CO_2-Triggered Switchable Solvent Systems and Their Applications

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Abstract

This thesis begins with the introduction of solvents and their classification. The two solvent system studied here are switchable polarity solvents (SPS). A switchable polarity solvent is a liquid where its polarity can change between two forms by a trigger. These two solvent systems have several similar characteristics. First, they both require CO_2 as the switching agent, which can be switched back by its removal with heat or N_2. The first project is the continuation of previous work with using an amidine and alcohol mixtures as a switchable polarity solvent. The second project was the development of a new switchable polarity solvent that is based on the reaction of a secondary amine with CO_2. Both solvent systems are fully characterized by many analytical techniques and examples of applications in chemical reaction and separation are outlined.

The final project involves using these solvent systems, among others, in the separation of soybean oil. The aim was to use SPS technology to extract soybean oil from the bean flakes, and then separate the oil from the extracting solvent.

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List of Abbreviations

Abbreviation	**Meaning**
VOCs	Volatile organic compounds
E factor	Environmental factor
EPD	Electron pair donator
EPA	Electron pair acceptor
NR	Nile Red
DBU	(1,8-diazobicyclo-[5.4.0]-undec-7-ene)
SPS	Switchable polarity solvent
ROH	Alcohol
HexOH	n-hexanol
t-BuOH	t-butanol
n-PrOH	n-propanol
$[DBUH]^+$	DBU cation
$[OCO_2R]^-$	Alkyl carbonate anion
MeOH	Methanol
EtOH	Ethanol
$E_T(30)$	Reichardt's dye
GXL	Gas expanded liquids
M_n	Molecular number
M_w	Molecular weight
PDI	Polydispersity index
DIMCARB	Dimethylammonium dimethylcarbamate
NHBuEt	N-ethyl-N-butylamine
NHBzMe	N-benzyl-N-methylamine
$NHPr_2$	Dipropylamine
NHBuMe	N-butyl-N-methylamine
$[NH_2R'R'']^+[Cl]^-$	HCl salts of the corresponding secondary amine
FTIR	Fourier Transform Infrared Radiation
DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
Cr(salen)Cl	N,N'-bis(3,5-di-ter-butylsalicyliden)-1,2-ethylenediimine
$[PPN]^+[N_3]^-$	bis(triphenylphosphoryl)idine
UCST	Upper critical solution temperature
Et_3N	Triethylamine
IR	Integration ratio
Wt. %	Weight percent

Chapter 1: Introduction to Solvents

1.1 Solvents in Green Chemistry

1.1.1 Solvent use and the 12 principles of green chemistry

Solvent use is possibly the most important factor in synthetic chemistry because of its volume. We can already see how this solvent issue can potentially be problematic when we think of the waste and money involved in cleaning up or disposing the solvents after the work is done.

As new environmental restrictions and cost cutting issues are becoming increasingly important to companies, they must strive to reduce costs and follow the environmental guidelines set by governing bodies. Furthermore, being an environmentally friendly corporation can result in better business appeal. More and more companies are taking big measures to meet to these demands. One area of cost cutting is to reduce the total amounts of solvents used. As outlined by Anastas and Warner,[1] reduced solvent usage is one of the twelve principles of green chemistry (**Table 1.1**).

Table 1.1 The twelve principles of green chemistry.[1]

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

The 5th principle considers solvent as an auxiliary substance, meaning solvent only plays a supporting role in the synthesis of a product. Despite the fact that solvent is secondary, the quantities used are so large that its waste production is substantial. Not all solvents are created equal, some are more toxic than others, and some can cause severe environmental damage. For example, halogenated solvents (ie: chloroform, perchloroethylene, carbon tetrachloride, and methylene chloride) are all possible carcinogens. Other solvents such as hexanes or volatile organic compounds (VOCs) can have great effects on smog generation.[1]

It is vital for chemists to make careful choices when choosing solvents for their work. The use of a less toxic, benign, and recyclable solvent will reduce or eliminate risks and environmental damages.

1.1.2 E-factor and green chemistry

It has been over a decade since the concept of E Factor was first introduced by Roger Sheldon.[2] E(nvironmental) factor is a simple mathematical equation used to compare the amount of waste generated to produce a chemical product, (kg waste/kg product). **Table 1.2** outlines some E factors for different chemical industries.

Table 1.2 E factors for chemicals in various industries.[3]

Industry	Weight of Product	E Factor
Oil refining	10^6-10^8	<0.1
Bulk chemicals	10^4-10^6	<1-5
Fine chemicals	10^2-10^4	5-50
Pharmaceuticals	10-10^3	25-100

It can be understood how the fine chemicals and pharmaceutical industries exhibit such a large E factor. The processes in these two industries usually take many steps and require additional steps that involve washing and purifying their target compounds or intermediates. It should be noted that the E factors for the pharmaceutical industry could be actually higher if you take into account the E factor of their drug precursors. It has been proposed that up to 85 % of the waste generated in the pharmaceutical industry arises from solvent use.[4] This number is extraordinarily high, but a pharmaceutical process has many steps, where each step can require many different solvents for washing, extracting and removal of compounds and wastes. Therefore, one area for major improvement for this industry is the way they utilize their solvents. Many companies have made great improvements in their choice of solvents and have reduced the volume of solvents to reduce the E factor. For example, the solvent waste from Pfizer's synthesis of Sildenafil (Viagra©) went from 1,700 L/kg down to only 7 L/kg.[5] They reorganized their synthetic route and moved some strategic reactions to earlier steps, they used expensive reagents that lead to cleaner reactions, and were also able use one solvent for three different steps. All these strategies and reductions ultimately reduced the E factor of Sildenafil to 6.

1.1.3 Classification of solvents

There are many different solvents being used by many industrial processes, which makes it a non-trivial task to classify them. The most common way to classify solvent is by their physical and chemical properties.[6] There are three major classes of solvents; molecular liquids, ionic liquids and metals.

The majority of solvents fall in the molecular class, which is further divided into other categories.[7] The categories and descriptions of the solvents under this class are listed below.

Inert/low polarity: an unreactive solvent that has zero or low dipole moment, also has low polarisability. Examples are hydrocarbons and fluorocarbons.[6]

Inert-polarisable: solvents that are aromatics or polyhalogenated hydrocarbons. Examples are benzene and tetrachloromethane.[6]

Protogenic: solvents with hydrogen bond donating capability. An examples is trichloromethane.[6]

Protophilic: solvents with hydrogen bond accepting capability. Examples are tertiary amines.[6]

Dipolar-aprotic: neither protogenic nor a protophilic, but has substantial dipole moments. Examples are DMF and acetonitrile.[6]

An overlapping category is electron-pair donors (EPD), which means the solvent is composed of molecules with a free pair of electron capable of exhibiting hydrogen bonding, such solvents are ketones, ethers and nitriles.[6] Sulphur dioxide is categorized as electron-pair acceptor (EPA), which can act to accept electrons for hydrogen bonding.

Polarity is another way to classify solvents. A solvent can range from non-polar to extremely polar, such as hexane and water, respectively. Polar solvents are used to dissolve polar solutes, and similarly, a non-polar solute is soluble in a non-polar solvent, giving the traditional saying "like dissolves like" (**Figure 1.1**). One way to measure the polarity of a solvent is to look at its dielectric constant, which is the property of an electrical insulating material equal to the ratio of the capacitance of a capacitor filled with the given material to the capacitance of an identical capacitor in a vacuum without the dielectric material.[8] Polar solvents, such as water, tend to have a high dielectric constant, while non-polar solvents, such as hexane, have a low dielectric constant.

Another way of quantifying solvent polarity is to look at its Hildebrand's parameter, which is the measurement of the cohesion of a solvent, the energy required to create a cavity in the solvent.[9] If two solvents have similar Hildebrand parameters, then it tells us how these two solvents will behave when mixed together (**Figure 1.1)**. For example, water and 1,2-ethanediol are totally miscible with each other, while water and n-heptane are immiscible (biphasic) at certain portions. A mixture of water and 2-butanone shows mild miscibility, while one of water and ethyl acetate has little miscibility.

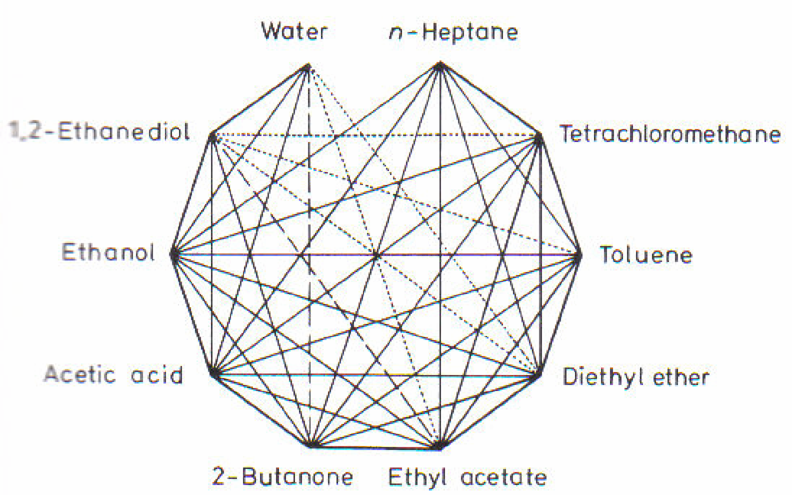


Figure 1.1 Miscibility chart for organic solvents. Solid lines indicate miscibility at all portions; dashed lines indicate limited miscibility; dotted lines indicate little miscibility; no line indicate immiscibility.[10]

1.1.4 Solvent recovery strategies

The reduction of wastes generated from solvent use can be achieved by recycling the solvent. In his book about solvent recovery, Ian Smallwood gave many strategies for recovering solvents for many chemical processes.[14] For example, some separation methods to remove solvents from water include extraction, membrane separation, air stripping, salting out, and distillation.[14]

One advantage of solvent recovery is to reuse it for other processes. This helps alleviate the costs of buying new solvents.[14] There are cases where the recycling of the solvent is not applicable, and the only method of clean up is through incineration. This is seen in the cleaning of ground water contaminated with many different solvents.[14] After the solvents are removed, they are incinerated rather than recycled for reuse.

1.1.5 Solvation

The term solvation means the encapsulation of a dissolved molecule or ion (solute) within a shell of solvent molecules. What exactly happens when a solute dissolves in a solvent? How does the dissolution change the molecular structure of both species? What are the interactions when we have dissolution or insoluble solute? To answer these questions, refer to **Figure 1.2** below.

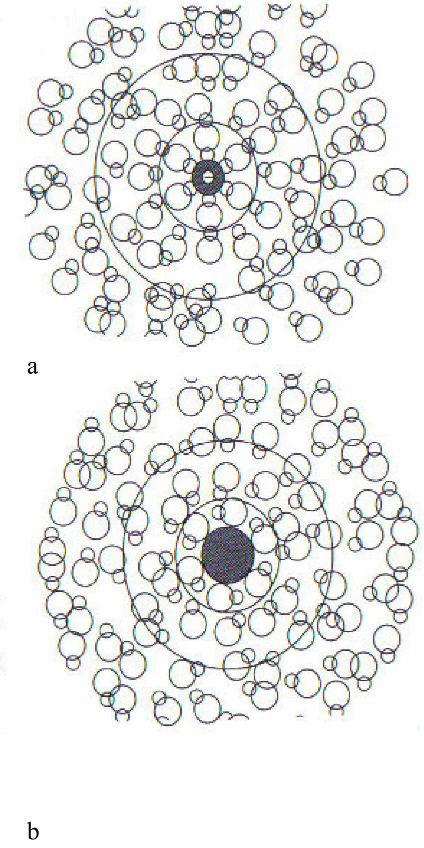


Figure 1.2 a) The interaction between a charged solute in a polar solvent; b) the interaction between a non-polar solute and a polar solvent.[6]

Let us look at the first case (**Figure 1.2a**), where a charged solute is dissolved in a polar solvent (a simple example would be NaCl dissolved in water.) The salt ions are very dilute compared to the solvent, so we can assume that the interaction between salt ions is negligible,[6] while the interaction between the solvent and ions is dominant. The region surrounding the solvated solute where the solvent molecules exhibit an ordered alignment is called the cybotactic region. More specifically, the coordination sphere of the ion is the area in which the solvent is strongly interacting with the ion. As we move further from the ion center, the solvent molecules become more disordered because these outer molecules feel weaker interactive forces from the ion, and making the solvent orientation more randomized. In such a case of dissolution, the entropy of the solution is lower within the cybotatic region, while the outer regions have higher entropy.[6]

If we look at the second case (**Figure 1.2b**), where a non-polar solute is in a polar solvent, such a phenomenon can be called the hydrophobic effect.[6] We can imagine this case to be an oil solute in a water solvent. The non-polar oil has favourable interactions with the polar water. To minimize the energy of this system, the water molecules interact with each other, and create a cavity where the oil molecule can be stored. Although there is no inner coordination sphere for this case, the water molecules encapsulating the oil do exhibit some form of order, while outside this encapsulating layer, the water molecules are randomly oriented. In such a case, the enthalpy and entropy of the system are decreased.

1.1.6 Solvatochromism and solvent polarity

The solvents studied in this thesis are unique in that they can change their polarity by adding a triggering agent. We saw that they have effectively increased in their polarity with the use of a solvatochromic dye. Before we go any further, we must first become familiarized on how these dyes can be used to quantify solvent polarity. The term “solvent polarity” was defined by Reichardt[11] to be the solvation power of a solvent including all molecular interactions between the solute and solvent. Dyes used to quantify the solvents are called solvatochromic dyes. The term “solvatochromism” describes a phenomenon in which the UV/Visible spectrum of a compound is altered by the surrounding solvent.[12] The change can include such things as absorption intensity, absorption shape and intensity maxima of the spectra. An explanation of how these dyes work is shown in **Figure 1.3** below.

