix gel that is an effective barrier to prevent CEES vapor and decontaminate a CEES-contaminated coupon. The design, synthesis, and development of new, functional RTIL-based monomers to enable the demonstration of this new curable coating material for CWA mitigation are also described.

Chapter 6 contains a summary of conclusions based on the research described in Chapters 2–5. Chapter 6 also provides specific recommendations for further research into gel RTIL systems for membrane and CWA mitigation coating applications.

Several appendices are also included at the end of this thesis that discuss tangential research with CO₂ separation materials unrelated to RTILs and gels that was performed as a part of new collaborative effort. This additional research involved testing new organic framework-based sorbent materials for CO₂ capture prepared and provided by the group of Prof. Wei Zhang in the Dept. of Chemistry and Biochemistry at CU Boulder. The documents within these appendices list step-by-step instructions regarding: experimental procedures used, calculations for permeability measurements and decontaminating-barrier measurements, and ongoing gas adsorption studies with rigid organic frameworks.

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Chapter 2

Physically Gelled Supported Ionic Liquids: Solid Membrane Materials with Liquid-like CO₂ Gas Transport

Abstract

A room-temperature ionic liquid was combined with a low molecularweight organic gelator to form a cuttable, soft gel solid. When used as a supported membrane, this material has enhanced transport properties for CO₂ gas separations compared to traditional supported liquid membranes, while showing increased mechanical stability.

2.1 Introduction

CO₂ separation is needed in many industrial applications (e.g., natural gas sweetening, respiratory gas enrichment in life-support systems, and CO₂ scrubbing of power plant combustion exhaust).¹ Currently, there are three primary methods of gas separation: cryogenic condensation, pressure-swing adsorption, and aqueous amines.² Each method has significant energy costs for refrigeration or regeneration of the separation medium. Membranes represent a fourth mechanism for gas separations that may offer significant operating cost savings over the three prior methods because it only requires a pressure differential.³

2.2 Dense Polymer Membranes and Room-temperature Ionic Liquids

In dense solid polymer membranes, separation is afforded by differences in the solubility (S) of each gas in the polymer and/or differences in their diffusivity (D) through the membrane material.⁴ In this solution-diffusion (S-D) mechanism, the permeability ($P = S \cdot D$) is the pressure gradient-normalized flux of gas through the media, and gauges how easily gas moves through a dense material to separate it from other gases in the same mixture. Unfortunately, there is typically a trade-off between gas flux and separation selectivity for dense polymer membranes which is linked to the limitation in the S-D mechanism of gas transport.⁵ In many cases, if a liquid is used as the active separation medium, diffusion, and in turn permeability, will be greater than in a dense, solid membrane. Despite greater transport properties the liquid-phase separation material must be supported in a solid porous matrix to prevent flow under applied pressure. As a consequence, supported liquid membranes (SLMs) must operate at low differential pressures (0.1–1 MPa), to avoid forcing the liquid material out of the pores of the support.⁶ Another disadvantage of SLMs is loss of liquid to the gas phase through evaporation.

RTILs (i.e., organic salts that are liquid at 1 atm and 25 °C)⁷ are promising materials for SLMs for light gas separations. RTILs have negligible vapor pressure, and as a result, there is no solvent loss to the gas phase. Gas solubility and selectivity in RTILs can be easily tuned by modifying the structure of the RTIL cation and anion to select for certain gases.⁸ Previous studies with supported ionic liquid membranes (SILMs) have shown enhanced selectivity and good *P* values compared to conventional polymer membranes.⁹ While SILMs do not suffer from the evaporation problem that SLMs based on conventional liquids have, they still suffer from being displaced at low differential pressure. *The ideal SLM material should be non-volative, and have the transport properties of an RTIL but with the mechanical stability of a solid polymer membrane.* Progress in combining liquid-like and solid-like properties in a single RTIL gas separation material has recently been achieved by blending RTILs with polymerized RTILs.¹⁰

Herein, we present a new type of RTIL material for CO_2 separation applications based on physical gelation of a common RTIL, 1-hexyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide [C₆mim][Tf₂N], with a small weight percent (1.5 wt %) of the low molecular weight gelator (LMOG), 12hydroxystearic acid (Figure 2-1). The resulting RTIL gel has good mechanical stability (i.e., it is a firm, gelatinous, cuttable solid), while maintaining liquid-like gas transport properties similar to that of the neat RTIL. Because it is >98 wt % liquid, the RTIL gel exhibits CO_2 gas permeability on par with traditional SLMs. Initial tests also show that CO_2 permeability in this gel in a supported membrane

format is two orders of magnitude higher than similar RTIL-based solid polymers. The gel's CO_2/N_2 selectivity is similar to the neat $[C_6mim][Tf_2N]$, lower than other neat RTILs and near the upper limit for flux-selectivity for known dense, CO_2/N_2 separation materials. The RTIL gel also has increased mechanical stability with little loss in CO_2 gas selectivity. This unique combination of performance properties suggests that RTIL gels are promising new membrane materials for gas separations that bridge functional liquids and solid polymers.



Figure 2-1: Structures of the RTIL [C₆mim][Tf₂N] and LMOG (12-hydroxystearic acid) components of the RTIL gel.

2.3 Results and Discussion

By way of background, LMOGs are small molecules that can solidify organic liquids at very low loading levels via physically bonding with each other through H-bonding, van der Waals forces, and/or and π - π bond stacking.¹¹ This affords a non-covalent network that immobilizes the surrounding liquid, affording

a stable gel that will not flow, with a thermally reversable sol-gel phase transition. Although a large number of LMOGs are known that gel water¹² and conventional polar organic solvents,¹³ only four examples of LMOGs that can gel an RTIL have been reported.^{14,15,16,17} However, none of these RTIL gel systems have been examined for their gas separation properties.

 $[C_6 mim][Tf_2N]$ was selected for this proof-of-concept gas separation study because it is a commonly available and easily-synthesized RTIL with inherent solubility selectivity for CO₂ over N₂. While other RTILs would have better selectivity, they did not form a gel with 12-hydroxystearic acid. Imidazoliumbased RTILs in general have excellent solubility and solubility-selectivity for CO₂ over N₂.⁸



Percent mass fraction of 12-hydroxystearic acid

Figure 2-2: Phase diagram of [C₆mim][Tf₂N] and 12-hydroxystearic acid.

Figure 2-2 shows the phase diagram for the $[C_6 mim][Tf_2N]/12$ hydroxystearic acid system. The maximum loading of 12-hydroxystearic acid in $[C_6 mim][Tf_2N]$ was found to be approximately 1.5 wt %, above which two phases formed: a RTIL-rich phase and an LMOG-rich phase. The minimum LMOG concentration needed to form a gel was found to be 0.5 wt %, indicating a maximum gelation efficiency of 400 $[C_6 mim][Tf_2N]$ ion pairs for every 12hydroxystearic acid present. The resulting RTIL gels are soft solids that are able to support their own weight and do not phase-separate or lose any mass over many months at room temperature.

The most mechanically and thermally stable gel was found to exist at a maximum LMOG loading level of 1.5 wt % with a temperature of gelation of 67 °C. As such, this gel composition was selected for the subsequent gas solubility and permeability performance studies. The solubility of gas in the gel and neat $[C_6 mim][Tf_2N]$ was determined for CO₂ and N₂ using a gas adsorption unit. As seen in Table 2-1, the RTIL gel has a CO₂ solubility of 2.2 cm³ gas at 1 atm/cm³ RTIL and a N₂ solubility of 0.070 cm³•atm/cm³. These values are slightly lower than those of neat $[C_6 mim][Tf_2N]$. However, the CO₂/N₂ solubility selectivity is approximately the same for both the gel and neat RTIL. These similarities in gas solubility performance are not unexpected because the two materials are compositionally very similar (i.e., the gel is 98.5 wt % [C₆mim][Tf₂N]). Compared to some typical organic solvents (Table 2-1),¹⁸ the observed CO₂ solubility of the gel and pure RTIL are lower. However, their CO_2/N_2 selectivity values are in the middle of the range. Despite their lower CO₂ solubility, RTIL-based materials have an important advantage in membrane operation compared to regular solvents: they have no evaporative loss due to the negligible vapor pressure of RTILs.

Material	Gas Solubility (cm ³ •atm/mL)		Solubility Selectivity
	CO ₂	N ₂	(CO ₂ /N ₂)
[C ₆ mim][Tf ₂ N] neat	2.68±0.02	0.082±0.002	33
[C ₆ mim][Tf ₂ N] gel	2.2±0.1	0.070±0.005	31
<i>n</i> -Hexane	2.1 ^a	0.24 ^a	8.8
Acetone	6.6 ^ª	0.17 ^ª	40
Acetonitrile	7.1 ^ª	0.11 ^a	64

Table 2-1. Solubility of CO_2 and N_2 in the RTIL gel, neat RTIL and other organic solvents. The ideal solubility selectivity is the ratio of the solubilities of the gases obtained from single-gas experiments.

(a) Data obtained from reference 18.

Table 2-1 shows the results of CO_2 and N_2 gas transport studies on the supported gel and pure RTIL test membranes. The permeability of CO_2 was determined to be 650 barrers for the gelled [C_6 mim][Tf₂N] membrane and 700 barrers for the neat [C_6 mim][Tf₂N] membrane. The permeability of N_2 was also similar, 29 barrers for the gel and 31 barrers for the neat RTIL membrane. The supported gel and neat RTIL membranes exhibited similar permeability selectivity for CO_2/N_2 of 22 and 23, respectively. These observed permeability and selectivity values are exceeded by only three polymer membranes in the literature (polymers containing intrinsic micropores (PIM-1, PIM-7)¹⁹ and aminomodified poly(dimethylsiloxane)).²⁰ Also listed is an example of a recent PEO composite membrane.²¹

Table 2-2. Permeability and selectivity of CO_2 and N_2 in the RTIL gel, neat RTIL, the 3 known polymers with better gas transport properties, and recent PEO composite. The ideal permeability selectivity is the ratio of the permeability values of CO_2 and N_2 from single-gas experiments.

Material	Gas Permeability (barrers)		Permeability Selectivity
	CO ₂	N_2	(CO ₂ /N ₂)
[C ₆ mim][Tf ₂ N] neat	700±10	31±1	23
[C ₆ mim][Tf ₂ N] gel	650±10	29±1	22
PIM-1	2300 ^a	92°	25
PIM-7	1100 ^a	42 ^a	26
Modified PDMS	2000 ^b	59 ^b	34
PEO composite	238 ^c	4.9 ^c	49

(a) Data obtained from reference 19 (b) Data obtained from reference 20 (c) Data obtained from reference 21.

The gas transport properties of this new supported RTIL gel membrane can be compared to other types of membranes using a "Robeson plot" (Figure 2-3), which tracks permeability vs. the selectivity on a log-log scale.²² The resulting plot has an empirical upper-bound for dense polymer membranes (•) illustrating a well-established flux-selectivity trade-off.⁵ Any material at or above this line (i.e., in the upper right quadrant) is considered to have good transport properties (i.e., high permeability and high selectivity).