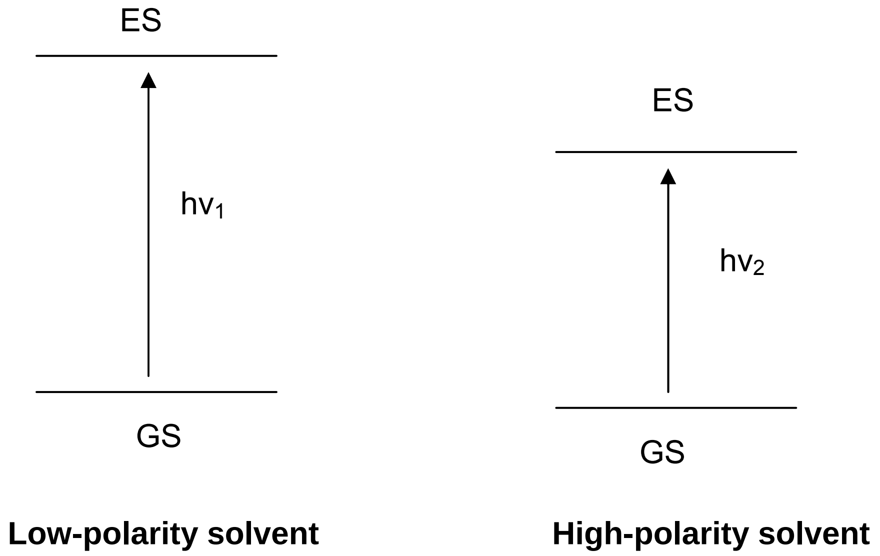


Figure 1.3 The excitation of a solvatochromic dye that leads to a $\pi \rightarrow \pi^*$ transition. GS: ground state, ES: excited state. The transition energy in a low-polarity solvent is larger than in a high-polarity solvent ($h\nu_1 > h\nu_2$) because the energy of the ES is lower in a high-polarity solvent (from favourable interaction of dye and solvent). Higher energy means shorter wavelength, meaning low-polarity solvents have smaller λ_{max}.

NR is classified as a negative solvatochromic dye, which means its λ_{max} is larger for more polar solvents. When a solvatochromic dye is excited by UV/Visible light, it becomes excited and exhibits a shift in its λ_{max}; this transition is known as $\pi \rightarrow \pi^*$ transition.[13] For most solvatochromic dyes, the excitation starts with the electron donating nitrogen atom, and because of the conjugated structure of the dye, this charge eventually ends up in the electron withdrawing group, the oxygen atom. The measurement of wavelength change is correlated to π^*, which measures the inductive, polarisability and interactions of the solvent and dye. This π^* (dipolarity/polarizability of the solvent)[9] is a solvatochromic scale developed by Kamlet and Taft, and is based on the transition average of seven solvatochromic dyes.[13] The π^* value for cyclohexane is 0.00, and the value for DMSO is 1.00. The reason why NR was chosen over π^* is because NR absorbs in the visible regions. The dyes used to calculate π^* absorb in the UV region, which exhibit overlaps with absorbed CO_2 used for the work.

1.1.7 Things that switch

Although the concept of a switchable solvent is quite new, the concept of switching things from one form to another has been established in the literature. For example, there has been work with switchable fluorinated solvents,[15] in which the application of 20-70 bar CO_2 induces the dissolution of fluorinated compounds. Crystals of these compounds can be collected upon the release of the CO_2 pressure. X-ray crystallographic studies on the following structures of $Rh_2(O_2CCF_2CF_2CF_3)_4(DMF)_2$, $Rh_2(O_2C(CF_2)_9F)_4(MeOH)_2$, $Cr(hfacac)_3$,and $P\{C_6H_3(3,5\text{-}CF_3)_2\}_3$ were done via this switching strategy.[15]

Another switchable solvent is piperylene sulfone (**Figure 1.4**). Piperylene sulfone is a liquid that has a melting point of -12 °C. The solvent is made via reaction of *trans*-1,3-pentadiene and sulphur dioxide. This solvent is a liquid and is reversible at 100 °C to the two gases, the solvent has many similar characteristics to the more common solvent DMSO.

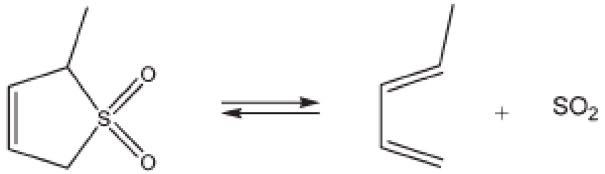


Figure 1.4 Piperylene sulfone switchable solvent.[16]

Other areas of switchability include surfactants, homogeneous catalysts and surfaces. A series of switchable surfactants have been studied by Liu et al.[17] where the surfactants can be switched "ON" and "OFF" to stabilize or destabilize a water-oil emulsion. A catalyst that exhibits the ability to become homogeneous or heterogeneous has been demonstrated by Ablan et al..[18] Another area of switchable catalysts is from the work by Bergbreiter et al.;[19] where the solubility of these catalysts can be switched by changing the temperature. Work by Langer et al.[20] has shown that an electric current can reversibly switch a surface from being hydrophilic to hydrophobic.

Another similar concept of switchable solvents is tunable solvents. The difference between a switchable solvent and a tunable solvent is that a switchable solvent exists in only two forms, while a tunable solvent can be tuned to any point between the two forms.

One example of a tunable solvent is CO_2 gas expanded liquids (GXLs). A GXL is formed by the dissolution of a gas, in most cases CO_2, in an organic solvent, which causes volumetric expansion. As the organic solvent is being expanded with CO_2, many of the solvent's physicochemical characteristics are changed (such as solvation, polarity, and dielectric constant). Some applications of GXLs are in areas of crystallization[21] and homogeneous catalysis.[22]

1.1.8 Solvents used in this thesis

The work of this thesis is aimed at satisfying the 5th principle of the 12 principles of green chemistry. Despite the fact that the work for this thesis still requires solvents, the solvents are easier to recycle and are capable of being used over more than one step in a synthesis. These solvents are classified as switchable polarity solvents. They are fully characterized and described. Chapter 2 outlines a solvent system composed of an alcohol and an amidine, which can exhibit a polarity change by the addition or removal of CO_2. In Chapter 3, we describe the second solvent system. This solvent system is based on the reaction of a secondary amine with CO_2 to form a carbamate salt, which is more polar than the neutral amine. Chapter 4 sees the application of these SPS systems in the separation of soy oil. Other strategies are also explored in their ability to separate soy oil

Chapter 2: A Two Component Switchable Polarity Solvent System

2.1 Introduction

2.1.1 Ionic Liquids

Ionic liquids are becoming increasingly popular as solvents for many applications. Their physical characteristics of being non-volatile, nonflammable, polar, conductive, thermally stable at high temperatures, have a wide liquid range, and environmentally friendly make them highly favourable and easy for researchers to work with. The term "ionic liquid," means a salt with a melting pointing below 100 ^{o}C, while the expression "molten salt" means one with a melting point above 100 ^{o}C. These solvents are not composed of individual molecules, but rather the liquid is made up of pairs of ions.

Ionic liquids have been known for almost a century. An early ionic liquid was Walden's[23] $[EtNH_3]^+[NO_3]^-$, which has a melting point of 12 °C. The first attempt to use ionic liquids was by Hurley et al., as liquid electrolyte for electrochemistry.[24] But it was in 1992 that the first air stable, water-insensitive, aprotic ionic liquid was found.[25] Later that decade, an ionic liquid was commercially applied in the Difasol/Dimersol process,[26] where a homogeneous metal-catalyst is immobilised in the ionic liquid that has been designed to interact with the catalyst for optimal activity.

Due to the wide variety of cations (e.g.: NR_4^+, PR_4^+, imidazolium and pyrrolidinium) and anions (e.g.: BF_4^-, PF_6^-, NO_3^-, SO_4^{2-}, $CF_3SO_3^-$. $CuCl_2^-$, $AlCl_4^-$) that can be synthesized and combined, overall there is a large number of possible ionic liquids.

Physical properties of ionic liquids are hard to predict. Predictions of melting points, ion volumes,[27] and volatility[28] have been somewhat successful. However, to truly identify all the physical characteristics of an ionic liquid, it must be synthesized and studied.

Most current ionic liquids are rather difficult to purify, which is a significant issue. For some applications, totally pure ionic liquids are not essential, but for uses in areas such as biology[29] and electrochemistry,[30] extremely pure solvents are required. For example, the commercially available 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide is sold as a slightly yellow liquid, whereas its pure form is clear; therefore, purification of this ionic liquid[31] is necessary before any it can be used.

Ionic liquids are presently being used as solvents for numerous coupling reaction, such as Stille type reaction with aryl bromides and aryl iodides,[32] Suzuki cross coupling reactions,[33] Grignard reactions,[34] and some examples of olefin metathesis with ruthenium carbene complexes.[35] Deng et al., have done extensive work using ionic liquids, their research demonstrated that ionic liquids can be used as both green reaction catalysts and reaction media.[36] Some examples of their work include cyclization, cycloaddition of CO_2, oxidative carbonylation, and hydroesterification.

2.1.2 Switchable polarity solvents

A switchable solvent[37, 16] is a solvent where one of its physical characteristics can be switched from one form to another. These could be conductivity, polarity, solubilizing capability, fluorophilicity or viscosity.

Conventional solvents as media for reactions or separations are disadvantageous compared to switchable solvents. For example, in a multi-step chemical process, it is often the case that each step requires a different solvent for optimal activity; hence a new solvent must be used for each step, and must be completely removed before the next step is carried out. This increases the production cost and environmental waste for the entire process.[38] However a switchable solvent could carry out more than one step before it needs to be replaced. For example, a switchable solvent could be used as a reaction medium, after which the solvent is changed to another form that is more appropriate for the next step, such as an extraction or separation. Such a solvent is depicted in this chapter, where the solvent can go from a relatively low polarity into another that is more polar, with the addition of CO_2.

Some examples of solvents that exhibit physical changes are supercritical fluids, such as CHF_3,[39] or CO_2-expanded liquids,[40] but the trigger for change in these systems only happens with pressures higher than 40 bar. It was not until the work of Xiaowang Li in the Jessop group that a solvent was found that requires only mild conditions to trigger such a change.[37] This solvent system is an improved version of the examples above in that it can be “switched” under ambient temperature and pressure. An equimolar mixture of DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene) and 1-hexanol results in a non-ionic, low polarity liquid. However, after exposure to one atmosphere of CO_2, the mixture turns into a viscous ionic liquid. This behaviour is similar for a variety of DBU/alcohol mixtures. The ionic form can be easily converted back to the neutral form by bubbling N_2 or argon through the solution and/or heating the solution to 60 °C.

Our switchable ionic liquid can be classified as a switchable polarity solvent (SPS), because its polarity swing is similar to a change from that of DMF to that of MeOH. This system is composed of two simpler components, an amidine (1,8-

diazabicyclo-[5.4.0]-undec-7-ene) (DBU) and a linear alcohol. The high-polarity (ionic) form is achieved by adding CO_2 to the low-polarity (non-ionic) form. Removing the CO_2 by bubbling N_2 and/or heating the ionic liquid form to 60 ^{o}C can reverse this process.

The switching process, previously studied by Xiaowang Li, included analytical techniques[37], such as, ^{1}H and ^{13}C NMR spectroscopy, UV/VIS spectroscopy, FTIR spectroscopy. Further characterization by viscosity, and conductivity, and an example of the use of this ionic liquid in separation and polymerization were done in this thesis.

2.2 Experimental Section

Organic liquids from Aldrich (DBU, t-BuOH, n-PrOH, n-HexOH, MeOH, EtOH), solids from Aldrich (cellulose, tetraethylammonium-p-toluene sulfonate, sodium toluene sulfonate, poly(sodium-4-styrene sulfonate), polyacrylic acid sodium salt, glucose, tetracosane, polystyrene MW 2,000 and 100,00, ibuprofen, (vinylbenzyl)-trimethylammonium chloride, stilbene, mesitylene, benzylbenzamide, benzyltriethylammonium chloride, and NR dye), CO_2 from Praxair (supercritical fluid chromatography grade) and N_2 (99.98%) were used as received, unless otherwise specified. Spectra were obtained with a 400 MHz NMR spectrometer.

2.2.1 Drying DBU

A 2-necked 250 ml flask under N_2 containing 100 ml of DBU and 1.0 g of crushed powder CaH_2 was stirred for 2 h. DBU was distilled under vacuum into another 2-necked flask. CO_2 was bubbled into the collection flask for 2 h and the dried DBU was filtered through a Shlenck filter apparatus under inert atmosphere.

2.2.2 Switching DBU/ROH mixtures from nonionic to ionic form and back again

In the N_2 atmosphere of a glove box, dried DBU and an alcohol were charged into a 4-dram vial, in a 1:1 molar ratio. CO_2 was bubbled through the liquid for 2 h while it was stirred. This yielded the ionic form, $[DBUH]^+[OCO_2R]^-$. To turn it back into the nonionic form, the vial was heated to 50-65 °C with N_2 bubbling through the solution.

In Xiaowang Li's work with the system of DBU/HexOH, the hexylcarbonate anion was detected by mass spectroscopy.

$[DBUH]^+[O_2CO(CH_2)_5CH_3]^-$: ^1H NMR ($CDCl_3$) 3.90 (t, 2H, hexyl C-1), 3.49 (m, 4H, DBUH C-2 and C-11), 3.43 (t, 2H, DBUH C-9), 2.81 (br, 2H, DBUH C-6), 2.00 (quintet, 2H, DBUH C-10), 1.75 (br, 6H, DBUH C-3, C-4, and C-5), 1.58 (quintet, 2H, hexyl C-2), 1.37 (m, 2H, hexyl C-3), 1.29 (br, 4H, hexyl C-4 and C-5), 0.87 (t, 3H, hexyl C-6); $^{13}C\{^1H\}$ NMR ($CDCl_3$. referenced to $CDCl_3$ at 77.2 ppm) 164.9 (DBUH C-7), 158.7 ($O_2\mathit{C}OR$), 64.6 (hexyl C-1), 53.5 (DBUH C-2), 48.1 (DBUH C-11), 38.6 (DBUH C-9), 32.3 (DBUH C-6), 31.5 (hexyl C-4), 29.4 (hexyl C-2), 28.8 (DBUH C-4), 26.8 (DBUH C-3), 25.5 (hexyl C-3), 24.0 (DBUH C-5), 22.2 (hexyl C-5), 19.7 (DBUH C-10), 13.7 (hexyl C-6); IR (neat) 2938 (m), 1648 (s), 1613 (s), 832 (m), 688 cm^{-1} (m); MS/MS (ESI, negative mode) 145.1 (M, $C_6H_{13}OCO_2^-$), 101.1 (M-CO_2), 99.1 (M-H_2CO_2), 83.0 (M-H_2CO_3), 60.0 (CO_3^-).