Supported neat $[C_6 mim][Tf_2N]$ (\otimes) and the $[C_6 mim][Tf_2N]$ gel (\otimes) membranes are located to the upper-right of most dense polymer membranes. They have good transport properties even without optimization. Other SILMs (\blacksquare)

have similar permeability values but much higher selectivity values due to lower N₂ solubilities.⁹ Recent examples of solid-state, poly(RTIL) membranes (\blacktriangle)²³ retain the high CO₂ solubility of conventional liquid RTIL materials, but suffer from lower *D* and *P* values because of their dense solid natures. These materials are also below the empirical upper-bound line. Recently, liquid RTILs have been combined with poly(RTIL)s to generate composites with higher gas permeabilities without sacrificing selectivity. These RTIL-based solid-liquid (i.e., 20% liquid) hybrid materials () show a pronounced shift to the right on the Robeson plot compared to the parent solid poly(RTIL)s.¹⁰ However, as demonstrated in Figure 3, the $[C_6 mim][Tf_2 N]$ gel (\otimes) exhibits a CO₂ permeability that is ca. 100 times higher than that of chemically similar imidazolium-based polymers and only a slightly lower CO_2/N_2 selectivity. Moreover, the [C₆mim][Tf₂N] gel also shows a ca. 12 times higher permeability than a similar poly(RTIL)+RTIL solid-liquid composite. The observed selectivity and permeability for the solid RTIL gel are both virtually identical to those of pure liquid [C₆mim][Tf₂N] in an SLM configuration.





The Robeson plot is good for comparing transport properties; however, it does not take into account other physical properties that are essential for a membrane material to be considered industrially viable. For instance, the supported RTIL gel membrane has better mechanical stability compared to conventional SILMs. In conventional SILMs if enough pressure is applied, the active liquid component will be expelled out the permeate side (i.e., burst pressure). It was found that the burst pressure for a neat [C₆mim][Tf₂N] SLM on Supor support was 2.2 ± 0.1 MPa. In contrast, the burst pressure for the

supported [C₆mim][Tf₂N] gel membrane was found to be 2.7 \pm 0.2 MPa (23% higher). While the absolute value is lower than other SLMs, this can be attributed to the relatively large pore size.⁶ This combination of better solid-like mechanical stability and liquid-like gas permeability makes these RTIL gels valuable new platforms for RTIL-based CO₂ separation systems.

This initial proof-of-concept study successfully demonstrates that commercial LMOGs can be used to form stable RTIL gels that *simultaneously* exhibit liquid-like gas transport properties and the solid mechanical properties desired for membrane applications. The gas selectivity of these RTIL gels may be improved by using functionalized RTILs with better targeted selectivity for certain gases. For industrial applications, a membrane that is stable up to 150 °C is desirable in order to withstand the temperature of hot flue gases. Increased thermal and mechanical stability in these RTIL gels may be accomplished by synthesizing new LMOGs with stronger non-covalent gelling interactions. Our research group is currently pursuing both these directions.

2.4 Supporting Information: Materials and General Procedures

12-Hydroxyoctadecanoic acid (i.e., 12-hydroxystearic acid) (99% pure) was purchased from Sigma-Aldrich (catalog # 219967, CAS 106-14-9), and used without any further purification. The CO_2 and N_2 test gases were ultra high purity (99.999%) and purchased from AirGas. Supor 200 (a porous membrane support

made from hydrophilic poly(ether sulfone)) was obtained from Pall Corp. and used as received. Supor 200 has a porosity of 0.8, an average pore size of 0.2 μ m and a film thickness of 145 μ m. All manipulations and procedures were performed in the air on the bench top, unless otherwise noted.

1H NMR spectra were obtained using a Bruker AMX-300 (300 MHz) spectrometer, or Varian Inova 500 (500 MHz) and Inova 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm relative to residual nondeuterated solvent. Powder X-ray diffraction (XRD) spectra were obtained with an Inel CPS 120 diffraction system using monochromated Cu K radiation. XRD measurements on samples were all performed at ambient temperature (21 ± 1 °C). Polarized light microscopy (PLM) studies were performed using a Leica DMRXP polarizing light microscope equipped with a QImaging MicroPublisher 3.3 RTV assembly. Gas solubility measurements were performed using a custom-built stainless steel gas sorption apparatus containing a PX303-015A5V pressure transducer from Omega Engineering Corporation, a 47mm membrane holder catalogue number XX4404700 from Millipore Corporation, and Swagelok tube fittings and valves. The data was acquired by a ADAC DagBoard Pci5500MF from Abu Dhabi Airports Company and processed with Labview 7 Express from National Instruments. This setup has been used in prior publications (Figure S1).²⁴



Figure 2-4: Schematic diagram of the gas solubility apparatus used in this research.

Gas permeability studies were performed with a custom-built, stainlesssteel apparatus consisting of PX303-015A5V pressure transducer from Omega Engineering Corporation, a 47mm membrane holder catalogue number XX4404700 from Millipore Corporation, and Swagelok tube fittings and valves. The data was acquired by a ADAC DaqBoard Pci5500MF from Abu Dhabi Airports Company and processed with Labview 7 Express from National Instruments as described in prior papers from our group (Figure S2)²⁵



Figure 2-5: Schematic diagram of the gas permeability flow apparatus used in this research.

1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

 $[C_6mim][Tf_2N].^{26}$ This compound was synthesized according to literature procedures. Spectroscopic data for this compound were consistent with those published in the literature,²⁶ and the sample purity was confirmed to be >99% by NMR analysis.

Preparation and Characterization of [C₆mim][Tf₂N] / 12-

hydroxystearic acid RTIL gels. The RTIL gel was formed by heating measured amounts of 12-hydroxystearic acid (12-hydroxyoctadecanoic acid) and $[C_6mim][Tf_2N]$ in a water bath maintained at 80 °C. Upon cooling the homogenous clear sol phase became an opaque, white soft solid gel. When viewed under standard optical microscopy the sample appears to have entangled fibers and fibrils (Figure S3a,c). When viewed under PLM, the gel showed disordered dark regions with ordered fibers the rotate polarized light (Figure 2-6 a-d). The presence of these macroscopic fibers throughout the RTIL gels is what accounts for the cloudy white, non-transparent appearance of these gels. However, powder XRD analysis of the gels showed no <u>detectable</u> periodic order on the molecular and mesoscopic levels; only a broad amorphous halo was present (Figure 2-7).



Figure 2-6. Microscopy images of (a) and (c) the standard optical magnification of gel, showing networked fiber structure; (b) and (d) the PLM textures of the same gel. Magnification = 6.3x for (a) and (b); 12.6x for (c) and (d). Standard length = $0.125 \mu m$ for (a) and (b); 0.1 μm for (c) and (d).



Figure 2-7. XRD profile of $[C_6 mim][Tf_2N]$ gel sample containing 1.5 wt % 12-hydroxystearic acid.

Phase diagram. The phase diagram of the $[C_6 mim][Tf_2N] / 12$ -hydroxystearic acid system was constructed by tracking the average temperature of gelation of multiple samples of $[C_6 mim][Tf_2N]$ with incremental loadings of 12-hydroxystearic acid, from 0 to 2 wt %. The vials were immersed in a stirred oil bath that was slowly heated and cooled at ~5 °C min. The gelation temperature was determined when the sample went from clear to opaque, and checked for the absence of flow when inverted.

Supported membrane preparation. The supported membranes of pure RTIL and RTIL gel were made using microporous Supor 200 poly(ether sulfone) membrane (Pall Corporation) as a porous support (0.2 µm pores, 0.8 porosity, 47 mm diameter, 148 µm thickness). The neat RTIL or RTIL gel were applied to the support as it was

heated to 80 °C. The resulting fluid samples were then spontaneously drawn into the pores of the support via capillary forces. The resulting dense membranes were then slowly cooled to room temperature. In the case of the supported RTIL gel membranes, the gel reformed inside the support pores upon cooling. The membranes are white, dry to the touch and flexible (see Figure 2-8).



Figure 2-8. Photograph of a supported RTIL gel membrane on Supor 200 support.

Gas solubility measurements on bulk materials. The solubility of CO₂ and N₂ were determined for the gelled RTIL and neat RTIL materials using the gas adsorption unit shown schematically in Figure S1 above. Gas solubility measurements were made as follows: Approximately 8 mL of bulk test sample were placed in the sample cell and evacuated overnight to remove all gas. The lower portion was closed off while the upper reservoir was charged with gas. The run was started when the lower valve is quickly

opened and closed allowing the test gas into the lower portion with the sample. The pressure drop was then measured as a function of time as the sample absorbed the gas. Figure 2-9 shows a typical pressure vs. time plot for a gas solubility run as described above.



Figure 2-9. Typical pressure vs. time plot for determining gas solubility and diffusion.

Once equilibrium (i.e., steady-state) was reached, the amount of gas absorbed into the sample was determined from the pressure drop using the Ideal Gas Law (eq. 2-1).

$$so \text{ lub} ility = \frac{\frac{\Delta PV}{RT} \bullet \frac{22400 cm^{3}_{gas(atm)}}{mole}}{mL_{solvent}}$$

Equation 2-1: solubility equation

The initial pressure drop observed with an unstirred sample was used to estimate diffusion of the gas through the sample (see Figure 2-9).

Gas permeability studies on membrane samples. The permeability of gases (e.g., CO_2 and N_2) through supported membranes of the test samples was measured using the gas solubility apparatus schematically in Figure S2. Gas permeability measurements were made as follows: The test membrane was loaded and sealed in the membrane holder. The entire system was then placed under vacuum to remove all dissolved gas from the membrane. The lower and middle valves were then closed to isolate the membrane in vacuum while the upper portion was charged with gas. The run was started by opening the middles valve and recording the pressure rise on the permeate side of the membrane. The pressure rise measured on the permeate side of the membrane. The pressure rise measured on the permeate side of the membrane.

representative data plot using the apparatus and procedures described above. The flux and permeability can be determined from the slope of the linear portion of the pressure vs. time plot at pseudo-steady-state, where the pressure increase is constant, using eq. 2 below.



Figure 2-10: Typical pressure vs. time plot for determining gas permeability and diffusion rate.

$$permeability = \frac{Volume_{gas} \bullet Thickness_{memb}}{Area_{memb} \bullet Time \bullet \Delta P}$$

Equation 2-2: calculation for permeability through a membrane

Since permeability is the flux of a fluid through a solid or liquid membrane that has been corrected for thickness, difference in pressure, and area, the unit of permeability is a non-SI unit, barrer, defined as below.

$$barrer = \frac{10^{-10} \cdot cm_{gas(STP)}^{3} \cdot cm_{thickness}}{cm_{area}^{2} \cdot s \cdot cm_{Hg}}$$

Equation 2-3: units of barrer

Initially the pressure does not increase, because the gas has a certain amount of time to diffuse through the membrane, known as the time lag. The diffusion can be estimated from the time between the start of the experiment to the intercept of the pseudo-steady-state flux.

Burst pressure measurement. The maximum driving pressure that the test membranes could withstand was determined by slowly increasing the pressure difference in the gas permeability test apparatus (Figure S2) until the membrane failed. Membrane failure was defined as the moment there was a sharp increase in flux. After

membrane failure visual inspection revealed portions of the membrane to be a different shade of white, the same shade as the new, dry membranes.

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Chapter 3

Improved Physically Gelled Supported ionic Liquids: Soft-Solid Membrane Materials for CO₂ Separations

Abstract

There is an increasing need for separation of CO_2 from other light gases. One particular area is coal, natural gas and oil powered electric generation¹. These fossil fuel power plants generate billions of tons of CO₂ each year. The increase in CO₂ concentration in the atmosphere contributes to anthropogenic climate change, which has greater effects to the environment, habitable living areas and food production². The European Union has recently instituted a carbon economy based on the production and reduction of carbon dioxide emissions. For both ecological and economic motivations, there is a growing need for separating CO_2 from post-combustion flue gas. There are many current methods to perform a CO_2 separation (e.g., aqueous amine, pressure swing adsorption) however they are energy intensive processes. Membranes have recently been developed as a low-cost (both capital costs and operations costs) separation process. Membranes that are attractive to industry have high permeability and high selectivity. To achieve these two inversely linked goals, we have used room-temperature ionic liquids (RTILs) as the separation media,

which is inherently selective for CO_2 and has high permeability from liquid-like diffusion. One disadvantage of supported liquid membranes is their low mechanical stability. This is overcome by combining the RTIL with a solidifying agent to make a mechanically stable soft-solid, while maintaining the liquid matrix. This study develops a supported soft-solid membrane system composed of room-temperature ionic liquids for CO_2 separations from N₂.

3.1 Introduction

More power and power production is needed to supply ever increasing populations and in countries such as India and China, whose industrialization increases the power consumed per capita each year.² Most of the power supplied to the world comes from carbon fuels (i.e. coal, natural gas, and oil). These carbon-based power plants release 44 tons of carbon dioxide for every 12-14 tons of fuel they burn.¹ This large quantity of carbon dioxide has contributed to the dramatic increase in atmospheric CO₂ concentration during the last century.³ The increased CO₂ level has been linked to anthropogenic climate change, whose effects include: ocean acidification which leads to coral reef dieoff, glacier retreat and ice pack melting which causes rising sea levels, and more violent weather patterns¹. The European Union has already enacted a carbon trading system to encourage companies to reduce their carbon foot-print in an effort to curb CO₂ emissions. There is a strong effort to adopt a similar system in the United States and Australia. Clearly, for both environmental and economic

reasons, power plants should attempt to capture and sequester the carbon dioxide they produce^{4,5}.

The flue gas from a power-plant contain the by products of combustion, including any non-carbon compounds that exist in the feed stock. The majority of flue gas is nitrogen, then carbon dioxide and water. There are trace amounts of nitrogen oxides (NO_x), sulfur oxides (SO_x) and various heavy metals. Capturing the entire flue stream would have a significant mass of nitrogen which would increase sequestration costs. A more efficient method of reducing carbon capture costs is to separate the CO_2 from the N_2 . However, any method used must be able to tolerate the other trace components (i.e. water and acidic gases).

Current methods for CO_2 separation involve aqueous amine bubblers, cryogenic distillation, and pressure swing adsorption. Aqueous amine bubblers are a well established technology that uses alcohol amines (e.g. diethanolamine DEA, monoethanolamine MEA) in an aqueous solution⁶. The solution is passed through a liquid-gas contacted (bubbler) and the CO_2 reacts with the amine to form a carbamate salt in the aqueous phase⁷. Then the solution is heated under reduced pressure to reverse the reaction, releasing CO_2 and regenerating the amine. This method has a relatively high cost for energy to heat the solution, due to the high heat capacity of water. In addition, the aqueous phase is acidic and requires more expensive stainless steel piping. Cryogenic distillation is another method to remove CO_2 by cooling down the flue gas until each component, including CO_2 , freezes and the nitrogen can be removed. The

advantage of having an easy to transport frozen CO_2 (dry ice) does not outweight the enormous expense of refrigerating hot flue gas. The third method is to flow the flue gas across a large porous bed that will selectively adsorb CO_2 , once theflue gas travels to the end of the bed, most of the CO_2 will have been removed. After the bed reaches capacity, it is switched to high vacuum to dexorb the CO_2 , collect it and regenerate the bed. Normally, two beds are run side-byside alternating between flue stream and vacuum. This method requires a large quantity of adsorbent material which may be adversely affected by the acidic gases.

A promising alternative to the three methods listed previously are membranes^{8,9}. In a membrane system the flue gas is passes across a thin film of selective material while vacuum is applied to the other side¹⁰. CO₂ selectively permeates across the film down the pressure gradient to be sequestered. The flux across the membrane is inversely proportional to the thickness of the membrane, so membranes are usually between 0.1-1 μm thick, a trade off between thinness, mechanical stability and defect-free manufacturing. Because membranes are so thin, they use very little selective (i.e. expensive) material, unlike pressure swing adsorption or aqueous amines. The only operational cost with a membrane is the pressure differential across the membrane. This is a much cheaper endeavor than heating aqueous solutions or cooling to cryogenic temperatures. Thus, membranes offer an inexpensive operation and capital costs over other current technologies^{Error! Bookmark not defined}.



Figure 3-1: Chemical reaction for CO₂ scrubbing with aqueous amine solutions

As demonstrated, there is a need for a membrane material that will be stable under vacuum, high temperatures (hot flue gas), acidic environments (feed contaminants NO_x and SO_x), with high flux and low cost. Room temperature ionic liquids (RTILs) accomplish many of these requirements and should be considered as a part of any flue gas separation membrane material^{11,12}. An RTIL is an organic salt that is liquid at or below standard temperature and standard pressure (20 °C, 1 atm) ¹³. These salts usually have delocalized charges and have negligible vapor pressure.

Imidazolium based RTILs are particularly suited for CO_2 separation membranes. They have an inherent solubility selectivity of CO_2 over N₂ and are chemically stable¹⁴. The RTIL is also tailorable, with two independent amines to attach to and a choice of anion to pair with the imidazolium. If a bis(trifluoromethylsulfonyl)imide (Tf₂N) anion is selected the resulting RTIL is hydrophobic, and if dicyanoamide (DCA) is selected the RTIL has exceptional selectivity. Imidazolium RTILs are an excellent component to a separation membrane, because they are chemically robust, vacuum stable, heat tolerant, synthesized from cheap materials and have tailorable chemistry.

Supported ionic liquid membranes (SILMs) have been previously tested for CO₂/N₂ separations and determined to have good solubility and good permeability^{15,16}. However, liquid membranes can only withstand a small transmembrane pressure drop. If the applied pressure reaches above a certain threshold (approximately 1 atm) the liquid is expelled from the pores of the supported membrane and the membrane breaks. Also, the liquid must wicked inside a support, pure liquid membranes can not be cast in films thin enough for commercial applications. Conversely, polymer membranes are mechanically stable and castable, but have low permeability due to the gas diffusing through a solid. The best of both worlds, a liquid-like permeability and a solid-like mechanical stability can be achieved with a low molecular-weight organic gelator (LMOG).

LMOGs are small surfactant-like molecules with polar and non-polar moieties. They can be dissolved into a solution at elevated temperatures, and crash out when cooled. Due to their particular shape, when the solution cools, the LMOG molecules align themselves in one-dimentional strands through physical bonding (e.g. hydrogen bonding, pi-pi bond stacking, van der Walls interactions)¹⁷. These one dimensional strands become long enough to entangle into a three dimensional network that entrains the liquid forming a gel^{18,19}. This gel has a high liquid loading of >95% liquid, and consequently has liquid-like
solute diffusion, and solubility^{20,21,22,23}. However, it also has mechanical stability and will not flow under gravity. This will also allow the membrane to be spray cast as a thin film on a support, for a commercially thin membrane.

Herein, we shall demonstrate a supported gelled RTIL membrane for CO₂ separations from flue gas. The LMOG provides mechanical stability for thin film casting, and increased trans-membrane pressure. The RTIL provides high permeability and selectivity for CO₂. This work is accomplished in coolaboration with Los Alamos National Laboratories. They provide the thin film spray coating apparatus and techniques, while the University of Colorado provides materials and initial gas transportation measurements.

3.2 Experimental Methods

3.2.1 Materials

The aspartame derived LMOG **1** (figure 3-2), was synthesized from a modified method in literature^{24,25}. The imidazolium RTILs were all synthesized from literature²⁶. The gases CO_2 and N_2 were purchased from AirGas and at least 99% pure. The Supor 200 porous polyethersulfone membrane support was purchased from Pall.



Figure 3-2: Chemical structures of RTIL components and aspartame derived LMOG

3.2.2 Membrane Preparation

200 mg of LMOG **1** was added to 5 mL of each RTIL. The mixture was heated to 100 °C until a homogeneous solution formed. Then the sol was rapidly cooled in an ice bath to form a gel. This particular concentration of LMOG **1** (40 mg / mL RTIL) was chosen because the temperature of gelation for each gel was approximately 80 °C. The 47 mm diameter Supor membranes have a maximum operating temperature of 100 °C. A portion of the gel was placed on the support, on top of a temperature controlled heating plate. The plate was heated to 80 °C, or just when the gel would start to melt. A lid was helpful to expedite the gel melting. After a period of 1-3 minutes the gel will melt completely, and the sol will wick into the Supor support. The system was held at constant temperature for 3

minutes to allow the sol to permeate the membrane. Afterwards, the still hot membrane was blotted with a Kim-wipe to remove excess sol from the surface of the membrane. Finally, the membrane was removed off the hotplate and quickly cooled to room temperature. The gel formed inside the membrane pores. The finished membrane was dry to the touch and opaque white. The membrane was weighed to confirm that the entire pore volume was filled with gel RTIL.

The following RTILs were used to make both neat RTIL supported membranes and LMOG **1** gelled RTIL supported membranes: hmim/Tf₂N, emim/Tf₂N, emim/DCA, emim/triflate. The supported ionic liquid membranes were made in a similar fashion. Except, instead of a gelled RTIL, neat RTIL was used.

3.2.3 Gas Permeability Measurements

 CO_2 and N_2 gas permeability studies were performed on a dead end pressure cell, custom build with a dual o-ring seal and 47 mm membrane holder. The data was collected automatically from a Omega PX303 pressure sensor to National Instruments Lab View software. The membranes were gently loaded into the holder and placed under dynamic vacuum (<1 torr) for 4 hours to remove any gasses. The membranes were then tested for CO_2 and N_2 separately, with 1 bar of feed pressure and <1 torr permeate pressure. The flux (Q_i) for each gas

was calculated from the pressure rise for the permeate side of the membranes by applying the ideal gas equation.

$$Q_i = \frac{n_i}{A_{SA} \cdot t} = \frac{\Delta p \cdot V}{R \cdot T \cdot A_{SA} \cdot t} = \frac{V}{R \cdot T \cdot A_{SA}} \cdot \frac{dp}{dt}$$

Equation 3.1: Calculation of flux from change in pressure over time

The permeability (P_i) was calculated by normalizing the flux for membrane pressure drop or driving force (Δp) per thickness (I).

$$P_i = \frac{Q_i}{\Delta p/l}$$

Equation 3.2: Calculation of permeability from normalizing flux.

The dead-end permeability apparatus is able to determine diffusivity of the membrane from the characteristic time-lag before steady-state pressure rise. However, these membranes had a time lag of only a few seconds: too small to accurately determine diffusivity.