2.2.3 X-ray crystallography of $[DBUH]^+[O_2COMe]^-$

In a 4-dram septum-sealed vial, an equimolar mixture of DBU and MeOH was exposed to CO_2 bubbling for 30 min. The formation of a solid indicated the formation of the $[DBUH][O_2COMe]$. The crystal was kept in a freezer overnight before X-ray crystallographic analysis was done.

A crystal of the compound (colorless, plate-shaped, size 0.35 x 0.25 x 0.08mm) was mounted on a glass fiber with grease and cooled to -93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 4.52 ~ 50.00º. No significant decay was observed during the data collection.

Data were processed on a Pentium PC using the Bruker AXS Crystal Structure Analysis Package, Version 5.10.[41] Neutral atom scattering factors were taken from Cromer and Waber.[42] The raw intensity data were integrated using the program SAINT-Plus. Absorption corrections were applied using program SADABS. The crystal is monoclinic space group $P2_1/c$, based on the systematic absences, E statistics and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w\,(F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically. The positions for all hydrogen atoms were located gradually in difference Fourier map and their contributions were included in the structure factor calculations.

Convergence to final $R_1 = 0.0303$ and $wR_2 = 0.0592$ for 1550 ($I>2\sigma(I)$) independent reflections, and $R_1 = 0.0462$ and $wR_2 = 0.0632$ for all 2120 (R(int) = 0.0233) independent reflections, with 225 parameters were achieved.[43] The largest residual peak and hole was found to be 0.122 and – 0.151 e/Å^3, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles and hydrogen bond information are given in **Table 2.1** to **Table 2.7**. The molecular structure and the cell packing are shown in **Figure 2.2** and **Figure 2.3**.

2.2.4 Conductivity of DBU/HexOH in nonionic and ionic forms

A 4-dram vial containing 4.5 mL DBU and 3.6 mL hexanol (1:1 by moles) was placed in a glove box. A glass / platinum JENWAY 4071 Conductivity Meter conductivity probe was placed in the solution to measure the starting conductance. CO_2 was slowly bubbled into the solution, and the conductance was measured every 30 s until a constant value was obtained. To measure the conductance during the conversion back to the nonionic form, the contents of the vial were heated to 65 ^{o}C with stirring, and the conductance was periodically measured until it returned to the initial value. Conductance monitoring of the switching process was repeated twice more using the same solution.

2.2.5 Ultraviolet – Visible Spectroscopy Measurements

Ultraviolet absorbance spectra were acquired with Agilent Technologies ultraviolet/visible spectrometer 50-60 Hz with UV-Visible ChemStation software. A 1 cm optical glass cuvette was filled with an equimolar mixture of DBU/ROH. A small amount of solvatochromatic dye NR (enough to obtain an absorbance between 0.5 and 1) was added from the tip of a syringe needle. The UV/Visible spectrum was acquired and the λ_{max} of NR in the neutral form recorded, using a fresh DBU/ROH mixture as the blank. The cuvette was sealed with a septum and CO_2 was bubbled into the solution for 20 min to convert it to the ionic form, and the λ_{max} of NR in the ionic form was then measured.

2.2.6 Conductivity of DBU/t-BuOH

In the inert atmosphere of a glove box, 4.5 ml of DBU and 2.83 ml of anhydrous t-BuOH (1:1 by moles) were charged into a 4-dram vial. A glass / platinum JENWAY 4071 Conductivity Meter conductivity probe was placed in the solution to measure the starting conductance value then CO_2 was bubbled through the solution with the conductivity measured every 5 min intervals for 30 min, after which the conductivity was measured after longer time intervals.

2.2.7 Viscosity of neat DBU/n-PrOH

The viscosity of an equimolar mixture of DBU (12 ppm water) and n-PrOH (34 ppm water) was measured with a Cannon-Fenske viscometer in a dry-box containing a nitrogen atmosphere at 23 ˚C. The reported value is the average of three measurements of the same sample. Dry CO_2 was bubbled through an identical solution in a vial for 1 h to turn the liquid into the ionic form, after which the vial was capped and left for 1 h to temperature equilibrate. After this, the viscosity was measured again.

2.2.8 Solubility and miscibility tests

Under an N_2 atmosphere and room temperature, 1.5 ml of DBU, 0.72 ml of n-PrOH (1:1 by moles) and either 50 mg of the solid substrate or 0.5 ml of the liquid substrate were placed in a vial. Solubility or miscibility of the substrate was visually observed after the contents were stirred for 10 min. CO_2 was then bubbled through the vial for 1 h to turn the liquid into the ionic form and solubility or miscibility was checked again. The solid substrates were benzylbenzamide, benzyltriethylammonium, tetraethylammonium-p-toluene sulfonate, tetracosane, mesitylene, sodium toluene sulfonate, ibuprofen, poly(sodium-4-stryene sulfonate), polyacrylic acid sodium salt, polystyrene, glucose, cellulose, and trans-stilbene. The liquid substrates were: toluene, decane, and styrene.

2.2.9 Styrene polymerization in DBU/n-PrOH

Into a 2-necked flask under N_2 atmosphere containing 3.0 ml DBU and 3.6 ml n-PrOH (1:2.5 by mole), 50 mg of $K_2S_2O_8$ and 1.5 ml of distilled styrene were added. The flask was stirred with a condenser attached for 12 h at 50 ^oC. After the reaction was complete, the solution was slightly yellow. CO_2 was bubbled through the solution for 1 h to turn it into the ionic form. The polystyrene precipitated out and was filtered in an inert atmosphere Schlenk filter. The collected polystyrene was purified by washing with cold MeOH. The recovered ionic liquid was converted back to the nonionic form by heating to 60 ^oC with N_2 bubbling, then 1.0 ml of styrene, and 25 mg of $K_2S_2O_8$ were added to the recycled solvent and polymerization was carried out under the same condition. After CO_2 bubbling, 1.2 ml of n-PrOH was added to lower the viscosity and to make up for losses removed by filtration. The polymer precipitate was filtered and the recycle solvent was collected for the third cycle. The recovered ionic liquid was converted back to the nonionic form by heating to 60 ^{o}C with N_2 bubbling, then 1.0 ml of DBU was added to the recycled solvent, along with 1.0 ml styrene and 25 mg of $K_2S_2O_8$. Polymerization was carried out under the same condition. After CO_2 bubbling, 1.2 ml of n-PrOH was added to lower the viscosity and to make up for losses removed by filtration., and the polystyrene was filtered, with the solvent recollected for a fourth cycle. The recovered ionic liquid was converted back to the nonionic form by heating to 60 ^{o}C with N_2 bubbling, then 1.0 ml of DBU was added to the recycled solvent, along with 1.0 ml styrene and 25 mg of $K_2S_2O_8$. Polymerization was carried out under the same conditions. After CO_2 bubbling, 1.2 ml of n-PrOH was added to lower the viscosity, and the polystyrene was filtered and washed with MeOH.

The molecular weight of the polymer was measured using a GPC apparatus with the following details: Waters 515 HPLC pump, a 4.6 x 300 mm Waters Styragel HR 5E column, a 4.6 x 300 Water Styragel HR 4E column, a Waters 7.8 x 300 microStyragel 500 Å column, and a Waters 2410 Refractive Index detector. A 2.5 g/l tetrabutylammonium bromide salt solution in DMF at 0.4 ml/min was the eluent. The instrument was calibrated with commercially available polystyrene standards with molecular weights ranging from 770 to 6,500,000 g/mol. The unknown polymer samples were prepared by dissolving 20 mg of polymer in 2 ml of filtered HPLC grade 2.5 g/l tetrabutylammonium bromide salt solution in DMF. A 200 μL aliquot of the polymer solution was injected into the continuous flow of the eluent.

2.3 Results and Discussion

2.3.1 Drying DBU and its reaction with alcohol

The difficulty of working with DBU is that it must be extremely dried. If wet DBU is used, solid bicarbonate will form upon exposure to CO_2. The old purification technique involved pre-drying with CaH_2, then distilling DBU onto molecular sieves, but this did not sufficiently dry the DBU because when samples of DBU from this method, were exposed to CO_2, solid bicarbonate formed, clearly indicating that the DBU was still wet. A new method was developed using DBU itself as a drying agent. CaH_2 was still used as the pre-drying procedure, but after distillation, CO_2 would be bubbled into the distilled liquid; if the DBU were wet, then the reaction with CO_2 would form the bicarbonate precipitate. After filtering under inert atmosphere, the dried DBU has a water content of <50 ppm.

The reaction between DBU, alcohol and CO_2 is depicted below. If the alcohol is short, such as water, MeOH, or EtOH, then a solid is formed after CO_2 exposure. Longer alcohols result in an ionic liquid.

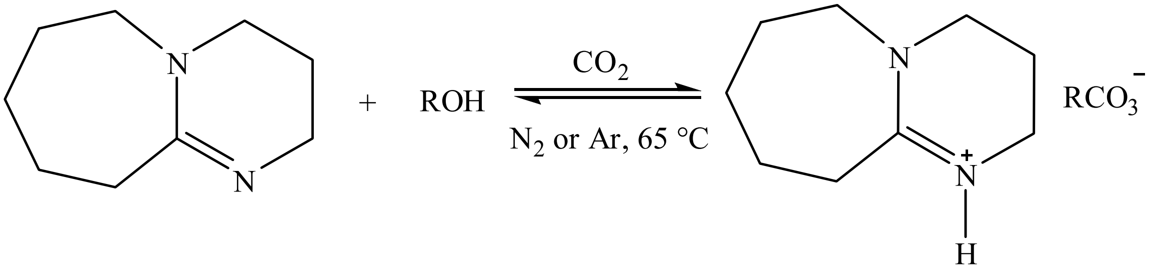


Figure 2.1. Reaction of DBU and ROH with exposure to CO_2.

2.3.2 X-ray crystallography of $[DBUH]^+[OCO_2Me]^-$

X-ray crystal structure analysis results (**Figure 2.2** and **2.3**) and data tables (**Tables 2.1** to **2.7**) are shown below. The X-ray crystal structure of $[DBUH]^+[O_2COMe]^-$ is different from that of $[DBUH]^+[O_2COH]^-$ by the fact that the bicarbonate exists as a hydrogen-bonded dimer,[44] essentially making it exists as $[DBUH]^+_2[O_2COH]^-_2$. A hydrogen bonding is between the cation and anion, another bonding is between two bicarbonate anions.[45] Our alkylcarbonate structure does not exist as a dimer because it lacks an acidic proton in the anion.

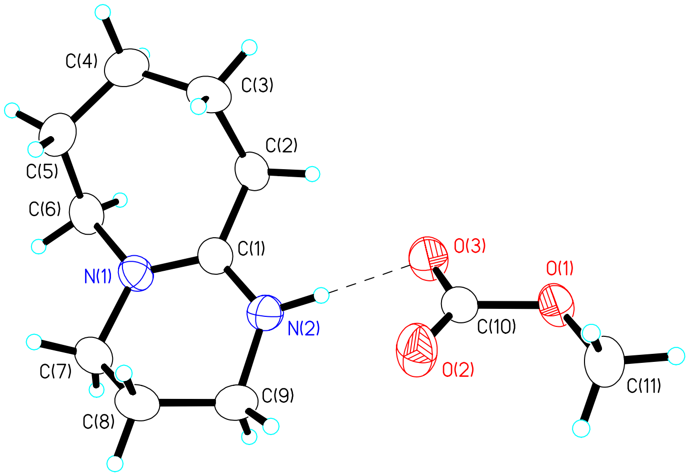


Figure 2.2. Molecular structure (Displacement ellipsoids for non-H atoms are shown at the 50 % probability level and H atoms are represented by circles of arbitrary size.)

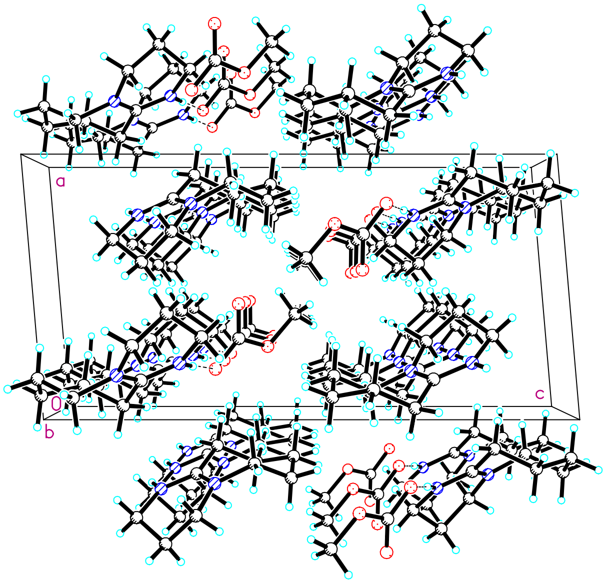


Figure 2.3 Unit cell packing of $[DBUH]^+[OCO_2Me]^-$.

Table 2.1 Crystal data and structure refinement $[DBUH]^+[O_2COMe]^-$.

Empirical formula	C11 H20 N2 O3	
Formula weight	228.29	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.9898(10) Å	α= 90°.
	b = 7.4386(8) Å	β= 94.892(2)°.
	c = 18.080(2) Å	γ = 90°.
Volume	1204.6(2) $Å^3$	
Z	4	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	496	
Crystal size	0.35 x 0.25 x 0.08 mm^3	
Theta range for data collection	2.26 to 25.00°.	

Index ranges	-10 ≤ h ≤ 10, -8 ≤ k ≤ 8, -20 ≤ l ≤ 21
Reflections collected	6837
Independent reflections	2120 [R(int) = 0.0233]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Empirical (Bruker SADABS)
Max. and min. transmission	1.0000 and 0.8311
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2120 / 0 / 225
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0592
R indices (all data)	R1 = 0.0462, wR2 = 0.0632
Largest diff. peak and hole	0.122 and -0.151 e.Å^{-3}

Table 2.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [DBUH]$^+$[OCO$_2$Me]$^-$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	-2026(1)	4539(1)	3185(1)	33(1)
N(2)	-2376(1)	2672(1)	2169(1)	36(1)
C(1)	-1796(1)	3000(2)	2847(1)	31(1)
C(2)	-868(2)	1559(2)	3233(1)	35(1)
C(3)	-1528(2)	809(2)	3922(1)	41(1)
C(4)	-1232(2)	1960(2)	4614(1)	44(1)
C(5)	-1882(2)	3846(2)	4546(1)	41(1)
C(6)	-1294(2)	4942(2)	3928(1)	38(1)
C(7)	-3045(2)	5920(2)	2841(1)	38(1)
C(8)	-4120(2)	5124(2)	2247(1)	41(1)
C(9)	-3300(2)	3965(2)	1730(1)	42(1)
O(1)	-2826(1)	-2364(1)	683(1)	36(1)
O(2)	-4393(1)	-340(1)	1116(1)	47(1)
O(3)	-2061(1)	-674(1)	1630(1)	41(1)
C(10)	-3152(2)	-1020(1)	1173(1)	30(1)
C(11)	-4012(2)	-2814(2)	139(1)	46(1)

Table 2.3 Bond lengths [Å] and angles [°] for [DBUH]$^+$[OCO$_2$Me]$^-$.