3.2.4 Phase Diagram Measurements

The phase diagram for these RTIL gels was determined by the 'test tube inversion' method. To date, there is no clear-cut definition of a gel. From

polymer theory a gel is when cross-linking density is greater than 1, from rheology it is when the G" is larger than G', from everyday interaction it is when the sol stops flowing. 1 ml of RTIL and 0-80 mg of LMOG 1 were mixed in a 10 mm diameter test tube. The test tube was heated until the phase was homogeneous then cooled in an ice bath for 30 minutes. The gels were then placed in a heated block. The temperature was incrementally raised 5 °C and held for 10 minutes, after which the test tubes were inverted to determine which gels had melted. Temperature of gelation (T_g) is reported as the last solid temperature.

3.3 Results and Discussions of Gelled RTIL Membranes

3.3.1 Phase Behavior of LMOG 1 Gels

The aspartame derived gelator, LMOG 1, is an improvement over the previous proof of concept gelator, 12-hydroxy stearic acid. LMOG **1** is able to gel multiple RTILs, not just hmim/Tf₂N. Also, the LMOG **1** loading in the RTIL (and consequently temperature of gelation) increases up to the decomposition temperature of the RTIL (Figure 3-3), as opposed to the 12-hydroxy stearic acid which is limited to 1.5 wt% loading before phase separation occurs. The 40mg / mL RTIL loading has a temperature of gelation near 80 °C. This is a good intermediate temperature for membrane processing that will prevent the Supor

support from melting before the gel does. All gas separation data on gels is performed with a LMOG concentration of 40 mg / mL RTIL.



Figure 3-3: Phase diagram of LMOG 1 for various RTILs

3.3.2 CO₂ and N₂ Gas Separation Performance

Presented next are a series of Robeson plots that include gelled and neat RTIL supported membrane data. The permeability data was taken at 20 °C and 70 °C.

First varying the temperature between 20°C and 70°C had a significant but predictable change. As temperature increases the solubility of CO_2 decreases in the RTIL due to unfavorable mixing parameters. In additional heat increases the permeability of N₂ and CO₂. So the entire set of data moves along the permeability/selectivity trade off toward the lower right of the Robeson plot. All membranes exhibited an increase in permeability and a decrease in permselectivity.



Figure 3-4: Effect of temperature on CO₂ permeability and CO₂/N₂ permeability-selectivity

The effect of gelation was not predictable nor followed a general trend Figure 3-5). Previous studies indicated a LMOG gel would lower permeability slightly and keep selectivity identical. In this study we found the effect of permeability of gelation dependent on the anion. For ionic liquid gels containing the Tf₂N anion (i.e.: emim/Tf₂N and diol/Tf₂N) the permeability of the gel as compared to the neat RTIL decreases and the perm-selectivity remains largely the same. This result is the predicted result. For ionic liquid gels containing the triflate anion (i.e.: emim/triflate) the permeability of the gel compared to the neat RTIL increases and the selectivity stays approximately the same. It is unknown why the permeability would increase for a soft solid over a liquid. One conjecture is the free volume fraction has increased; we do not have a method to measure the density of the separating layer inside the pores at this time. Lastly, and also counter-intuitive, the BF₄ containing RTIL gel (i.e.: emim/BF₄) shows an increase in selectivity and a constant permeability as compared to the neat RTIL. This result is particularly confusing, since the ionic environment of the selective layer is largely the same for the gel RTIL and neat RTIL form. The only theory at this point is that the emim/BF₄ causes the gel to aggregate in a unique fashion compared to the other RTILs. This different gel structure could cause amine groups on the gelator to be exposed to the RTIL phase rather than hydrogen bond with each other. The exposed amine groups would then positively interact with the CO₂, causing a higher loading and higher selectivity.



Figure 3-5: Effect of gelation on CO₂ permeability and CO₂/N₂ permeabilityselectivity

The effect of cation on gelled RTIL membranes is very distinct. All RTILs with the cation emim (i.e.: emim/Tf₂N, emim/triflate, emim/DCA) had both higher permeability and high selectivity than the diol cation and high selectivity than the hmim cation. The hmim based RTILs have a 6 carbon tail while the emim based RTILs have a two carbon tail. This extra alkyl length decreases the solubility of CO_2 and hence the permeability-selectivity of CO_2/N_2 . This is expected as increasing the tail length makes the RTIL more similar to polyethylene which has very poor selectivity. Or, in other words, the molar concentration of dipoles for



CO₂-RTIL quadrapole-dipole interaction is higher in emim RTILs than in hmim RTILs. This result confirms previously obtained solubility selectivity of the RTILs.

Figure 3-6: Effect of cation on CO_2 permeability and CO_2/N_2 permeability-selectivity

The effect of the anion is equally pronounced. Tf₂N has the highest permeability of 700-1000 barrers. The triflate RTIL has the next highest permeability between 400-600 barrers. Finally, the BF₄ anion has a permeability of 200-400 barrers. The diol/Tf₂N has a very low permeability of 60-110 barrers, most likely due to its high viscosity from hydrogen bonding. In general, excluding

the diol/Tf₂N, the selectivity of each RTIL is similar. The effect of the anion on permeability is largely due to the viscosity it imparts on the RTIL. The viscosity of emim/Tf₂N, emim/triflate and emim/BF₄ are 18, 34 and 43 mm/s respectively. The increase in viscosity is directly proportional to an increase in diffusivity which increases permeability.



Figure 3-7: Effect of anion on CO_2 permeability and CO_2/N_2 permeability-selectivity

The next phase of this research is to optimize the gel RTIL system for Los Alamos National Labs to make a sprayed thin film on a porous support. These results help guide a systematic design of a gelled RTIL system for the thin support and for future RTIL optimizations. The general conclusions we can draw from these results are as follows:

1. Low viscosity RTIL is better than high viscosity. This is most likely from higher diffusion increasing permeability. RTILs with a Tf₂N anion have some of the highest viscosities.

2. Longer alkyl groups decrease selectivity. The emim based RTILs have nearly twice the CO_2/N_2 permeability–selectivity as hmim based RTILs.

3. Higher temperature reduces selectivity and increases permeability. Due to the enthalpy of solution the CO_2 becomes less soluble in the RTIL and N_2 becomes more soluble. The RTIL viscosity decreases, which increases diffusion.

4. Gelation has a significant effect on permeability and selectivity. The gas permeation difference between the neat and gel RTIL is not predicable and must be tested for in any new system.

These 4 principles help guide material selection and design for the next phase. Low viscosity is the largest factor in increasing diffusivity and hence, permeability. The anion seems to have the greatest effect on viscocity and permeability; and the best anion candidate is Tf₂N. The Tf₂N based RTILs are chemically stable, relatively inexpensive, usually water imiscible and afford a permeability of 800 barrers. Other low viscosity RTILs that may work well are emim/dicyanoamide and emim/tricyanomethyl. The cation seems to have the greatest effect on permeability-selectivity; where the best performing cation is emim. RTILs based on an emim cation are also chemically stable, synthesized from cheap starting materials and have selectivity between 25 and 30 CO₂/N₂.

Designing for temperature will have two components: (1) increased temperature reduces selectivity and increases permeability, and (2) increased temperature will permit a higher LMOG loading in the sol. The polyethersulfone support used for gas permeation studies is limited to 100 °C and thus an LMOG loading of ~40 mg / mL RTIL. The spray-coating system at LANL uses a porous ceramic support that can withstand a thousand degree temperatures, much higher than the thermal decomposition of RTILs. So, the LANL system can use a higher loading of gelator, which will make a stiffer more robust gel. With regards to flue separation system processes, the flue gas should be cooled as much as possible before entering the separation process. The cooler the flue gas the more selective the CO_2/N_2 separation will perform. Finally, the gelator is a key component of this material that can significantly affect the gas permeation properties. Higher loadings of the LMOG will create a stiffer gel, but probably decrease permeability.

Based on these design concepts the first gel materials were sent to LANL for spray coating testing: emim/Tf₂N and emim/DCA with 40 mg gelator per 1 mL RTIL. After many variations, LANL was able to cast a gel membrane on a

porous support at ~50 μm thickness. The film did not flow under gravity but had a consistency described as "vacuum grease". When the coated fibers are handled the gel will smear off the fiber; this is too mechanically weak for industrial use. The membrane film must be mechanically stable enough to be handled without failure. The results from LANL are now being considered, and new materials are being developed that will be more mechanically stable.

3.4 Conclusions

This research improves and optimizes on the initial proof of concept gelator system: hmim/Tf₂N and 12-hydroxy stearic acid. The next generation system can be composed of a variety of RTILs; hmim/Tf₂N, emim/Tf₂N, diol/Tf₂N, emim/DCA, emim/triflate, emim/BF₄ and bmim/Tf₂N have all been used to make gels and gel supported membranes. Since the LMOG gels such a wide range of RTILs, it is most likely that functional RTILs, or RTIL blends can also be gelled. The next generation system has a larger temperature of gelation range. The proof of concept system had a maximum temperature of gelation of 68 °C because the 12-hydroxy stearic acid - hmim/Tf₂N sol phase would phase separate at 1.5 wt% loading of gelator. The new system has no such limitation and additional LMOG 1 can be added until the decomposition temperature of the RTIL is reached. In more practical terms, the temperature of gelation can be adjusted between 35 °C (just above room temperature) and 150 °C. These

temperatures are well above the application specification of hot flue gas which is usually around 80°C.

Many opportunities exist to advance the RTIL gel membrane system. As indicated from LANL there is a need for a more robust gel. Currently, CU is testing higher loadings of LMOG1 to see if good stability can be achieved. However, another approach is to use another LMOG. Because RTILs have a very high temperature tolerance, many previous molecules considered to be insoluble may indeed make good RTIL gelators. The amide moiety forms particularly strong bonds and could make a very robust LMOG (Figure 3-8). Previous research has concluded that such molecules bond too tightly and are insoluble in organic solvents up to the boiling point. Since RTILs can be safely heated to 300 °C the amide-containing LMOG may solubalize in RTILs at the elevated temperature. Another avenue of improvement is modifying the RTIL to have better gas transport properties. The anion could be changed to decrease viscosity, and increase diffusion. This would increase the permeability of all gasses. The cation could be modified with functional groups, such as amines, to increase CO₂ solubility and solubility-selectivity. All of these possibilities indicate further research into physically gelled RTILs warrants more research.

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Chapter 4

Ionic Liquid Gel-Based Containment and Decontamination Coatings for Blister Agent-Contacted Substrates

Abstract

Current methods to contain and decontaminate equipment and materials exposed to chemical warfare agents (CWAs) have disadvantages with regards to dealing with porous substrates, ease of delivery, and portability. Consequently, there is a need for a portable, easy-to-use material that will immediately act as a barrier to contain CWA vapors on contacted substrates and also decontaminate the substrate to allow a safer environment for military and first-responder personnel. Herein, we present a new type of decontaminating barrier system for blister agent CWAs made of three components: (1) a spreadable matrix based on a room-temperature ionic liquid (RTIL), (2) an organic gelator to act as a solidifying agent, and (3) a polyamine that acts as reactive agent to chemical degrade and help draw out the adsorbed blister agent. When applied to porous and nonporous substrates contaminated with 2chloroethylethylsulfide (CEES, a blister agent simulant), this coating mixture was found to act as an effective barrier material, immediately blocking 70–90% of the CEES vapor from entering the overhead space above the samples. Furthermore, this reactive gel RTIL coating system was able to remove (i.e., draw out) 70–95% of the liquid CEES that had soaked into the substrates over a period of 24 hours at ambient temperature as a static, single-application coating (i.e., without need for agitation).

4.1 Introduction

The ability to effectively contain and decontaminate chemical warfare agent (CWA)-contacted materials and personal equipment in the field is extremely important for maintaining the health and operational effectiveness of military personnel and firstresponders, especially when far from a base of operations where traditional CWA decontamination procedures can be implemented.¹ Highly toxic CWAs are generally categorized into two classes depending on their mechanism of action: (1) nerve agents (i.e., reactive phosphorus esters) that block neuroreceptor sites, and (2) blister agents (typically chlorinated thioethers) that alkylate and cross-link tissue and DNA.^{2,3,4} CWAs are usually delivered in vapor or aerosol form. Although protective garments can usually shield individuals from direct CWA exposure, CWAs can quickly adsorb into porous substrates such as wood, as well as nonporous but swellable substrates such as rubber paint.^{5,6} Unfortunately, current CWA decontamination methods have and disadvantages when dealing with materials that readily adsorb CWAs.^{7,8} Although these methods are effective for removing and deactivating surface-bound CWAs, they are not ideal for containing and efficiently removing or degrading soaked-in CWAs.^{9,10} Residual CWAs can still leach out from the interior of these materials in vapor and liquid form, causing problems with long-term safety and indirect exposure.^{11,12,13}

Traditional methods for decontaminating CWA-contacted materials have involved washing with reactive solutions that chemically degrade the CWAs, or evaporating the CWAs out with heated forced air.^{14,15,16} Current CWA decontamination solutions are based on aqueous strong bases or oxidizing agents.^{17,18} Although these wash solutions are inexpensive, they are not completely effective unless the contaminated object is immersed in the solution for long durations, which is not feasible for large items such as vehicles or buildings. In addition, many of these CWA decontamination solutions are heterogeneous in nature (i.e., emulsions) due to limited reagent solubility in the aqueous phase.¹⁹ This factor limits their reactivity and effectiveness in penetrating certain types of substrates. Hot air can also be forced into the contamination zone of the materials to drive out any adsorbed CWAs. Although this method works well for porous materials, it takes days or even weeks to reduce the CWA vapor concentration down to safe levels.⁹ Consequently, there is a need for new, portable, easily applied, and effective materials that allow military personnel and first-responders to rapidly contain and decontaminate CWA-contacted field equipment and materials.

Herein, we present a new type of decontamination material for blister agents (e.g., sulfur mustard and its analogues) that (1) acts as a non-volatile barrier that blocks hazardous vapors as soon as it is applied as a coating, and (2) actively removes/decontaminates soaked-in blister agent from the substrate interior over a period of 1–2 days. Afterwards, this coating can be removed and properly disposed of. This new spreadable coating material is a three-component gel system consisting of a room-temperature ionic liquid (RTIL) (1), a low molecular-weight organic gelator (LMOG) (2), and an organic polyamine tetraethylenetetramine (TETA), (Figure 1a) ^{20,21}.

The role of the major component in the system, the RTIL (i.e., a molten organic salt at ambient conditions with negligible vapor pressure), is to provide a very stable fluid medium that can envelop the contamination area, help extract out the CWA via solubilization, and depress the vapor pressure of any CWA underneath or dissolved in the RTIL.^{22,23} The role of the LMOG is to help solidify the RTIL at very low loading levels to form a soft solid with lower vapor diffusivity while retaining spreadability. This type of gelling occurs via the LMOG molecules physically bonding with each other (e.g., H-bonding, van der Waals forces, and/or π - π bond stacking) to create a thermoreversible, non-covalent network that immobilizes the surrounding liquid RTIL, and affords a more mechanically stable material that will not flow under gravity.^{24,25} Finally, the role of the organic amine is to act as a nucleophile and react with sulfur mustard and its analogues to degrade/deactivate them via nucleophilic substitution.⁷ The reaction of the blister agent with the sacrificial amine also creates a negative concentration gradient of the agent in the area in contact with the gel, thereby helping draw out soaked-in CWA from the substrate interior into the reactive coating layer. The liquid ionic environment provided by the RTIL may also afford a faster degradation reaction rate since RTIL as solvents are known to enhanced the rates of certain organic reactions with polar or ionic intermediates.²³ Initial studies with glass, wood, rubber, and painted steel substrates contaminated with the mustard agent simulant, 2-chloroethyl ethyl sulfide (CEES) (Figure 4-1), showed that applying a film of the gel RTIL + amine coating over the samples immediately reduces the CEES vapor concentration over the samples by 90% compared to uncoated control samples. In addition, the reactive gel RTIL + amine coating is able to extract / react away >98% of the CEES originally applied on the

surface of non-adsorbing substrates (e.g., glass) and 70–90% of the original CEES soaked into absorbing substrates (e.g., wood, rubber, and paint) after 24 hours of contact. Control studies with the various components of this reactive composite coating indicate the RTIL gel is responsible for a good part of the CEES vapor containment and extraction from the samples, but the reactive amine component provides even better vapor containment and extraction results.



Figure 4-1. (a) Chemical structures of the three components of the decontaminating barrier system (RTIL, LMOG and TETA) and the mustard simulant (CEES). (b) A cross sectional schematic of the CEES containment and decontamination test apparatus.

4.2 Experimental Methods

In order to demonstrate proof-of-concept for this approach, an initial RTIL, LMOG, and amine were chosen to prepare the reactive gel coating system. 1-Hexyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide (**1**), was selected as the RTIL component after preliminary studies showed that CEES is completely miscible with this RTIL. This RTIL also has the advantage of being commercially available and easily and cheaply synthesized. The aspartame-derived compound **2** was chosen as the LMOG because it has previously been shown to gel many different types of RTILs²¹. We also determined that **2** can also form a stable gel (>6 months) with varying mixtures of **1** and CEES, (i.e., from 1:0 to 0:1, mol RTIL:mol CEES), making it ideal for this application. The reactive amine component, TETA, was selected because CEES is known for reacting with amine-based nucleophiles, in particular because sulfur mustard will react with guanine and other biological amines.²⁶ Although stronger nucleophiles and bases could also be used, our premise was to keep the coating relatively non-reactive to most substrates and relatively non-toxic to dermal contact. The gel RTIL + amine coating system was prepared by mixing 960 μ L RTIL **1** + 40 μ L TETA + 40 mg LMOG **2**, such that a total of 1 mL of coating was applied to each CEES-contaminated test substrate coupon. Based on information found in the DTRA CWA Testing 2007 Source Document²⁷ glass (non-porous), wood disks (porous), tire rubber (swellable), and painted steel (dense but swellable) were chosen as the test substrates in order to mimic the range of materials often contacted by CWAs.

The CEES containment and decontamination testing apparatus is shown in Figure 4-1b. This lab-scale apparatus and the associated testing procedure described below were developed to be inexpensive and to allow for high-throughput, while providing a quantitative assay on both CEES vapor barrier effectiveness and liquid CEES desorption rate. The testing procedure used is described as follows: the substrates were first placed in small aluminum cups and allowed to sit overnight at ambient conditions. Subsequently, 20 μ L of CEES was pipetted directly onto the center of the substrates and allowed to soak into/equilibrate with the substrates for 1 min before 1.0 mL of the gel RTIL coating was applied over the center of the substrates. Although the same amount of gel RTIL coating was applied to each contaminated test substrate, the glass and painted steel samples had approximately a 2 mm-thick gel

RTIL coating, whereas the wood and rubber substrates had a 1-mm-thick coating due to the different dimensions of the substrate coupons. The coated substrates and aluminum cups were then each placed in a 140-mL EPA soil sample jar and sealed with Gas chromatography-mass spectrometry (GC-MS) analysis of the a septum. headspace in the sample jar was performed after 1–3 h and after 23–25 h to determine the concentration of CEES vapor released from the contaminated samples. The RTIL coating was then wiped away with a Kim-wipe until the substrates were dry to the touch. The substrates were subsequently placed in 10 mL of chloroform (which is not CEESreactive) for 24 h to extract any remaining liquid CEES from the samples. Again GC-MS analysis on the chloroform was used to determine the amount of CEES extracted from the samples. The final data obtained from this procedure include the ppm (parts per million) of CEES vapor in the headspace above the coated, contaminated samples (which is a direct measurement of the vapor barrier effectiveness of the applied coatings) and the amount of CEES remaining within the treated substrates (which is a direct measurement of soaked-in liquid CEES decontamination and desorption effectiveness).

Following the testing procedures described above, the CEES vapor containment and liquid CEES desorption performance results for the gel RTIL + TETA coating formulation on each of the four substrate materials are summarized in bar graph form in Figures 2 and 3, respectively. For comparison, performance data from control coatings consisting of [1 mL pure RTIL **1** (i.e., no gelator or amine)], [1 mL RTIL **1** + 40 mg LMOG **2** (i.e., no amine)], and [960 μ L RTIL **1** + 40 μ L TETA (i.e., no gelator)] are also included, along with data from the <u>uncoated</u> test substrates as benchmarks.

4.3 Results and Discussions

As can be seen from Figure 4-2, all four RTIL coating formulations substantially reduced the concentration of CEES vapor in the overhead space above the CEESwetted substrates compared to the uncoated reference samples. On average, the coated glass, wood and painted steel substrate samples had 10 times less CEES vapor in the headspace as compared to an uncoated control sample, while the rubber substrate samples had 5 times less (Figure 4-2). In general, the RTIL gel coatings performed better than non-gelled (i.e., liquid) RTIL coatings. This is mostly likely due to the gelled RTIL (semi-solid) having a lower diffusion coefficient compared to the less dense and more mobile liquid RTIL-based coatings. As expected, the coatings with TETA as an active reactant for CEES also performed better than the RTIL coatings without TETA added across all substrates. Of particular interest, the gel-RTIL + TETA system is able to quickly reduce the overhead CEES vapor concentration to ≤10% of that of untreated sample for all of the contaminated substrate types. These results demonstrate these RTIL-based coatings, and especially the gel RTIL system containing amine, act as effective vapor barriers for mustard-type compounds.



CEES in Headspace of Treated Samples



As can be seen in Figure 4-3, all four RTIL coating formulations also significantly reduced the amount of liquid CEES contained within the substrates after treatment compared to the untreated samples (as determined by CHCl₃ extraction of soaked-in CEES from the treated samples). Glass was used as a non-porous control substrate in order to determine if wiping the coupon removed the surface CEES. As expected, less than 0.5% of the CEES applied to the glass substrates in each treatment was seen in the post-treatment coupons, indicating almost all surface CEES was indeed removed.

The wood sample was used to test a common building material with a macroporous structure. CEES immediately adsorbs into the wood substrate when applied. After 24 hours, the uncoated wood coupon released 30% of the CEES applied into the chloroform. The other 70% of the CEES applied probably reacted with the nitrogen compounds in the wood substrate. The decontaminating coating reduces the amount of unreacted CEES in the wood sample to 6% of CEES initially applied. The coating reduces CEES contamination by 5 times in the wood substrate. The rubber sample is similar to the material of tire rubber: a swellable, dense material. CEES will slowly adsorb into the rubber sample when applied. After 24 hours, the uncoated CEEScontaminated rubber sample released 90% (almost all) of the applied CEES. This almost complete extraction of CEES out of rubber indicates the chloroform desorption method works well. This also shows how untreated rubber is a potential long-term hazard, slowly releasing unreacted CWAs. However, when a RTIL coating is applied to the contaminated rubber coupon, CEES-contamination is reduced to 25% of applied CEES. Lastly, the painted coupon is used to mimic painted vehicles: demonstrating how this decontamination system will work on paint coatings. The uncoated CEEScontaminated paint coupon released 40% of the CEES applied after 24 hours. The other 60% of the applied CEES probably reacted irreversibly with the paint coating, similar to the wood coupon. When a decontamination coating is applied, less than 1.5% of the applied CEES remains in the sample. This is a greater than 20 times reduction in CEES contamination.