N(1)-C(1)	1.3224(14)
N(1)-C(6)	1.4759(17)
N(1)-C(7)	1.4776(16)
N(2)-C(1)	1.3128(15)
N(2)-C(9)	1.4610(16)
C(1)-C(2)	1.4946(16)
C(2)-C(3)	1.5289(19)
C(3)-C(4)	1.5214(19)
C(4)-C(5)	1.521(2)
C(5)-C(6)	1.5146(19)
C(7)-C(8)	1.5035(19)
C(8)-C(9)	1.509(2)
O(1)-C(10)	1.3838(14)
O(1)-C(11)	1.4283(16)
O(2)-C(10)	1.2211(14)
O(3)-C(10)	1.2539(14)
C(1)-N(1)-C(6)	121.40(10)
C(1)-N(1)-C(7)	121.58(11)
C(6)-N(1)-C(7)	117.01(10)
C(1)-N(2)-C(9)	123.18(11)
N(2)-C(1)-N(1)	121.76(11)
N(2)-C(1)-C(2)	117.69(11)
N(1)-C(1)-C(2)	120.55(11)
C(1)-C(2)-C(3)	113.71(11)
C(4)-C(3)-C(2)	114.33(12)
C(5)-C(4)-C(3)	114.39(12)
C(6)-C(5)-C(4)	113.61(12)
N(1)-C(6)-C(5)	113.96(11)
N(1)-C(7)-C(8)	111.37(10)
C(7)-C(8)-C(9)	110.44(13)
N(2)-C(9)-C(8)	108.96(11)
C(10)-O(1)-C(11)	115.07(10)
O(2)-C(10)-O(3)	128.93(12)
O(2)-C(10)-O(1)	119.15(11)

O(3)-C(10)-O(1)	111.92(11)

Table 2.4 Anisotropic displacement parameters ($Å^2$ x 10^3) for $[DBUH]^+[OCO_2Me]^-$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	35(1)	27(1)	36(1)	-2(1)	0(1)	0(1)
N(2)	46(1)	31(1)	32(1)	-1(1)	0(1)	1(1)
C(1)	29(1)	29(1)	35(1)	0(1)	6(1)	-5(1)
C(2)	34(1)	31(1)	40(1)	-5(1)	-1(1)	2(1)
C(3)	44(1)	35(1)	44(1)	5(1)	-6(1)	-1(1)
C(4)	40(1)	53(1)	37(1)	4(1)	-3(1)	-1(1)
C(5)	33(1)	55(1)	35(1)	-7(1)	0(1)	2(1)
C(6)	35(1)	34(1)	44(1)	-10(1)	-1(1)	-1(1)
C(7)	41(1)	29(1)	44(1)	5(1)	7(1)	2(1)
C(8)	42(1)	37(1)	42(1)	10(1)	1(1)	2(1)
C(9)	51(1)	39(1)	35(1)	6(1)	-2(1)	1(1)
O(1)	38(1)	30(1)	41(1)	-6(1)	3(1)	4(1)
O(2)	34(1)	57(1)	50(1)	-15(1)	0(1)	12(1)
O(3)	36(1)	41(1)	45(1)	-7(1)	-5(1)	4(1)
C(10)	33(1)	27(1)	32(1)	2(1)	6(1)	1(1)
C(11)	49(1)	40(1)	46(1)	-12(1)	-1(1)	0(1)

Table 2.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for $[DBUH]^+[OCO_2Me]^-$.

	x	y	z	U(eq)
H(2N)	-2283(15)	1540(20)	1982(7)	51(4)
H(2A)	-769(13)	610(15)	2881(7)	35(3)
H(2B)	139(14)	2020(15)	3362(6)	37(3)
H(3A)	-1088(15)	-362(17)	4017(7)	43(4)
H(3B)	-2645(16)	609(15)	3810(7)	42(4)
H(4A)	-1653(15)	1346(18)	5056(8)	55(4)
H(4B)	-140(16)	2088(16)	4721(7)	43(4)
H(5A)	-2971(15)	3796(16)	4474(6)	40(4)
H(5B)	-1599(14)	4477(16)	5020(8)	48(4)
H(6A)	-183(15)	4791(15)	3904(6)	38(4)
H(6B)	-1485(13)	6253(17)	3992(6)	41(3)
H(7A)	-2420(13)	6861(17)	2634(6)	38(3)
H(7B)	-3576(14)	6419(16)	3243(7)	39(4)
H(8A)	-4850(16)	4404(17)	2471(8)	47(4)
H(8B)	-4622(14)	6093(17)	1960(7)	47(4)
H(9A)	-2652(15)	4731(17)	1439(7)	48(4)
H(9B)	-3976(14)	3293(17)	1382(7)	42(4)
H(11A)	-4848(19)	-3350(20)	408(8)	73(5)
H(11B)	-4368(15)	-1771(19)	-142(7)	50(4)
H(11C)	-3597(17)	-3740(20)	-180(8)	66(4)

Table 2.6 Torsion angles [°] for $[DBUH]^+[OCO_2Me]^-$.

C(9)-N(2)-C(1)-N(1)	0.76(19)
C(9)-N(2)-C(1)-C(2)	-179.85(12)
C(6)-N(1)-C(1)-N(2)	-176.11(11)
C(7)-N(1)-C(1)-N(2)	4.84(18)
C(6)-N(1)-C(1)-C(2)	4.52(18)
C(7)-N(1)-C(1)-C(2)	-174.53(12)
N(2)-C(1)-C(2)-C(3)	-115.88(13)
N(1)-C(1)-C(2)-C(3)	63.52(16)
C(1)-C(2)-C(3)-C(4)	-80.88(16)
C(2)-C(3)-C(4)-C(5)	61.24(18)
C(3)-C(4)-C(5)-C(6)	-59.57(18)
C(1)-N(1)-C(6)-C(5)	-70.66(16)
C(7)-N(1)-C(6)-C(5)	108.43(13)
C(4)-C(5)-C(6)-N(1)	80.53(16)
C(1)-N(1)-C(7)-C(8)	20.09(18)
C(6)-N(1)-C(7)-C(8)	-159.01(12)
N(1)-C(7)-C(8)-C(9)	-48.17(16)
C(1)-N(2)-C(9)-C(8)	-30.00(18)
C(7)-C(8)-C(9)-N(2)	52.16(16)
C(11)-O(1)-C(10)-O(2)	0.63(16)
C(11)-O(1)-C(10)-O(3)	-179.14(12)

Table 2.7 Hydrogen bonds for $[DBUH]^+[OCO_2Me]^-$. [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...O(3)	0.911(14)	1.785(15)	2.6964(14)	178.6(14)

2.3.3 ^{1}H NMR spectroscopy characteristics of DBU/ROH system

The switchability of this SPS system was studied by several different methods. We will first look at the ^{1}H NMR spectroscopy (**Figure 2.4 and 2.5**) and FTIR differences between the two forms of the system.

^{1}H NMR spectroscopy of a mixture of n-PrOH and DBU (2.5:1 by moles) in $CDCl_3$ at room temperature after exposure to CO_2 showed separate peaks for the carboxylated alcohol and free alcohol. The DBU (C-6) showed a shift from 2.48 ppm (before CO_2 exposure) to 2.60 ppm (after CO_2 exposure), this peak appears as a singlet, which arises from the fast proton exchange between a protonated and unprotonated (C-6) DBU. The n-PrOH (C-1) peak shifted from 3.51 ppm (before CO_2 exposure) to 3.40 ppm (after CO_2 exposure), a final ratio of 1:1.4 for attached alcohol to unattached alcohols. There is no significant shifting for the other protons of DBU or n-PrOH because they are too far from the reacting center.

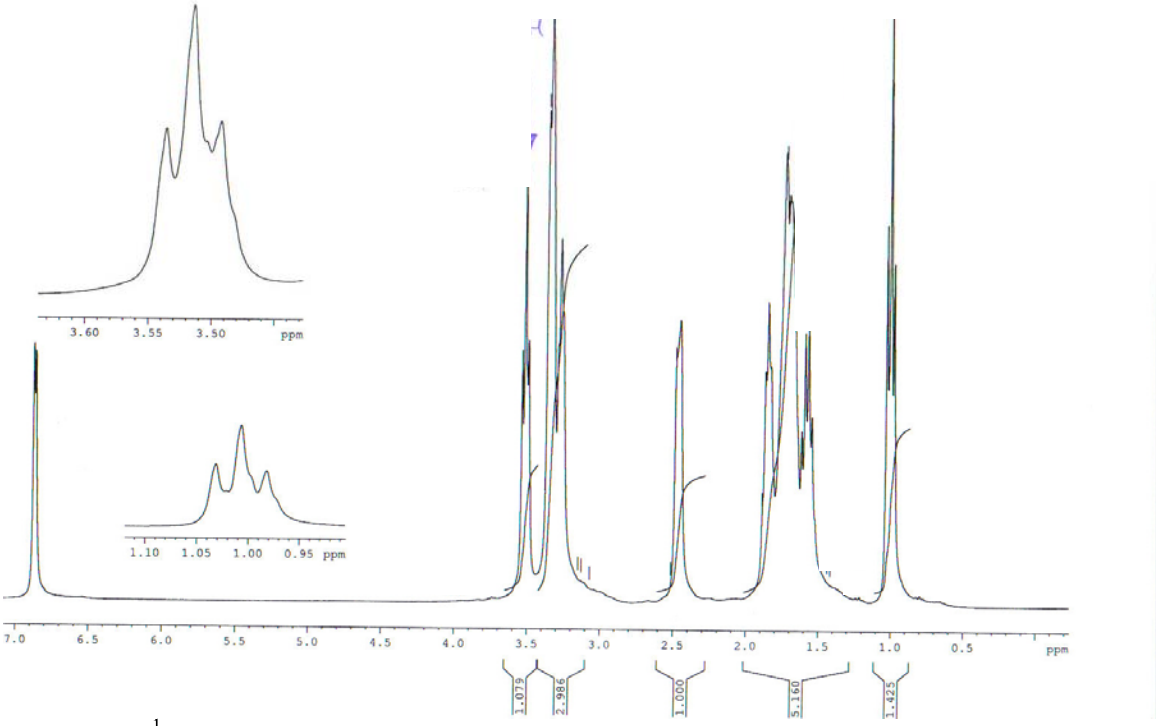


Figure 2.4 ^{1}H NMR spectrum of DBU:n-PrOH (1:2.5 by moles) in $CDCl_3$ in the absence of CO_2 at room temperature.

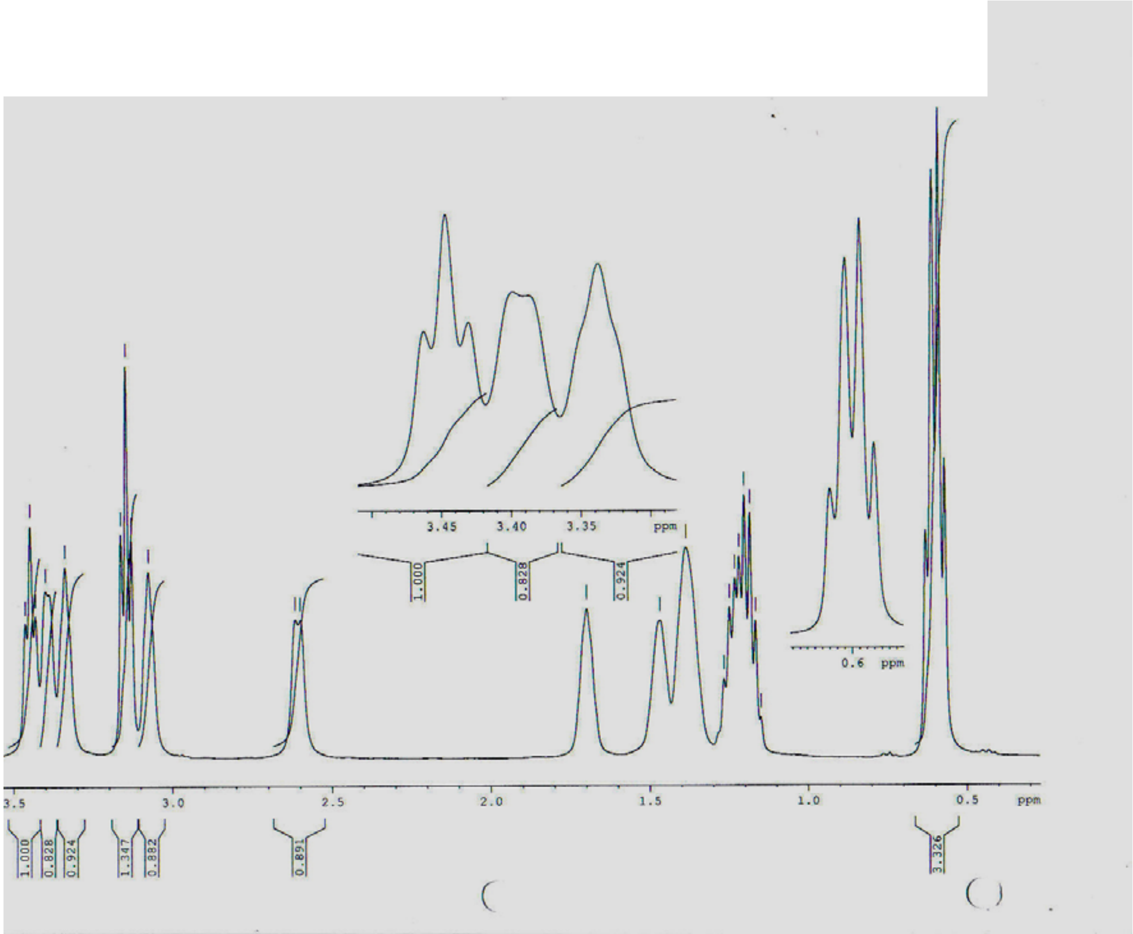


Figure 2.5 ^{1}H NMR spectrum of DBU:PrOH (1:2.5 by moles) in $CDCl_3$ after exposure to CO_2 at room temperature.