Again, the RTIL coatings containing the CEES-reactive TETA agent were the most effective for removing the applied CEES from within all of the test substrates

compared to the formulations without the reactive amine additive. However, the gelled RTIL + TETA coating achieved the best CEES depletion/decontamination results for the nonporous substrates (rubber and pained steel) whereas, the the ungelled (liquid) RTIL + TETA system was more effective in the case of wood, a very porous substrate. This can be rationalized by the fact that a more liquid-like medium is more able to penetrate a porous substrate and delivery the amine for reaction with the included CEES. Most impressive is the results from the painted steel substrates. An untreated paint sample will contain 40% of the CEES applied after 24 hours. But, the treated samples will contain less than 1.5% of the applied CEES; **a >95% reduction!** These results show the coating performs well in removing CEES from a porous substrate.



CEES Remaining in Substrate After Treatment

Figure 4-3: Ratio of CEES remaining in the substrate versus an untreated control after 22–24 h of treatment. Lower values are better, indicating that more CEES was decontaminated from the substrate into the coating.

In addition to 24-hour application study, a longer 96-hour application study of gelled RTIL + TETA was also performed on CEES-contaminated wood, rubber and painted steel substrates in order to determine the length of time needed for a single, static coating to deplete the CEES down to minimum levels. In all cases, the CEES vapor in the headspace over the contaminated sample slowly decreased every 24 hours in an exponentially decaying fashion. This is most likely due to the TETA chemically decontaminating (via nucleophilic attack on CEES²⁶) and reducing the total quantity of CEES in the sample and headspace above. The CEES extracted from the coupon also decreased every 24 hours in an exponential decaying manner (Figure 4-4). The CEES extracted from the painted steel sample decreased to 1% of the original applied CEES amount within 24 hours of application with the gelled RTIL + TETA coating. The wood substrate was decontaminated also quickly, and the CEES was reduced to 1% of the applied amount within 96 hours at ambient conditions. Finally, the CEES in the rubber substrate was reduced down to ca. 5% of the original applied amount within 96 hours.



CEES in Remaining in Substrate After Treatment

In summary, a new spreadable coating system based on a gelled RTIL containing an organic amine was prepared and evaluated as a containment and decontaminating coating for variety of common materials contacted by mustard-type agents When applied to a CEES-contaminated sample, this new reactive, non-volatile, gel coating has been shown to act as an effective CEES vapor barrier and immediately reduce the amount of CEES released in the overhead space above the sample. After the coating has been applied and removed, it was shown to be able remove most of the CEES from within macroporous samples (i.e., wood), from swellable dense samples (i.e., rubber), and from other coatings (i.e., painted steel). This new decontaminating barrier system is the first step in developing an easy-to-use product that could be used

Figure 4-4: Fraction of CEES remaining in substrate compared to original applied amount for a single static coating application, as a function of coating residence time. The rate at which the values approach zero indicate a faster decontamination rate.

by military and first-responders to treat mustard-agent contacted materials and equipment in the field.



4.4 Supporting Information

Figure 4-5: ppm of CEES vapor in the overhead of 5 CEES-contaminated rubber samples over a period of 96 hours. The decrease in CEES-vapor is probably due to a reaction with TETA in the gelled RTIL +TETA coating.

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Chapter 5

Two Component Ionic Liquid Polyurethane-Based Containment and Decontamination System for Blister Agent-Contacted Substrates

Abstract

Chemical warfare agents (CWAs) and toxic industrial compounds (TICs) pose a threat to military personnel and first-responder personnel. There are three current methods these people will use to mitigate and decontaminate a zone exposed to CWAs and/or TICs: (1) basic aqueous washes, (2) reactive adsorptive powders, and (3) heated forced air. Each of these methods have disadvantages, such as being non-portable, not feasible for application on vertical surfaces, unable to decontaminate porous or swellable materials, and/or requring a very long time for removal. Herein, we propose a new decontamination system that can be added to the current decontamination regime to fill in the gaps in hazard mitigation. This new system is composed of two parts, that when mixed, can be spread and quickly react to form a solid polymer network. The resulting solid film will immediately act as a barrier to reduce hazardous vapors and actively decontaminate and desorb the TICs from the substrate. This system is easily portable and can be applied quickly after a

spill. The decontaminating barrier has two parts that form a polyurethane system, (i.e., a polymer network formed by condensation reaction). In the first part of this combination system, there is a diol monomer, free room-temperature ionic liquid (RTIL), a step-growth polymerization catalyst, and reactive decontaminating component. The second part consists of a diisocyanate monomer, and free RTIL for solubility compatibility. The resulting curable coating has been tested using 2-chloroethyl ethyl sulfide (CEES, a sulfur mustard simulant) on 4 different substrates: glass, wood, rubber, and painted steel. The cured coating effectively acted as a barrier by reducing the overhead concentration of CEES vapor by a factor of 5 compared to uncoated substrates. The coating also exhibited good decontamination performance by desorbing 80% of the CEES out of substrates containing soaked-in CEES within 24 hours.

5.1 Introduction

The ability for first responder and military personnel to maintain a safe operational environment is their first responsibility when working in a hazardous situation. If the environment is unsafe a first-responder is trained to take life-saving measures for themselves, and then consider helping their partners, other victims, and property: in that order. A common, and unfortunate, situation can involve the unintentional or intentional spill of hazardous chemicals. Many protocols have been developed for the different classes of chemicals^{1,2,3,4,5}.
First responders should use a NIOSH-approved chemical, biological, radiological, nuclear (CBRN) self-contained breathing apparatus (SCBA) with a Level A protective suit when entering an area with an unknown contaminant or when entering an area where the concentration of the contaminant is unknown. For a hazardous gas or vapor release, personnel are evacuated to an open area upwind of the release. Then a protected first responder will enter the hot-zone and remove or mitigate the source of the gas release. Next, the area is quarantined and ventilated with industrial fans to remove any gas in stagnant areas. After many days of monitoring the decreasing concentration of the hazardous gas, the area is removed from guarantine when the concentration is in an acceptable range. For solid hazards, just the immediate area is evacuated. Then a CBRN-protected first responder will enter and evaluate the chemical hazard. The solid contaminant will be cleaned in a variety of methods including: bulk removal, decontaminating basic or aqueous washes, and/or soak up in an oil-based solution. While a danger, gaseous and solid hazardous chemicals are relatively straight-forward to mitigate and decontaminate.

The greatest complications arise from liquid hazardous chemicals. A liquid will flow into crack and crevices of the building and environment^{2,3}. A hazardous liquid can soak into porous and swellable substrates via absorption (i.e., chemical reaction) and adsorption (i.e., physical uptake) ^{6,7}. The liquid may have a low vapor pressure and continually release a hazardous vapor. The liquid may also be able to rapidly soak into protective garments. The current methods

to clean up a hazardous liquid involve aqueous washes, adsorbent powder, and heated forced-air^{2,3}.

Aqueous washes are one of the most common methods to clean up a hazardous liquid spill. Basic or acidic salts are dissolved in water and sprayed onto the contaminated zone^{8,9}. Then brushes are used to mix the water phase with the hazardous liquid to speed up the decontaminating reaction of the active component in the aqueous phase and the agent. This method is very inexpensive and works well for surface contaminants. However, there are many disadvantages to this system. The solution will quickly run off of vertical and slanted surfaces, possibly leaving un-decontaminated agent due to the short time available for reaction. The water system does not work well on porous materials. In porous materials, hazardous agents can soak into the pores and slowly leach out after the contaminant on the surface has been cleaned. Many materials and areas are not conducive to being submerged for days to remove the soaked-in agent. Lastly, many liquid toxic agents are immiscible with water, which yields a slow heterogeneous decontaminating reaction¹⁰. Surfactant can help mitigate this disadvantage but not completely.

Adsorbent powders are effective decontamination systems for large pools of hazardous liquids. They are commonly composed of reactive metal oxides (e.g., MgO, Al₂O₃, MnO) or adsorptive powders (e.g., starch, cellulose, CaCO₃). The metal oxides both adsorb and react to decontaminate many types of hazardous liquid materials, while the adsorptive powders only soak up the liquid.

The adsorptive powders are typically poured or placed onto the spill in an effort to turn liquid hazard into a solid hazard. This method works well for large bulk but cannot easily be applied to vertical surfaces. The adsorptive material may still release hazardous vapors until it can be properly disposed. This method will only partially desorb hazardous liquid from porous samples because the total contacted surface of a particle to another surface is low.

The last method to decontaminate a hazardous liquid spill is forced heated air. Large fans with heating coils, similar to the ones used to dry large floors, are set such that heated air is continuously blown through the contaminated zone⁴. There is an extreme hazard from the exhaust and the entire area must be under quarantine until the process is complete. The mechanism for this method is simply speeding up natural processes by increasing air-flow and increasing temperature. Many hazardous liquids are reactive enough to decompose in atmospheric oxygen. The increased temperature and fresh supply of oxygen increase the decomposition reaction rate. The increased air-flow increases the rate of evaporation of the contaminant. This method will eventually work for all types of hazards, even in porous or swellable substrates; however, this process may take weeks or months to complete^{11,12,13}.

Each of these methods has advantages and disadvantages and each is usually used in series to clean up a large spill of hazardous liquids. First, the area is evacuated and first responder personnel are equipped and assess the situation. Then adsorptive powders are applied to soak up the bulk of the spill.

After the soaked powders have been removed in airtight containers, an aqueous wash is scrubbed in the area to remove any contamination left over. Finally, the area is dried by heated fans that also remove any residual contaminant. The use of all three decontamination methods works well for many situations, but all three methods have drawbacks with regards to vertical surfaces, soaked-in materials, rapid containment and portability. There exists a need for an additional option that can be applied quickly, can immediately reduce the amount of hazardous vapor released, can desorb and decontaminate hazardous liquid out of porous and swellable substrates, and can be applied to a wide variety of materials and locations.

Herein, we present a new decontamination system for mustard-type CWAs. This is a two-part system that when mixed will quickly form a solid coating. The coating has a reactive component that will chemically react with the chemical hazard and decontaminate the area. This reaction creates a negative concentration gradient which will drive the hazard out of porous and swellable substrates. The coating has an entrained room-temperature ionic liquid (RTIL) that will provide an ionic environment that is conducive for many reactions with high diffusivity for a faster rate of decontamination^{14,15}. RTILs are liquid salts at ambient temperature that have negligible vapor pressure, a feature that can depress the vapor pressure of the liquid hazard and let the coating remain effective as a barrier indefinitely¹⁶. The entire system is held in place with a polymer network composed of ionic monomer. This two-component cross-linked polymer network is similar to polyurethane glues that have one highly reactive

diisocyanate in one solution and a multi-functional amine or alcohol in the other solution. The ionic polymer network is necessary to maintain a homogeneous material that retains all the free RTIL.