Other systems of DBU and alcohols have been previously characterized by Xiaowang Li; the ^{13}C NMR and ^{1}H NMR shifts of various $[DBUH]^+[O_2COR]^-$ salts are shown in **Table 2.8** and **Table 2.9**, respectively.

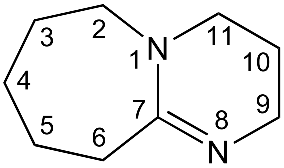


Figure 2.6 Numbering schemes of DBU for ^{1}H and ^{13}C NMR assignments.

Table 2.8 ^{13}C NMR chemical shifts of $[DBUH]^+[O_2COR]^-$ salts relative to $CDCl_3$ at 77.0 ppm.[38]

	Alcohols, R =						
Carbon	H	ethyl	1-propyl	1-butyl	1-hexyl	1-octyl	1-decyl
O_2COR	161.1	158.6	158.6	157.8	158.7	157.5	158.3
DBU C-2	53.2	53.5	53.9	52.9	53.5	52.6	53.3
DBU C-3	29.7	27.1	26.9	28.1	26.8	26.7	26.4
DBU C-4	28.3	28.9	28.9	23.5	28.8	23.3	23.7
DBU C-5	25.7	24.4	25.9	26.2	24	28	28.6
DBU C-6	36.6	33.1	31.5	31	32.3	31.8	31.7
DBU C-7	162.6	164.4	164.9	164.2	164.9	163.6	164.8
DBU C-9	43.1	39.4	38.4	38.1	38.6	38.2	38
DBU C-10	22	20.1	19.5	19.1	19.7	19	19.2
DBU C-11	48.5	48.2	48.5	47.5	48.1	47.2	47.8
ROH C-1	N/A	60	65.7	63.5	64.6	63.5	64.2
ROH C-2	N/A	15.1	31.5	31.7	29.4	28.6	28.6
ROH C-3	N/A	N/A	19.1	18.3	25.5	25	25.3
ROH C-4	N/A	N/A	N/A	13	31.5	28	29
ROH C-5	N/A	N/A	N/A	N/A	22.2	28	29
ROH C-6	N/A	N/A	N/A	N/A	13.7	30.5	29
ROH C-7	N/A	N/A	N/A	N/A	N/A	21.3	29
ROH C-8	N/A	N/A	N/A	N/A	N/A	12.8	31.1
ROH C-9	N/A	N/A	N/A	N/A	N/A	N/A	21.9
ROH C-10	N/A	N/A	N/A	N/A	N/A	N/A	13.4

N/A: not applicable

Table 2.9 ^{1}H NMR chemical shifts of [DBUH][O_2COR] salts relative to $CDCl_3$ at 7.25 ppm.[38]

	Alcohols, R =					
Carbon	H	ethyl	1-butyl	1-hexyl	1-octyl	1-decyl
DBU C-2	3.39	3.61	3.54	3.49	3.53	3.53
DBU C-3	1.72	1.74	1.73	1.75	1.70	1.76
DBU C-4	1.65	1.74	1.73	1.75	1.60	1.76
DBU C-5	1.72	1.74	1.73	1.75	1.75	1.76
DBU C-6	2.71	2.86	2.79	2.81	2.77	2.84
DBU C-9	3.39	3.42	3.40	3.43	3.39	3.43
DBU C-10	1.94	2.05	2.01	2.00	2.00	2.02
DBU C-11	3.39	3.61	3.54	3.49	3.53	3.53
ROH C-1	N/A	3.91	3.88	3.90	3.88	3.89
ROH C-2	N/A	1.19	1.6	1.58	1.58	1.59
ROH C-3	N/A	N/A	1.41	1.37	1.36	1.27
ROH C-4	N/A	N/A	0.92	1.29	1.28	1.27
ROH C-5	N/A	N/A	N/A	1.29	1.28	1.27
ROH C-6	N/A	N/A	N/A	0.87	1.28	1.27
ROH C-7	N/A	N/A	N/A	N/A	1.28	1.27
ROH C-8	N/A	N/A	N/A	N/A	0.88	1.27
ROH C-9	N/A	N/A	N/A	N/A	N/A	1.27
ROH C-10	N/A	N/A	N/A	N/A	N/A	0.88

N/A: not applicable.

The C-1 methylene proton resonance in DBU/n-hexanol showed a shift from 3.58 ppm in $CDCl_3$ in the non-ionic form to 3.90 ppm in the ionic form, this is comparable to that of $CH_3C(O)O(CH_2)_5CH_3$ at 4.05 ppm[46] or dihexylcarbonate at 4.13 ppm.[47] The ^{13}C NMR peak of the carbonate at 158.7 ppm and the C-7 of $[DBUH]^+$ at 164.9 ppm are comparable to those of $[NBu_4]^+[O_2COMe]^-$ at 158.2 ppm,[48] and $[DBUH]^+[O_2COH]^-$ at 162.6 ppm,[49] respectively. The FTIR spectrum of DBU/n-HexOH in its ionic form showed a ν(C=N) strong peak at 1648 cm^{-1}, which is very close to that of the $[DBUH]^+[Cl]^-$ frequency at 1645 cm^{-1}.[49]

Work by Hori et al.[45] have shown the reaction of DBU/EtOH and CO_2 in toluene went to 80 % conversion, but we have shown that neat mixtures of DBU and linear alcohols, such as n-propanol and n-hexanol, proceed to greater than 90 % conversion with CO_2. ^1H NMR integration in $CDCl_3$ after CO_2 exposure, of the methylene of the alcohol showed 93 % and 92 % conversion for neat mixtures of DBU/n-HexOH and DBU/n-PrOH, respectively. Reactions of DBU with branched alcohols such as i-PrOH or t-BuOH and CO_2 showed a lower conversion, 68 % and <10 %, respectively. This could be due to the steric effect of a branched species, making the ion interaction more difficult. Also, branched alcohols may not be acidic enough, thus making the reaction with the base less favourable.

2.3.4 Melting points of DBU/ROH

Not all combinations of DBU and alcohols result in an ionic liquid after CO_2 exposure. For short chains (water[45, 44, 49], MeOH[50,51] and EtOH) the carbonate is a solid at room temperature. The melting points of the various $[DBUH]^+[OCO_2R]^-$ are shown in **Figure 2.7**.

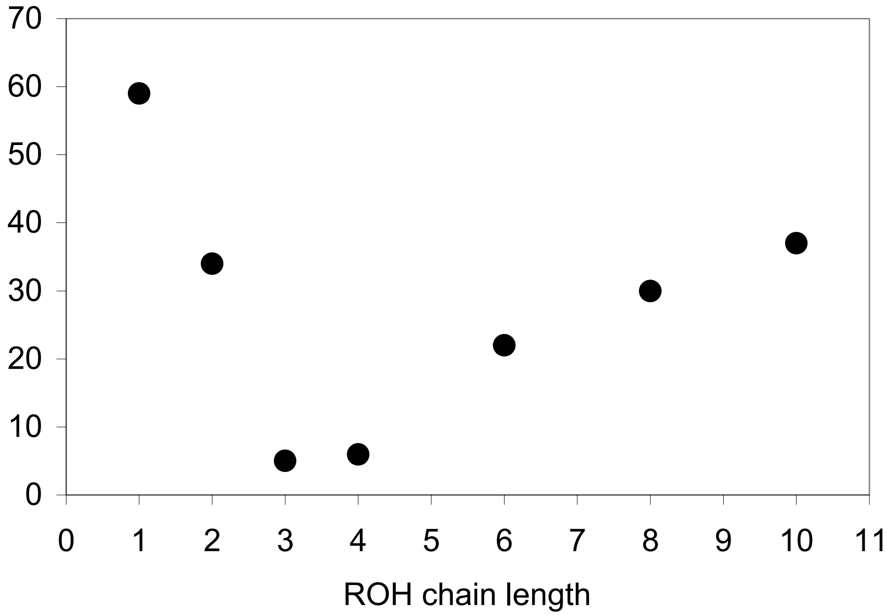


Figure 2.7 Melting points of $[DBUH]^+[O_2COR]^-$ from CO_2 bubbling into a equimolar mixtures of DBU and linear alcohols.[38]

Melting point measurements showed that the $[DBUH]^+[OCO_2Me]^-$ and $[DBUH]^+[OCO_2Et]^-$ are 60 °C and 33 °C, respectively. The lowest melting point is exhibited by the $[DBUH]^+[OCO_2Pr]^-$, at 6 °C, then as the alcohol chain increased, the melting point of the respective salt also increased.

2.3.5 Conductivity of neat DBU/HexOH before and after CO_2 exposure

The conductivity measurement of DBU/n-HexOH was done in an inert atmosphere because of the preference of the DBU to form the bicarbonate over alkylcarbonate if water is present. The conductivity profile is shown in **Figure 2.8**. For Trial 1, the non-ionic had a starting conductivity of 7 μS/cm, which rose to 187 μS/cm after reaction with CO_2. Although the conductivity was not measured during the reverse reaction, the conductivity was returned close to the starting value of 7 μS/cm. In Trial 2, however, the starting value was 37 μS/cm; this can be attributed to Trial 1 not having been totally reversed to the original point. For Trial 3, the solution was completely reversed before CO_2 was added.

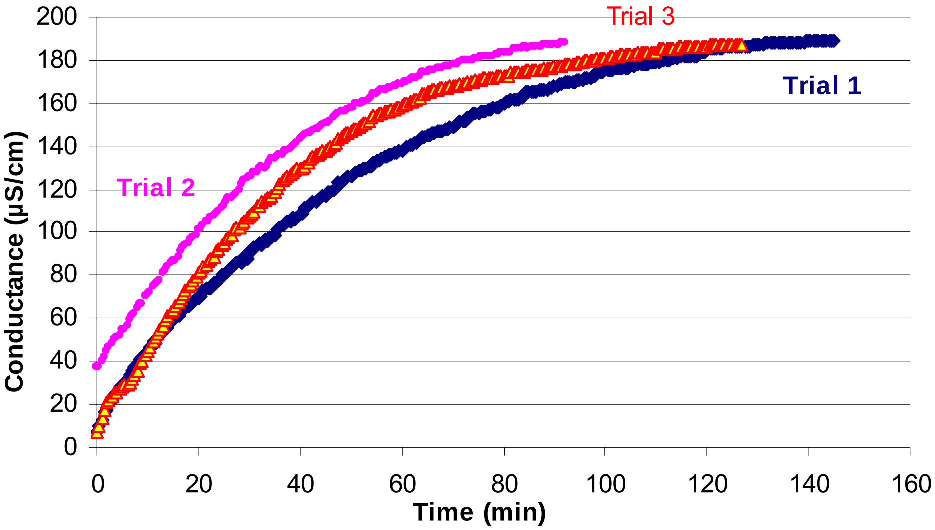


Figure 2.8 Conductivity profile of neat DBU/n-HexOH as it is being turned into the ionic form by CO_2 bubbling.

We have seen by ^{1}H NMR spectroscopy that reactions between DBU and branched alcohols have less conversion, possible due to the steric effects of the branching and the low acidity of the alcohols. The conductance profile of DBU/t-BuOH system does show some degree of conversion, as there is an increase in conductivity over time (**Figure 2.9**).

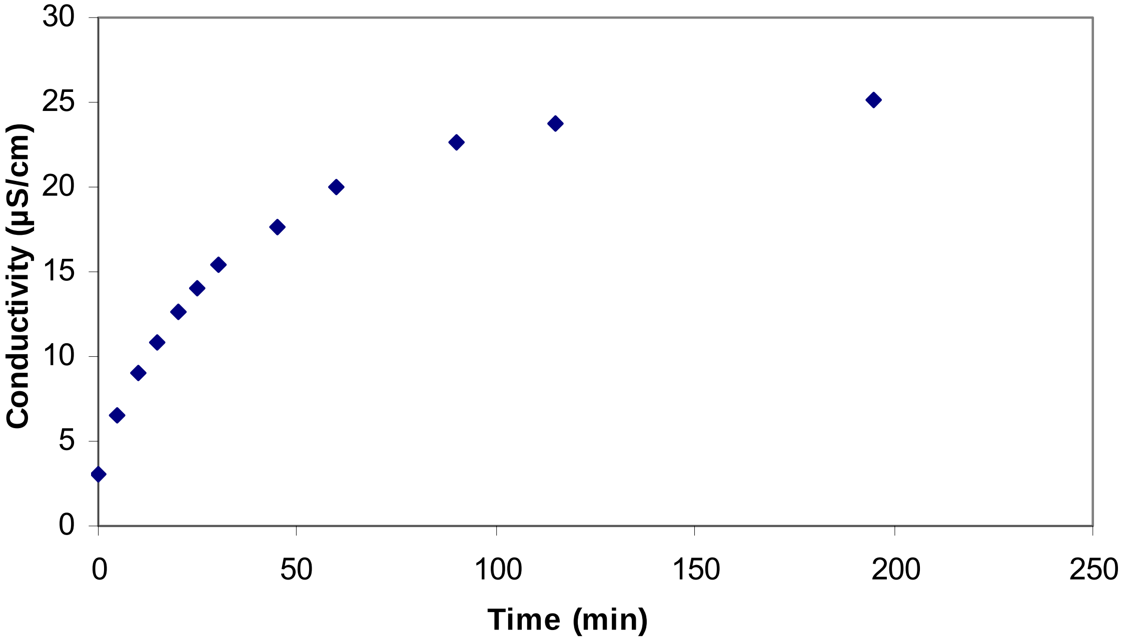


Figure 2.9 Conductivity of equimolar mixtures of DBU/t-BuOH with exposure to CO_2 at room temperature.

The final conductance value of the ionic form for DBU/t-BuOH was 25 µS/cm, which is very low when compared to that of DBU/PrOH (187 µS/cm.) This could be due to two reasons, the first is attributed to the low conversion, as there are fewer ions present to conduct electrical current, and the second could also be caused by viscosity issues. The low conversion is most probable because the viscosity of the mixture did not show dramatic increase upon visual inspection.