5.2 Experimental Methods

5.2.1 Materials

The coating system has 5 essential components. An alcoholfunctionalized imidazolium monomer is needed as a bifunctional step-growth monomer to form the chain of the condensation polymerization network. The diol-functionalized RTIL 1 (Figure 3.1) was selected because it was easily synthesized as described in literature¹⁷. Other alcohol-functionalized RTILs may work as well or better but would require more complex synthesis. The second monomer of the condensation polymerization network was a multi-isocyanate functionalized organic molecule. The diol-functionalized RTIL and diisocyanate monomers will react in a fashion similar to polyurethane chemistry. Toluene diisocyanate (TDI) was selected because it is an inexpensive and common organic compound already used in industrial polyurethane synthesis A 'liquid' component is needed to increase diffusion, reaction rate, adsorption rate and chemical compatibility between monomers. The alkyl-functionalized RTIL 2 was selected for this role because it has been shown to readily dissolve all components of the system and is easily synthesized as described in literature¹⁸.

The free RTIL **2** is entrained in the polymer network by Coulumbic interactions with the cationic charges from the ionic polymer repeat units. Without these strong attractive ion-ion interactions, the free RTIL **2** will slowly leach out of the network, as observed when mixed with a non-charged polymer network. Because diisocyanates arehighly reactive and difficult to synthesize, we determined it easier and safer attach the alcohol functional groups to an imidazolium unit and purchase TDI without further synthesis or purification.



Figure 5-1: Chemical structures of RTIL A, RTIL 2, TDI, DABCO, CEES and TETA.

Triethyltetraamine (TETA) was selected as the reactive decontaminating agent for mustard-type CWAs and the polymer-network cross-linker. 2-Chloroethyl ethyl sulfide (CEES, a mustard agent simulant is known to react with the amine groups in guanine and will also react with TETA in an RTIL environment. A stronger base/nucleophile could be used to greater effect, but TETA was selected because as a relatively weak base it would have reduced reactivity towards substrates and skin. TETA is also reactive with the TDI monomer and will function as a cross-linker in the condensation polymerization. Finally, TETA is also an inexpensive, commercially available and familiar industrial compound. The ratio of the two step-growth monomers (i.e. **1** and TDI) and the cross-linker (i.e. TETA) was determined by polymer network theory for the minimum conversion required to form a gel network. Simply stated, the degree of conversion to reach the gel point is minimized when the number of moles of the two reactive groups in a cross-linking step-growth polymerizationare equal (i.e., number of isocyanate groups equals the sum of alcohol and amine groups).[ref?]

The isocyanate with alcohol reaction is normally violently exothermic and very rapid, however, in an ionic environment with these monomers, the reaction is much slower. The addition of a catalyst is necessary to reduce the time to gelation from hours to minutes. Triethylenediamine (DABCO) is a common industrial dual-site catalyst that activates the alcohol for reaction with an isocyanate via hydrogen-bonding.[ref?] One disadvantage of the alcohol monomer, **1**, is the two alcohols groups can hydrogen-bond to form a 5-

membered ring. One obvious improvement for this system is to synthesize an imidazolium monomer with separated alcohol groups,. Such a diol-RTIL monomer may reduce the reaction time from minutes to seconds. Both RTILs were determined pure via NMR analsyis. TDI, TETA, CEES, and DABCO) were all purchased from Sigma-Aldrich and used as received.

The sample coupons were prepared from materials purchased from a local hardware store (Figure 5-2). The glass coupon was a 1 inch mirror. The rubber coupon was a 24-mm diameter disc punched out of a truck tire tube. The wood coupon is a 1/8-inch thick disc cut from a 15/16-inch diameter oak dowel. The painted steel coupons were prepared by cutting out 20-mm octagons from a sheet of 316 stainlesssteel. The surface of the steel was roughed with 300 grit sandpaper before painting. Three coats of Rust-Oleum Specialty Camouflage spray paint was applied with time to dry between each coat. This particular paint has a non-reflective finish similar to 'egg-shell' latex paints.



Figure 5-2: Four coupons used for barrier decontamination testing.

5.2.2 Sample Preparation and Barrier Measurements

The two parts of the coating were prepared in separate vials to prevent premature polymerization. Part 1, contained a mixture with a ratio of 1 mol RTIL **1**: 0.5 mol RTIL **2**: 0.05 mol TETA: 0.02 mol DABCO. Part 2 contained a mixture with a ratio of 1 mol TDI: 0.5 mol RTIL **1**. The two parts were mixed such that the final polymerization coating had 1 mol RTIL **1** : 1.1 mol TDI. This ratio creates a 1:1 ratio of alcohol+amine reactive groups to isocyanate reactive groups, which from polymer network theory will create a cross-linked network with the lowest conversion.



Figure 5-3: Testing materials used for barrier and decontamination testing method.

The coupons were placed in a small aluminum cup and left at ambient conditions overnight. Next, 20 μ L of CEES was pipetted onto the center of the coupon and allowed to soak into the coupon for 5 minutes. During this time, the two-part coating mixture was combined such that there was a total of 1 mL of coating solution and vortexed for 5 seconds to mix. The solution became slight viscous. Next, the polyurethane coating was poured onto the center of the CEES-contaminated coupon. The coating hardened in 2 minutes after application under ambient conditions. Finally, the aluminum cup with coated contaminated-coupon was placed in an EPA soil sample jar and sealed with a septum top.

The samples were left undisturbed for 24 hours before gas chromatography-mass spectrometry (GC-MS) analysis was performed on the head space above the coated coupon. This is a direct measurement of the quantity of CEES vapor in the headspace of the sample and measures the barrier effectiveness of the coating. Next, the coating was wiped off with a Kimwipe until the coupon was dry to the touch. The CEES-soaked coupon was then placed in 10 mL of chloroform (a solvent non-reactive to CEES). Any CEES in the coupon was allowed to desorb into the chloroform for 24 hours. Again, GC-MS analysis was used to measure the amount of CEES extracted into the chloroform, so as to determine the amount of CEES remaining in the coupon. This is a direct measurement of the decontamination capabilities of the coating.

5.3 Results and Discussions

The RTIL-based decontaminating barrier performed well as both a barrier and as a decontaminating film. The coating reduced the amount of CEES vapor in the overhead sample after 24 hours by 13–28% for all coupons as compared to untreated CEES-contaminated coupons (Figure 3.3). The coating also decontaminated and leeched the CEES out of the coupons, reducing the amount of CEES in the coupons by 12-20% as compared to untreated CEEScontaminated coupons (Figure 3.4).

Figure 5-4 shows the concentration of CEES vapor in ppm above the sample in the headspace of the EPA sample jar. CEES on the coupon has moved through the barrier film and volatilized into the headspace of the jar. This measurement is a direct coorelation to how well the coating performs as a barrier. A lower concentration of CEES vapor in the headspace is considered better.

As shown, the coatings reduced the CEES vapor to a little over 250 ppm. The glass control had 2035 ppm of CEES in the headspace, and a coating reduced the CEES vapor to 250 ppm, a 8.2 times reduction. The wood control coupon had CEES-vapor of 2015 ppm. A coating on the wood coupon reduced the concentration of CEES vapor by a factor of 80, down to an absolute concentration of 25 ppm. The huge decrease in CEES vapor seen in the wood coupon but not other substrates is probably due to the macro porous nature of the wood. When CEES is applied to the wood coupon, within seconds all of the

contaminant is sorbed into the substrate. The coating applied on top does not mix with the CEES. This indicates that a two coating method would greatly improve the barrier effectiveness of the coating. The first application is to contain and entrain the CEES in the polymer matrix, and the second coating to prevent CEES vapors from escaping. The rubber control sample had a lower concentration of CEES vapor in the headspace, most likely from the CEES adsorbing and soaking into the rubber polymer. The rubber control had 510 ppm of CEES vapor and the coating reduced that by 2.4 times to 210 ppm. Finally, the painted steel coupon had 1720 ppm of CEES vapor above the control coupon, and the coating reduced the CEES vapor by 9 times to 191 ppm. The CEES vapor in the headspace of barrier protected coupons reduced to ~220 ppm for all coupons. This may be due to a partition equilibrium between the gas volume and the coating volume. This theory merits further studies which could provide data for an improved barrier mechanism.





The amount of CEES remaining in the coupon was greatly reduced by the 24 hour application of the RTIL-based decontaminating barrier coating for all porous or swellable coupons (Figure 5-4). Since glass is a non-porous material, it was used as a control substrate for the coating removal process. All of the CEES is removed from the surface of the coupon when wiped with a Kim-Wipe for both the control and treated substrates. Since glass is non-porous, all CEES should be removed by this wiping process, and indeed we see only a trace of CEES remaining on both the coated and uncoated sample, 0.2% of the initial 20

μL of CEES applied. The untreated wood sample released 16% of the initial CEES applied, the other 84% probably reacted with the wood itself. If a coating is applied to a CEES-contaminated wood sample the amount of CEES remaining is reduced to 9%. The rubber coupon released 74%, almost all of the CEES applied. The CEES readily adsorbs into the dense rubber material, and remains unreacted. This demonstrates the hazard that rubber can pose, as CEES slowly leaches back out of the rubber despite removal of all surface CEES. However, if the coating is applied for 24 hours, the remaining CEES is only 31% of the applied CEES, a 2.5 times reduction. With the paint coupon, an untreated coupon will release 30% of the CEES applied. The other 70% of the applied CEES is likely reacting with the paint coating. But, if a coating is applied for 24 hours, the CEES in the paint is reduced to 6% of the applied CEES. This 5 times reduction indicates the coating will perform excellently on painted substrates.

These results indicate that this new reactive polymer-RTIL gel system performs as a better barrier material and worse decontamination material compared to the physically gelled LMOG-RTIL systems discussed in Chapter 4. Here we see evidence of a trend between solid-like and liquid-like properties. The physical gels are more liquid-like and perform better as a decontamination material, likely due to the increase in diffusion and reactivity. But, the polymeric gels are more solid-like and perform better as a barrier material, again likely to the *decrease* in diffusion preventing CEES vapor from escaping. The performance of the gel material can be tailored along the continuum of liquid and

solid properties by adjusting the ratio of its components to find optimum bulk properties.



Figure 5-5: Fraction of CEES remaining in treated and untreated coupons after the RTIL-based decontaminating barrier material has been applied for 24 hours and physically removed.

In conclusion, a new type of reactive poly(RTIL)/RTIL-based

decontaminating barrier coatings has been shown to effectively reduce the

amount of CEES vapor released from contaminated substrates of glass, wood,

rubber, and painted steel. These coatings have also been proven effective in

desorbing and decontaminating CEES from porous substrates (i.e., wood),

swellable substrates (i.e., rubber) and other coatings (i.e., paint). The new coating system is composed of two parts that can be safely stored until use. When mixed these two components are easily applied and quickly harden into a stiff polymer network. This new decontaminating barrier system is another step in developing an easy-to-use product that could be used by military and first-responders to treat mustard-agent-contacted materials and equipment in the field.