2.3.6 UV/Vis spectroscopy of DBU/ROH mixtures

The switch from non-ionic to ionic form can be monitored by UV/Vis spectroscopy. The use of a solvatochromatic dye can be used to monitor solvent polarity, as indicated by changes in the λ_{max} of the dye in the solution**.** For these measurements, the dye was Nile Red (NR). A table of λ_{max} of NR for some conventional solvents for comparison purposes is shown in **Table 2.10**. A graph depicting the changes in NR λ_{max} of DBU/n-ROH from non-ionic to ionic forms are shown in **Figure 2.9**.

Table 2.10 Polarities of solvents in two solvatochromic dyes

Solvent	$E_T(30)$, (kcal/mol)	NR λ_{max} (nm)
Diethyl ether	35.5[13]	504.4[52]
$CHCl_3$	39.1[13]	537.6[52]
DBU	39.4	545.8
Quinoline	39.4[13]	548.4
CH_2Cl_2	40.7[13]	535.2[52]
DMF	43.2[13]	541.2[52]
n-OctOH	48.1[13]	544.0[52]
n-PrOH	50.7[13]	545.6[52]
[bmim]PF_6	52.3[53]	547.5[54]
MeOH	55.4[13]	549.6[52]
[eim][BF_4]	--	562.9[55]

[bmim] = N-butyl-N’-methylimidazolium, [eim] = N-ethylimidazolium

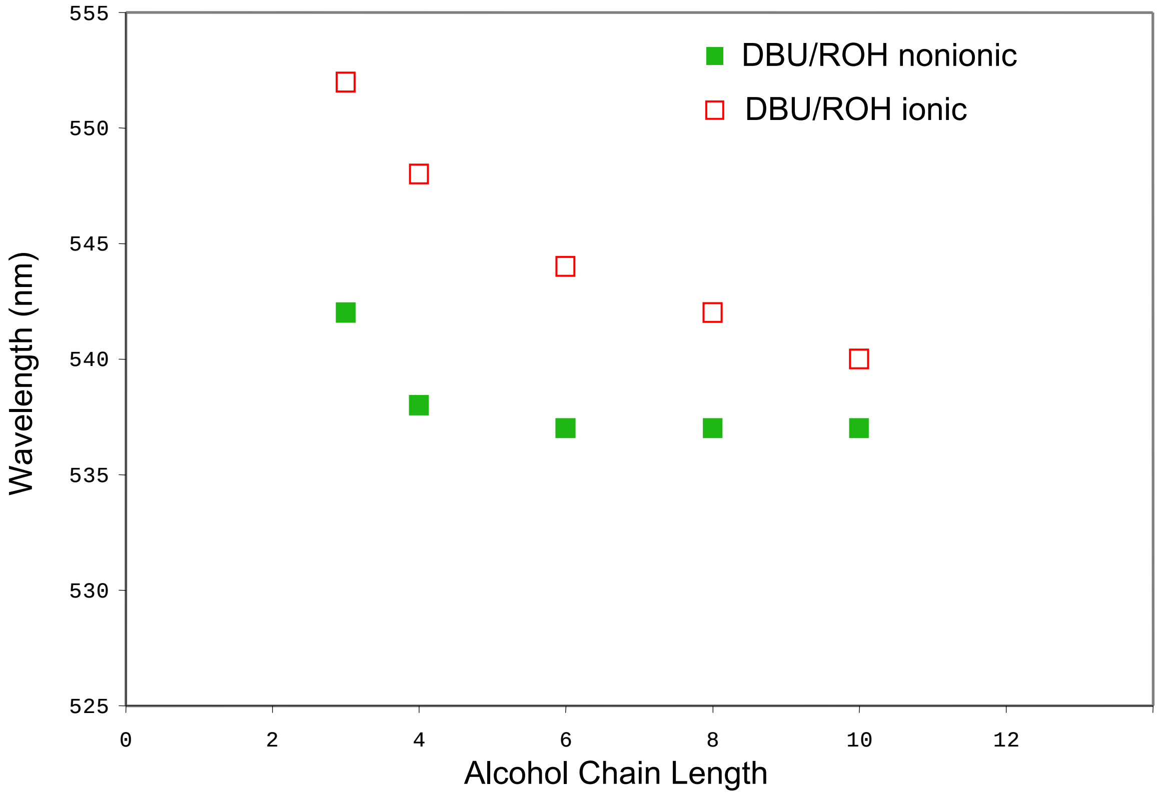


Figure 2.10 The λ_{max} of NR for equimolar DBU/ROH mixtures before and after CO_2 exposure.[38] The black boxes represent non-ionic form, the white boxes represent the ionic form.

Nile Red (NR) was chosen over another popular dye, Reichardt's dye or "$E_T(30)$", because Reichardt's Dye is bleached to yellow when the solvent is in the ionic form. This is probably due to protonation or hydrogen bonding of the dye with the acidic proton on the $[DBUH]^+$. It should be noted that NR overestimates the polarity of cyclic amines; the $E_T(30)$ data for pyridine showed that it is less polar than i-PrOH and EtOH as one would expect, but the NR values showed the opposite.[52]

The NR λ_{max} of equimolar mixtures of DBU and various alcohols was measured before and after exposure to CO_2. The polarity of these series of switchable solvents greatly depends on the chain length of the alcohol, with the neutral forms always having a lower λ_{max} than the ionic form. Shorter alcohols gave a greater NR λ_{max} change than longer alcohols; for example, when looking at **Figure 2.10**, one can see that the overall increase for DBU/n-PrOH is much bigger than that of DBU/n-OctOH.

DBU and n-PrOH individually have a NR λ_{max} of 546 nm and 546 nm, respectively, but when mixed in their non-ionic form, the NR λ_{max} is 542 nm. This is explainable because of solvent interaction between the DBU and alcohol, such as hydrogen bonding, which can mask the overall basicity, resulting in a lower NR λ_{max}. Similar results were observed by Kipkemboi and Easteal,[56] where the NR λ_{max} of a water and t-butylamine mixture showed a slight decrease when compared to each individual component. Upon CO_2 bubbling through a mixture of DBU/n-PrOH, the λ_{max} shifted to 552 nm, which is an overall increase of 10 nm. This increase is roughly equivalent of going from the polarity of DMF to slightly higher than that of methanol. Ogihara et al.[55] have demonstrated that solvents with acidic protons tend to have a higher NR λ_{max}.

2.3.7 Viscosity differences between the non-ionic and ionic form

As the equimolar mixture of DBU/n-PrOH reacts with CO_2, the viscosity of the liquid can be seen to dramatically increase. Measurements, at room temperature, of the non-ionic and ionic forms were done using a Canon-Fenske viscometer. The viscosity of the non-ionic form is 5.5 cP at 23 ^oC, and dramatically increased to 499.7 cP in the ionic form. For a mixture DBU/n-PrOH (by 1:2.5 moles), the non-ionic form has a viscosity of 3.9 cP, while and the ionic form was 133.5 cP. All ionic liquids generally have high viscosities because of the strong ion-ion intermolecular forces.

2.3.8 Miscibility and solubility tests

One potential use of the DBU/ROH system is to selectively dissolve certain compounds. This can be done because of the change in polarity from the non-ionic form to the ionic form. Therefore, it is reasonable to see a non-polar substance be soluble in the non-ionic form, and that same substance be precipitated or separated out when the mixture is in the ionic form.

The effectiveness of the polarity swing of DBU/n-PrOH was tested in a series of solubility experiments. Each substrate was tested to see whether it dissolved (for solids) or is miscible (for liquids) with the non-ionic form, then after the addition of CO_2, the dissolution or miscibility was observed. These results were visually determined, therefore it should be noted if not all of the solids, the result was concluded as undissolved, **Table 2.11** shows the results of these experiments.

Table 2.11 Dissolution results of 0.5 g of various solids in the non-ionic or ionic form of 1.5 ml of DBU and 0.723 ml of n-PrOH (1:1 by moles) at room temperature.

Solute	Non-ionic form	Ionic Form
Cellulose	X	X
Tetraethylammonium-p-toluene sulfonate	X	X
Sodium toluene sulfonate	X	X
Poly(sodium-4-styrene sulfonate)	X	X
Polyacrylic acid sodium salt	X	X
Glucose	X	X
Tetracosane	X	X
Polystyrene MW 2,000	√	X
Polystyrene MW 100,000	√	X
Ibuprofen	√	X
(Vinylbenzyl) trimethylammonium chloride	√	√
Stilbene	√	√
Mesitylene	√	√
Benzylbenzamide	√	√
Benzyltriethylammonium chloride	X	√

√: totally dissolved; X: insoluble or has some undissolved solids remaining.

Table 2.12 Miscibility results of 0.5 mL of various liquids in the non-ionic or ionic form of 1.5 ml of DBU and 0.723 ml of n-PrOH (1:1 by moles) at room temperature.

Solute	Non-ionic form	Ionic form
[b]Toluene	√	√
[b]Styrene	√	√
[b]Decane	√	X
[b]Hexadecane	√	X
[b]Propylene carbonate	√	X

√: miscible; X: immiscible;

There are some trends that can be observed from the results above. First, it seems that very high polarity compounds are insoluble in both forms. It could be that because the ionic form of DBU/n-PrOH is not polar enough to dissolve these compounds. Polar and non-polar aromatic compounds are soluble in both forms, while substances with intermediate polarity (with the exception of decane and hexadecane) are soluble only in the non-ionic form, but insoluble in the ionic form.

There are some exceptions to the trends observed. For example, tetracosane is a non-polar solid that is insoluble in both forms, but decane and hexadecane (also non-polar, but are liquids) are miscible in the neutral form and immiscible in the ionic form. Ibuprofen is a polar acid that is may have an acid/base reaction with the DBU.
Overall, the switching behaviour could be useful in practices where a separation of a mixture of compounds is required. For example, one can separate a mixture containing glucose, decane and benzylbenzamide. The non-ionic form would dissolve decane and benzylbenzamide, allowing the glucose to be filtered out. Once the solvent is switched to the ionic form, the decane would separate out, and leave the benzylbenzamide in the solution. Then the final step would be to distill out the DBU/n-PrOH to recover the final

compound. So in general, the selective solubilization behaviours of this switchable polarity solvent could be used to separate a mixture of three different compounds.

2.3.9 DBU/n-PrOH as a medium for polymerization and separation

We have previous outlined the advantage of using a switchable solvent in a chemical process, where it takes out the wasteful separation processes. Imagine we have a reaction where the reactants are soluble in one form of our solvent, and the products are insoluble in the other form, therefore, we can use the switching to trigger the precipitation or separation of our product after the reaction has been completed. From the solubility experiments Section 2.3.7, it was found that polystyrene was soluble in the non-ionic form of DBU/n-PrOH mixture, and was insoluble in the ionic form. This behaviour was tested in the polymerization of styrene to demonstrate the usefulness of solvent switching. The polymer product was separated upon the polarity switch of the solvent. The overall reaction schematic and recycling of the system is outlined in **Figure 2.11**.

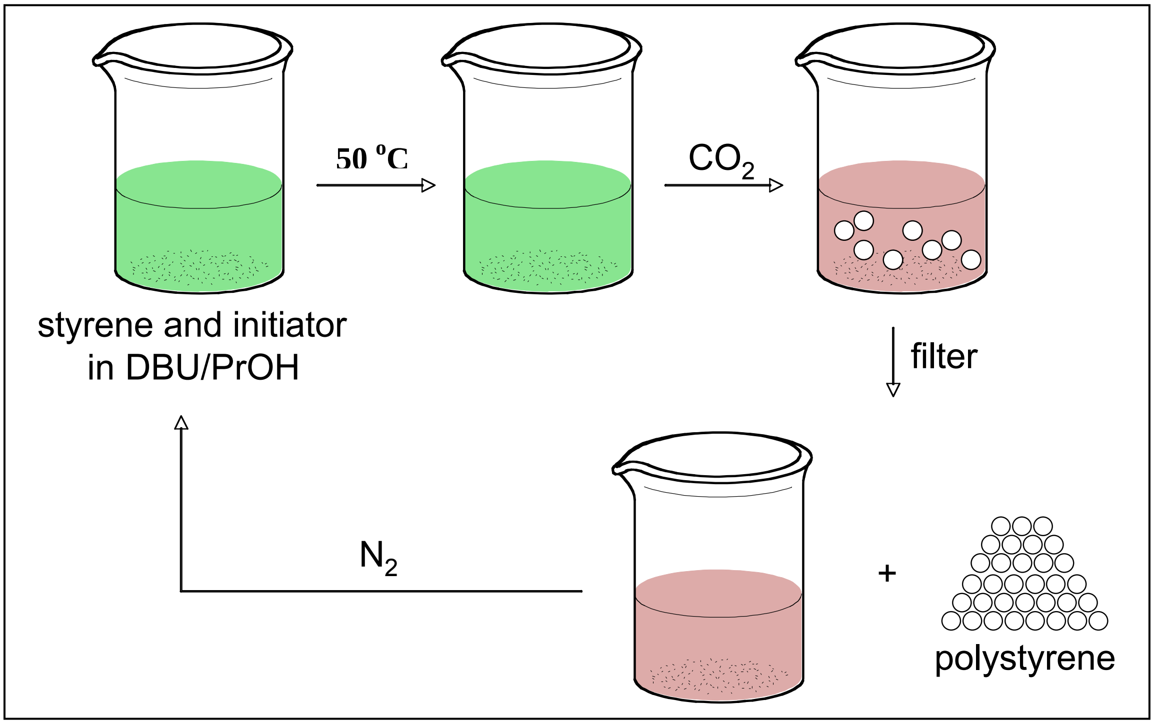


Figure 2.11 Schematic of using DBU/n-PrOH as a switchable solvent for the polymerization of styrene, and separation of polystyrene.

The ratio of DBU to n-PrOH was adjusted to get the optimum performance. A mixture of DBU/n-PrOH (1:2.5 by moles) was found to give the desired precipitation behaviour of the polymer. A 1:1 ratio was too viscous in its ionic form for filtration to be adequate, and a ratio of 1:3 was not sufficiently polar to induce polystyrene precipitation in the ionic form. A 1:2.5 ratio gave the desired solubility of the polymer in the non-ionic form, and was polar enough to cause polymer product to precipitate out of solution when CO_2 was added.

Styrene was polymerized with $K_2S_2O_8$ initiator in the non-ionic form of the 1:2.5 mixture at 50 °C. After polymerization, the solvent was switched to its ionic form by CO_2 bubbling, causing the polystyrene to precipitate out of solution. The polymer was collected by vacuum filtration while still under CO_2 atmosphere. The recovered solvent was reconverted back to its non-ionic form at to 60 ^{o}C with N_2 bubbling before another polymerization cycle was done. More n-PrOH was added after filtration for the second cycle to reduce viscosity and to make up for solvent loss in the filtration step. The make up of DBU was added before the third cycle was carried out to restore the 1:2.5 mole ratio. The yield and polymer characteristics for all four cycles are shown in **Table 2.13**.

Table 2.13 Yield and characteristics of polystyrene prepared in DBU/n-PrOH switchable solvent.

Cycle	Styrene (mL)	Yield %	M_n	M_w	PDI
1	1.5	42	21,142	40,800	1.93
2	1.0	172	11,941	17,561	1.47
3	1.0	50	16,775	28,457	1.70
4	1.0	151	12,457	18,235	1.46

The overall yield of polystyrene over the four cycles was 97 %. The yield for each cycle was calculated based on the amount of styrene added. It seems that the first cycle gave only 42 % yield, but this low yield was compensated when the second cycle resulted in a higher yield than the 1.0 mL styrene added. This showed that there could have been some unreacted styrene or unprecipitated polystyrene from the first cycle that remained in solution. This amount precipitated out in Cycle 2, explaining why its yield was 172 %. The same behaviour is seen for subsequent cycles. The PDI also exhibited s pattern, where the PDI for cycles 1 and 3 are higher than those of cycles 2 and 4.

2.4 Conclusions and Future Work

A series of switchable solvents that can be triggered to change their polarity has been described. This amidine-based solvent can go from its non-ionic form to a more polar ionic liquid form with the application of CO_2. It can be easily reversed to the non-ionic form by simply heating to 60 °C and/or bubbling N_2 through the solution. The main component of the system, DBU, can be combined with various linear alcohols from n-propanol to n-decanol to obtain different polarity ranges. The switching of polarity was confirmed by many methods: ^{1}H and ^{13}C NMR spectroscopy, the λ_{max} of NR solvatochromic dye, FTIR spectroscopy, viscosity measurements, and conductivity measurements. X-Ray crystallography also confirmed the formation of the $[DBUH]^{+}[OCO_2Me]^{-}$ after exposure to CO_2.

The inherent reactivity of DBU can limit the use of this system, and the necessity of being moisture free also makes it difficult to handle. Another impediment is that this system requires two components in a controlled ratio; hence for a reaction or process that has high temperatures, the loss of one of the components to evaporation is hard to track. Nonetheless, this novel switchable polarity solvent system has been proven to be useful for certain chemical processes. Polymerization of styrene was done over many cycles without the need of other solvents to purify or separate the compounds.

Although the use of this switchable polarity solvent was proven in the polymerization and separation of styrene, there is no doubt that other chemical reactions can be applied. A possible polymer synthesis can be tried, such as polymethylmethacrylate, polyacrylamide or any coupling reactions that make a compound that would precipitate or separate out in the ionic form. All the work done in this thesis used only n-PrOH and n-HexOH, and we have seen that even with just these two alcohols, these SPS systems exhibited a wide range of polarities. Therefore, even though certain solids can precipitate out of solution with DBU/n-PrOH, there could be a very different set of behaviours when a different alcohol is used. On the other hand, works done by our collaborators at Georgia Institute of Technology have shown that a different base (amidine or guanidine) can be used to get a different range of polarity.

Finally, the mechanism of how DBU/ROH reacts with CO_2 should be investigated. We know this happens, but a clear mechanism of the forward and reversed reaction has yet to be determined.

Chapter 3: Switchable Polarity Solvent Using Secondary Amines

3.1 Introduction

3.1.1 The need for another switchable polarity solvent

As good as the DBU/ROH system is, there are three main issues that make it difficult to work with. The first issue is sensitivity to water, the system only works well under anhydrous conditions; therefore all solvents and reactants need to be purified and must be anhydrous before they can be used. The second issue is that this system is composed of two liquids, where each individual liquid has different physical properties. One important difference is the volatility; DBU is less volatile than any of its alcohol partners, which makes it difficult to maintain the one to one ratio that is crucial for the system to work. The final problem is the polarity of this system. The change in polarity of this system is dependent on the alcohol; hence the maximum polarity that can be reached is slightly higher than methanol when n-PrOH is used. Furthermore, the non-ionic form of this system is still quite polar, therefore, when we want to use a truly low polar SPS, this system fails to satisfy that need; limiting this system for uses in certain applications or chemical processes.

3.1.2 Secondary amines as switchable polarity solvents

Amines react with CO_2 to form carbamate salts via carbamic acids (**Figure 3.1**). In order for such this solvent system to be classified as a SPS,[37, 38, 57] the carbamate salt and the amine must be liquids and exhibit a significant change in polarity. Primary amines form solid salts,[58, 59] while some secondary amines give liquid salts.

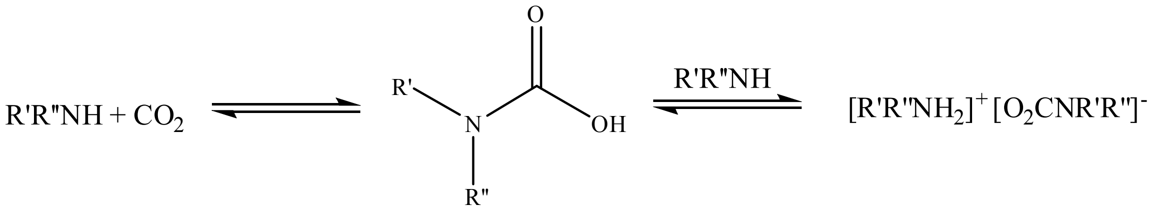


Figure 3.1 Reaction of a secondary amine with CO_2 to form a carbamic acid then a carbamate salt.

The secondary amines discussed in this chapter indeed exhibit changes in polarity. Many liquid secondary amines were tested for their ability to form liquid carbamate salts. The majority did, while a few gave solid carbamate salts, which does not allow them to be considered as SPS at room temperature. Ionic liquids from carbamate salts are not unusual, the carbamate salt of dimethylamine, called dimethylammonium dimethylcarbamate (DIMCARB) has been extensively studied over several decades.[58] The advantage that our carbamate salt ionic liquids have over DIMCARB is that these are SPS, whereas DIMCARB is not. The neutral amine that forms DIMCARB is a gas, dimethylamine, at ambient temperature and pressure. Another advantage is that our SPS can easily be switched back into its liquid non-ionic neutral amine form, while dimethylamine is difficult to collect when DIMCARB is reversed into its non-ionic form.

The reaction between primary or secondary amines with CO_2 is spontaneous and thermally favourable. There have been numerous studies in the identification of which species are formed during the reaction. The prominent species in the reaction are: the free amine, the carbamic acid, and ions of the carbamate salt. Aresta et al.[59] found that $(PhCH_2)_2NH$ reacts with CO_2 to form $(PhCH_2)_2NCO_2H$ at 10.3 °C, which was detected by an FTIR ν(CO) band at 1640 cm^{-1}. The reaction of isopropyl amine with CO_2 in DMSO was studied by Dijkstra et al.,[60] where they found a new δ(O-H) at 9.2 ppm that is indicative of the carbamic acid. By ^1H NMR integration, this group found that the ratio of carbamic acid to amine was 0.92, which is consistent with these two species existing as a hydrogen-bonded pair. The detection of a new C=O at δ(C=O) at 158 ppm[60] in the ^{13}C NMR spectrum also supports the formation of carbamic acid. The carbamate anion was detected by FTIR as a ν(CO) band at 1575 cm^{-1} , while the ν(CO) band for carbamic acid appears at 1650 cm^{-1}. The formation of the carbamic acid is favoured in dipolar aprotic solvents, for example, in DMSO, the carbamic acid of isopropyl amine/CO_2 were detected by FTIR. Similar results were found with silylmonoalkylamines (e.g. $H_2N(CH_2)_3Si(OMe)_3$) where the reaction with CO_2 at 297 K in THF forms the carbamate salts of the silylmonoalkylamines, while the product at 273 K was the carbamic acid of silylmonoalkylamine.[61]

DIMCARB has been extensively studied by ^{1}H and ^{13}C NMR spectroscopy.[62] The carbamic acid peak at 12.8 ppm when done at 173 K and in $CDCl_3$, but this peak slowly disappears when the analysis is done at a higher temperature. For example at 233 K, two peaks with similar integration appeared at 2.47 and 2.76 ppm, corresponding to the carbamate ions, and no peaks for the carbamic acid was found. Theoretical prediction of the FTIR spectra was done by Jamroz et al.,[63] where they found a favourable interaction between the acid and free amine (in a 1:1 mole ratio), with a stabilization energy of this complex being -11.5 kcal/mol.

From the literature sources cited above, it can be concluded that different analytical techniques are used to detect the species at different conditions. FTIR can be used to detect the carbamic acid and carbamate anions and NMR spectroscopy can be used to detect the carbamate salt ions and free amines, although later technique can also detect the carbamic acids when done at lower temperatures. In our studies, we also employed these analytical techniques at room temperature, but we were still successful in identifying all the mentioned species.

This chapter will discuss and identify the secondary amines that give liquid carbamate salts. The methods of turning the non-ionic form to the ionic form and their reversing are outlined, as well as studies of the changes in polarity, viscosity, and conductivity of the liquids. Applications in separation and polymerization are also discussed.

3.2 Experimental Methods

Amines from Aldrich (methylaniline, benzylmethylamine, methylpropylamine, methylbutylamine, methylpentylamine, ethylbutylamine, dipropylamine, propylbutylamine, ^{sec}butyl-n-propylamine, and ^{tert}butyl^{iso}propylamine) were all used as received. All other compounds such as organic solids, dyes, CO_2 (supercritical fluid chromatography grade) and N_2 (99.98%) were used as received (see Section 2.2). Spectra were obtained with a 400 MHz NMR spectrometer.

3.2.1 Using CO_2 to turn secondary amines from non-ionic to ionic form.

To a septum-capped vial, 2 mL of NHBuEt was charged and flushed with N_2. CO_2 was bubbled into the solution for at least 20 minutes, until the vial was cooled to back room temperature. This produced the ionic form of the amine. To reverse this process, the vial was heated to 65 ^{o}C under N_2 and stirred until no more CO_2 evolved from the solution. Similar procedures were carried out for NHBzMe, $NHPr_2$, and NHBuMe.

3.2.2 ^{1}H NMR profile of $NHPr_2$ as it is being turned into its ionic form

A standard 5 mm NMR tube was half-filled with $CDCl_3$. Three drops of $NHPr_2$ were added to the tube, which was then sealed with a septum. CO_2 was bubbled into the solution. ^{1}H NMR spectra were acquired after every minute of CO_2 exposure for 5 minutes.

3.2.3 Synthesis of $[NH_2R'R'']^+[Cl]^-$ salts

The $[NH_2R'R'']^+[Cl]^-$ salts of the secondary amines were prepared for comparison with their ionic forms. HCl (4 M in dioxane) was added drop-wise to a vial containing 1 ml of the secondary amine until all precipitates stopped forming. The solid was then washed with hexane and collected on a medium fritted filter.

3.2.4 UV/Visible spectroscopy measurements

Ultraviolet absorbance spectra were acquired on an Agilent Technologies ultraviolet/visible spectrometer using UV-Visible ChemStation software. A 1 cm glass cuvette was filled with 3 ml of the amine. A solvatochromatic dye, NR, was added from the tip of a syringe needle (amount used was enough to get the absorbance between 0.5 and 1.0). The NR λ_{max} of this neutral form was measured, using fresh 2^o amine as the blank. The cuvette was sealed with a septum and CO_2 was bubbled through the solution for 20 minutes, following which the UV/Visible spectrum was re-acquired. The amine was reversed back to the neutral form by heating to 60 ^{o}C with N_2 bubbling, and the UV/Visible spectrum was taken again.

3.2.5 Viscosity measurements

A Cannon-Fenske type viscometer of appropriate range was placed in a water bath, thermally equilibrated for 20 minutes, and purged for 10 minutes with N_2 immediately before use. 7.0 mL of secondary amine was charged into the viscometer and the viscosity measurement was taken. CO_2 was bubbled through the solution for 1 hour, and the viscosity was measured again.

3.2.6 Conductivity measurement of neat NHBuEt

CO_2 was bubbled through a 10 mL sample of NHBuEt in a 4-dram vial. The conductivity was measured every few minutes, using an Orion 4 Star pH/conductivity probe, until a constant value was obtained. To reverse the conductance N_2 was bubbled through the solution at 55 °C until the conductivity returned to 0 μS/cm.

3.2.7 Conductivity of NHBuEt in DMSO with different ratios of CO_2:N_2

The following procedure was done with the help of Colin Eddie. Four separate 4-dram vials containing 12.0 mL of a mixture of DMSO:NHBuEt solution (5:1 by moles) was prepared. To each vial, a gas mixture containing a specific ratio of CO_2:N_2 gases was bubbled through. The partial pressures of the two gases (CO_2:N_2), in bar, were 10:40, 20:30, 30:20, 40:10. The conductivity of each mixture was measured until a constant value was obtained.

3.2.8 Solubility and miscibility tests in NHBuEt

To a vial containing 1.5 mL of NHBuEt, 50 mg of the solid substrate or 0.5 mL of the liquid substrate was added. The solubility or miscibility of the substrate was visually checked. CO_2 was then bubbled through the vial for 20 min to turn the NHBuEt to the ionic form, and solubility or miscibility was checked again. To determine whether the solubility or miscibility change is reversible, the vial was heated to 60 ^{o}C with N_2 bubbling and stirred for 2 h. For all tests that showed a change in solubility or miscibility after CO_2 treatment, reversing the solvent to the non-ionic form causes a reversal in the solubility or miscibility of the solute, with the exception of glucose where it still remained dissolved after the solvent was reversed back into the non-ionic form.

The solid substrates were benzylbenzamide, benzyltriethylammonium, tetraethylammonium-p-toluene sulfonate, tetracosane, mesitylene, sodium toluene sulfonate, ibuprofen, poly(sodium-4-styrene sulfonate), polyacrylic acid sodium salt, polystyrene, glucose, cellulose, stilbene, and cholesterol. The liquid substrates were: toluene, decane, hexadecane, styrene, 5-trans-decene, propylene carbonate.