Future developments can include incorporation of a pH-sensitive dye molecule that will change color in the presence of acidic compound such as mustard agents. Also the reaction rate of polyurethane usually requires retardants or cooling baths because the reaction is fast and exothermic. Oddly, in an RTIL environment the reaction is slower (as observed between TDI and triethanolamine). The reaction is likely further depressed by the diol-RTIL hydrogen bonding with itself to form a stable 5-membered ring. The synthesis of a alcohol functionalized imidazolium with an alcohol on each nitrogen and spaced by 3-4 carbons would alleviate both problems. Hopefully, this new RTIL will react, with the help of a catalyst, fast enough to form a gel network in seconds. With a fast reacting system, the two part system can be used in a dual sprayer configuration for easy application.

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Chapter 6

Conclusions and Recommendations

This work focused on the application and development of gelled roomtemperature ionic liquid (RTILs) soft-solid materials and their uses. The two applications explored were supported membranes for light gas separation and decontaminating barrier coatings for chemical warfare agents (CWAs).

Proof of concept studies for supported gelled membranes demonstrated that low molecular-weight organic gelators (LMOGs) can be used in a porous membrane support to separate CO₂ from other light gases. This initial study on gelators used commercially available 12-hydroxy stearic acid to gel hexylmethylimidzolium bis(trifluoromethylsulfunyl)imide (hmim/Tf₂N). When compared to neat hmim/Tf₂N supported liquid membranes the gelled version had 10% less permeability of all gases and the same permeability selectivity. As expected the entrained RTIL had a lower diffusion and hence lower permeability but since the selective media was 98% RTIL the solubility selectivity remained the same. The gel was also shown to have a higher burst pressure, (i.e., the trans-membrane pressure at which the gel or liquid is expelled out of the membrane support) than the neat RTIL supported membrane. The 12-hydroxy stearic acid based gel worked well in proving the feasibility of gel membrane

systems, however, this LMOG has sever limitations of a maximum LMOG loading of 1.5 wt% before phase separation, a 68 °C maximum temperature of gelation and is only able to gel imidazolium RTIL that have long alkyl chains such as $hmim/Tf_2N$.

The next gel system examined was developed in response to the drawbacks of the first RTIL gel system. The aspartame-derived LMOG was synthesized from literature and was already known to gel many classes of RTILs (e.g., ammonium, phosphonium, imidazolium, pyridinium). A new synthesis method was developed to handle a much larger batch size (10g) of aspartamebased LMOG. This LMOG was able to gel all imidazolium-based RTILs (i.e., hmim/Tf₂N, emim/Tf₂N, emim/triflate, emim/DCA, diol/Tf₂N) used in this study. The temperature of gelation could be controlled between 30 °C and 160°C by loading an increasing concentration of the LMOG. These RTIL gels were tested for gas transport properties in a custom gas permeation apparatus. All the gas transport properties of the supported gel RTIL membranes were similar but statistically different to the supported neat RTIL membranes. In general, the viscosity of the neat RTIL had the most significant effect on permeability of CO_2 with the Tf_2N anion and emim cation performing the best. The most selective membranes were those with an emim cation, probably due to the higher molar concentration of dipole interaction from the RTIL. All of the membranes had increased permeability and decreased selectivity when heated from 20 °C to 70 °C. The best performing candidates (i.e., emim/Tf₂N and emim/DCA) were sent to Los Alamos National Laboratories (LANL) for membrane coating testing.

LANL collaborators, used the gelled RTIL in a pressure spray coater to layer a finely atomized membrane onto a porous support. Their feedback indicated the gel membrane, while mechanically stable enough to not flow under gravity, was not stable enough to be handled. They requested a more stable gelator system that could withstand handling of coated fibers. The next steps for this project are to develop a more robust gelator, possibly using a repeating amide moiety, and the high temperature stability of the RTIL to form a robust gel.

The second application for gel RTIL systems was a decontaminating barrier film for mitigation and desorption of CWAs in porous substrates. The proof-of-concept system used the aspartame-based LMOG and hmim-Tf₂N on glass, wood, rubber and painted steel substrates contaminated with chloroethylethylsulfide (CEES). Hmim/Tf₂N was determined to be a good solvent because it is miscible with CEES and the aspartame-based gelator was determined to be an excellent LMOG because it could gel pure hmim/Tf₂N to pure CEES. The coating consisted of hmim/Tf₂N (for liquid-like diffusion), aspartame-based LMOG (for solid-like stability), and triethyltetraamine (TETA) for reactive decontamination. A new testing method was developed from the military Source Document 2007 to provide a quantitative assay of barrier and desorption effectiveness of the coating. The film was shown to reduce the CEES vapor in the headspace above the coated sample by at least 5 times for every sample. The coating was also able to desorb at least 80% of the soaked-in CEES from the coupons, and in the case of the painted coupon it was able to desorb >98% of the applied CEES.

An alternate coating technology was also tested using a two part system based on polyurethane chemistry. The first part has 4 components: diol/Tf₂N (monomer), hmim/Tf₂N (for liquid diffusion), catalyst and TETA (reactive crosslinker). The second part has 2 components: toluene diisocyanate (TDI) and hmim/Tf₂N (solubility compatibility). When the two parts are mixed the isocyanate, alcohol and amine groups react to form a viscous liquid initially, and in about 4 minutes form a gel network. After 2 hours the barrier is stiff and very mechanically strong. This new decontaminating barrier was tested via the same method used before on the same glass, wood, rubber and painted steel coupons. The coating performed well as a barrier, and reduced the ppm of CEES vapor by 5 times to ~225 ppm. The coating also worked well to desorb the CEES out of the porous substrates by removing ~90% of the soaked-in CEES from the wood and rubber coupons and an impressive 98% from the painted steel. Future development of this system include adding a pH type color indicator to signal the presence of basic CWAs and to synthesize a new RTIL with alcohol groups further away from the imidazolium head-group. This new RTIL will most likely react faster with the isocyanate and be capable of being delivered via a dual spray system for easy application.

In general, there are many more RTIL chemistries and different gelled RTIL systems for a variety of applications. The single most important aspect of RTIL gels is their negligible vapor pressure. All other organic gels, even high boiling point temperature solvents, will slowly degrade and evaporate. Any application involving high diffusivity soft solids would benefit from a solvent that will effectively remain indefinitely. This unique material merits further study for different commercial applications.

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Appendix A

Organic Molecular Cages

A.1 Summary

Three-dimensional (3-D) shape-persistent cage compounds have attracted considerable attention due to their important applications as sensors, nanoreactors, delivery vehicles, gas storage and separation materials. A series of novel organic cage compounds **1-4** were synthesized through a dynamic covalent chemistry approach (imine condensation reaction). Covalently crosslinked cage framework **5** was obtained through the *cage-to-framework* strategy via the Sonogashira coupling of cage **4** with the 1,4-diethynylbenzene linker molecule. Cage compounds **1-4** and framework **5** exhibited exceptional high ideal selectivity (36/1-138/1) in adsorption of CO₂ over N₂ under the standard temperature and pressure (STP, 20 °C, 1 bar). Gas adsorption studies indicate that the high selectivity is provided not only by the amino group density (mol/g), but also by the intrinsic pore size of the cage structure (distance between the top and bottom panels), which can be tuned by judiciously choosing building blocks of different size.



Figure A1-1: Chemical structure of organic cages 1-4.

A.2 Low-Pressure Gas Adsorption Measurements

Ideal gas adsorption measurements were performed using a custom-built stainless steel gas sorption apparatus specifically designed for small (100-200 mg) samples; containing a PX303-015A5V pressure transducer from Omega Engineering Corporation, a 47mm membrane holder catalogue number XX4404700 from Millipore Corporation, and Swagelok tube fittings and valves. The data was acquired by a ADAC DaqBoard Pci5500MF from Abu Dhabi Airports Company and processed with Labview 7 Express from National Instruments. All samples were placed under vacuum between tests to remove all adsorbed gases, and kept at 20 °C for both adsorption testing and off-gassing

phases. CO_2 and N_2 were used unaltered from Airgas, Inc. in single gas experiments for ideal gas adsorption, no mixed gas studies were performed.

A.3 Gas Adsorption Results

The ideal selectivity in CO_2/N_2 adsorption was measured at 20 °C by using a specifically designed instrument (Figure A-2) for low-pressure gas adsorption with a small amount of samples. Cage samples for the gas adsorption study were prepared by direct removal of the solvent under high vacuum to give mostly amorphous materials. All the cage molecules and the cage framework showed excellent selectivities (36/1-138/1, Figure A-3, Table A-1) in adsorption of CO₂ over N₂, with cage **4** showing the highest selectivity (138/1) which is significantly higher than previously observed for anthracene-based molecular cage 2. These ideal selectivities are the highest reported to date under STP conditions for discrete organic molecules. Cage 4 cross-linked with diethynylbenzene showed an adsorption selectivity of 65/1, which is lower than the corresponding noncrosslinked cage 4. The adsorption capacity of CO₂ (mol %) was found to be similar for all the cages (1-4) with small variations (0.31-0.37 mol/mol). The calculated CO₂ weight percentages of these cages are 0.42 % to 1.02 %, which is comparable to other previously reported organic solids (e.g. 0.5 wt % for 1,2dimethoxy-p-tert-butylcalix[4]dihydroxyquinone at 298 K, 640 torr, or 0.5 mol/mol for tris-o-phenylenedioxycyclotriphophazene at 298 K, 640 torr). A few other organic cages have been reported to have higher adsorption capacities of CO₂ (e.g. 11 wt % for noria, at 298 K, 1 bar; 9.4 wt % for salicylbisimine cage at 273 K, 1 bar, and 13.2 wt % for imine-linked tetrahedral cage at 275 K, 1.12 bar), albeit still relatively low compared to MOFs and COFs. The CO₂ uptake of a non-cage control is 0.18 mol/mol, which is about two times less than that of other cage compounds (1-4). However, it should be noted the non-cage structure has half the amino groups as compounds (1-4). Cross-linked cage framework 4 shows two times higher CO₂ adsorption capacity than that of other cage materials presented here. In all cases, under the STP condition the N₂ uptake is extremely low, and varies substantially (0.0024-0.0093 mol/mol) depending on the cage dimensions. Similar to the case of CO₂ adsorption, the cage framework 14 showed the largest N₂ uptake (0.0094 mol/mol).



Figure A-2: Gas adsorption apparatus for small (0.1g) powder samples.



Figure A-3. The adsorption isotherms of CO_2 and N_2 for cages **1-4**, **2'**, half-cage control and crosslinked **4**..

l able A	-1. Gas	adsorption	capacity	and	selectivity	of	cages	1-4,	2′,	half-cage
control a	nd cross	slinked 4								

	CO ₂ adsorption			N ₂ adsorption		Pore	N ₂	Ideal
Compound	(1 bar, 20 °C)			(1 bar, 20 °C)		size	Interaction	selectivity
	Wt %	cc/g	mol/mol	cc/g	mol/mol	(Å)	energy	CO ₂ /N ₂
							(Kcal/mol)	
1	0.61	3.32	0.31	0.033	0.0031	6.03	-2.3	100
2	0.80	4.35	0.36	0.065	0.0053	6.27	-0.3	67
3	1.02	5.58	0.33	0.157	0.0092	6.72	-1.0	36
4	0.45	2.27	0.33	0.016	0.0024	5.27	-0.2	138
2'	0.84	4.56	0.37	0.117	0.0094	7.32	4.5	39
13	0.72	3.95	0.18	0.104	0.0048	-		38
14	0.84	4.27	0.61	0.065	0.0094	-		66