3.2.9 Polymer/catalyst separation in NHBuEt

This procedure was done by Jeremy Andreatta of Texas A&M University. N,N'-bis(3,5-di-ter-butylsalicylidene)-1,2-ethylenediimine (Cr(salen)Cl) (0.050 mg, 0.086 mmol) was stirred with bis(triphenylphosphoryl)idine ($PPNN_3$) (0.050 mg, 0.086 mmol) in CH_2Cl_2 for 30 min in a 30 mL glass vial and dried *in vacuo*. The "active" catalyst was dissolved in 10 mL of cyclohexene oxide and loaded via cannula into a 300 mL stainless steel Parr reactor at 80 ºC. The vial was rinsed with 10 mL of cyclohexene oxide; this was also loaded into the reactor. The reaction vessel was pressurized to 35 bar CO_2 and heated to 80 ºC for 4 h. The CO_2 was vented and the reactor placed under vacuum for 10 min to remove all traces of CO_2. 20 mL of degassed NHBuEt was loaded into the reactor via cannula and the reaction mixture stirred for 1 h. The reactor was opened and the contents emptied into a 125 mL Erlenmeyer flask, and washed with an additional 10 ml of degassed NHBuEt which was added to the flask. CO_2 was bubbled through the reaction mixture for 30 min resulting in the precipitation of the polymer. The polymer/catalyst/SPS slurry was mechanically stirred to ensure maximum catalyst removal and filtered using a Büchner funnel resulting in an off-white polymer and an orange-brown solution. This process was repeated to further purify the polymer and increase catalyst recovery yields. The catalyst was isolated from the SPS via vacuum distillation and combined with 0.037 mg (0.065 mmol) $PPNN_3$ in CH_2Cl_2, as previously described, in preparation for recycling.

3.3 Results and Discussion

3.3.1 Characterizing secondary amine SPS by ^{1}H NMR spectroscopy

The reaction of primary or secondary amines with CO_2 is depicted in **Figure 3.1**. CO_2 reacts with one molecule of the neutral amine to form a carbamic acid, then the carbamic acid reacts a free amine molecule to form the carbamate salt. When this reaction is done in a solvent, the formation of the carbamic acid is favoured in polar solvents, while the carbamate salt is favoured in less polar solvents.[59-61] Not all primary[57, 64] or secondary amines remain liquid after treatment with CO_2. The amines in our studies such as hexylamine, N-^{tert}-butyl-isopropylamine, and 1,3-dimethylbutylamine gave solid carbamate salts after the CO_2 treatment. Other amines such as allylamine,[65] piperidine,[66] pyrrolidine,[66] and benzylamine[67] also give solid carbamate salts after CO_2 treatment.

During the treatment with CO_2, the amine solution exhibited an increase in temperature. This is due to the exothermic reaction to form the carbamate salts. If the neutral amine is basic enough, then the carbamic acid will react with one molecule of the neutral amine to form the carbamate salt. One example where the secondary amine that is not basic enough to deprotonate its carbamic acid is aniline.[68, 69] The lone pair of aniline can form resonance structures through the aromatic ring by lone pair conjugation, thereby stabilizing the base; this limits its ability to abstract the proton from the carbamic acid; therefore, aniline could not form a solid carbamate salt.

There are drastic differences in the ^{1}H NMR spectra of the two forms of NHBuEt. **Figure 3.2** depicts the ^{1}H NMR spectrum (in $CDCl_3$) of the non-ionic form of NHBuEt, while **Figure 3.3** shows the ionic form. The non-ionic form shows clear splitting of the hydrogens that can easily be assigned. The ionic spectrum exhibits broad peaks, due to the increased in viscosity of the liquid in its ionic form. Furthermore, since there are two sets of peaks for this amine in the ionic form, we can say that one set is for the anion, and the other is for the cation. It is difficult to specifically assign which peaks arise from the anion, and which arise from the cation because there is a lot of overlapping. The terminal methyl group shows very little broadening or shifts in its position because it is so far from the actual reaction center of the molecule. In contrast, the methylene groups near the nitrogen all show significant shifting and broadening. This is shown in the neutral and ionic spectra of the two forms of NHBuEt, the terminal –CH_3 of the butyl side chain remains at 0.86 ppm and is still a clear triplet.

As a demonstration of the reversibility of NHBuEt, the ionic mixture was heated to 65 ^{o}C while being bubbled with N_2, and the resulting ^{1}H NMR spectrum is identical to that of the neutral amine in its non-ionic form; but there are still small peaks showing the presence of small amounts of the carbamate salts.

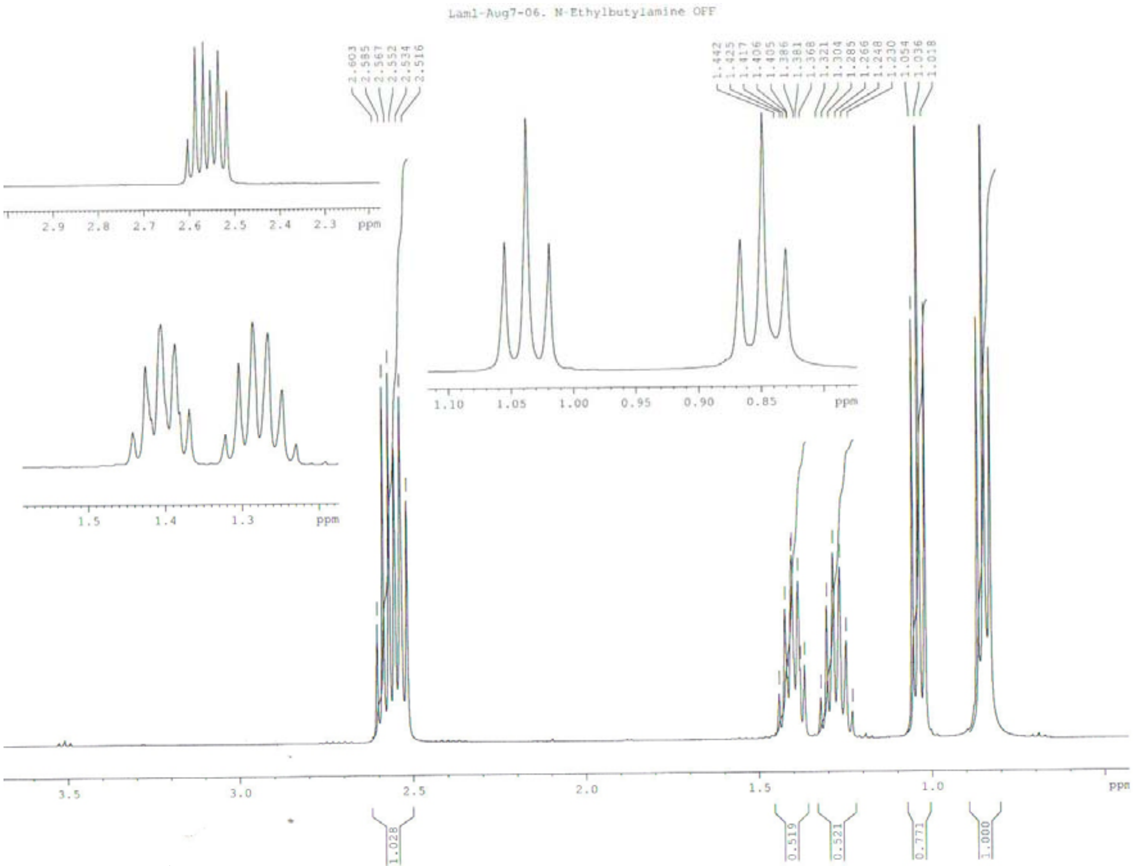


Figure 3.2 ^{1}H NMR spectrum of the non-ionic form of NHBuEt in $CDCl_3$ at room temperature. For peak assignments, see **Table 3.1**.

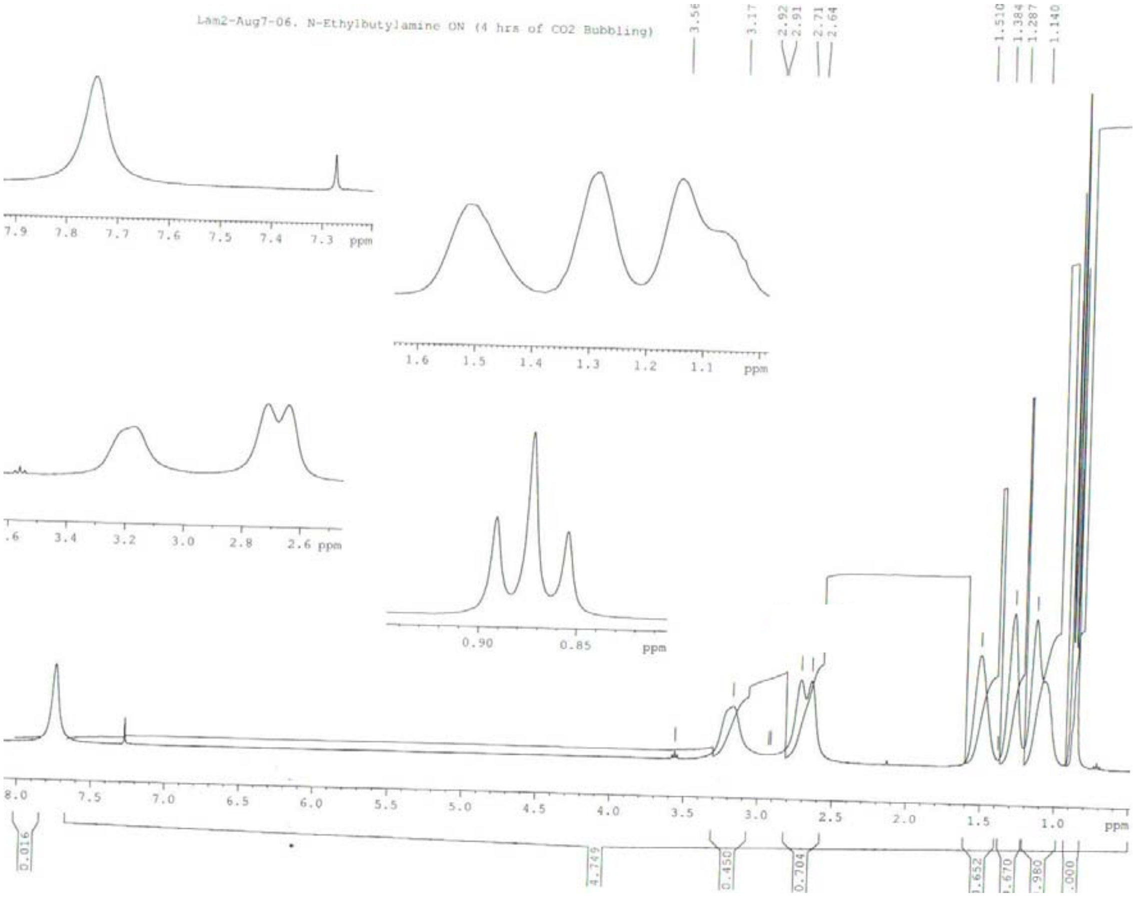


Figure 3.3 ^{1}H NMR spectrum of the ionic form NHEtBu from exposure with CO_2 in $CDCl_3$ at room temperature. For peak assignments, see **Table 3.1**.

Ionic liquids are generally very stable, but these carbamate salt ionic liquids may be exceptions because they are composed of amines, which are inherently reactive. The ionic forms of NHBuEt, NHBzMe and NHBuMe are all stable when exposed to atmospheric conditions. No changes were observed even after exposing these ionic liquids to normal atmospheric conditions over 24 h. This could be one positive aspect for these ionic liquids, as it is known that amines are quite reactive, and most will eventually react with the moisture in the air and form the carbamate bicarbonate salts.

Attempts in identifying specific melting points of the carbamate salt ionic liquids proved to be difficult. The carbamate salts of the amines were kept in a freezer at -78 ^{o}C overnight, after which the carbamate salts still remain as liquids. This may be attributed to a phenomenon called supercooling behaviour of viscous ionic liquids.[70] Supercooling is a process in which a liquid is cooled below its normal freezing point without actually being frozen. These carbamate salts exhibit such behaviour, which makes it difficult to identify their true melting points. It is valid for us to say that the true melting points of these carbamate salts are expected to be much higher, possibly somewhere closer to room temperature.[66]

The previous SPS system of DBU and alcohol has problems with water moisture, limiting its application to only anhydrous chemistry. One possible advantage of using secondary amines as switchable solvents is that they may be less sensitive to water, making them easier to handle under atmospheric conditions. When 4 mL of NHBuEt containing four drops of water was treated with CO_2, the appearance of a white solid was observed, this precipitate was identified to be bicarbonate salt of the NHBuEt when analyzed by FTIR (the reaction between water and amine is favourable). This precipitate disappears when the entire solution is reversed with heating to 60 ^{o}C and N_2 bubbling. On the other hand, when there is a significant amount of water present (1 mL water in 4 mL NHBuEt), the carbamate bicarbonate precipitate does not disappear. The melting point of this white salt was found to be 69 ^{o}C, and it showed the characteristic bicarbonate out-of-plan vibration band at 836 cm^{-1} in the FTIR spectrum.

The mass gained by the amine during its reaction with CO_2 should give an indication of the reaction stoichiometry; therefore, gravimetric measurements were done with NHBuEt. A sample of NHBuEt was weighed, and as CO_2 was bubbled through the solution, periodic mass measurements were taken until no significant changes were observed. The final amount of CO_2 taken up by NHBuEt was 0.61 mol of CO_2 per mol of NHBuEt. Of the 0.61 mol of CO_2, 0.55 mol can be accounted as the actual reaction with the amine (to form carbamic acid and carbamate salts), and the other 0.06 mol is attributed to CO_2 dissolved in the ionic liquid. When compared to other solvents with similar polarity, CO_2 dissolution is about 2 wt. %.[71] Therefore, we based the 0.55 mol of reacted amine to fit the 2 wt. % of CO_2 dissolution, making it comparable to other ionic liquids. If we assumed that exactly half of the NHBuEt reacted (meaning 0.11 mol of CO_2 is dissolved) it will make the wt. % of CO_2 to be much higher than the 2 wt. %.

A variety of secondary amines were studied under this project, the number and structural assignments of the other secondary amines are shown in **Figure 3.4**. A comparison table of the ^1H and ^{13}C NMR signals of the non-ionic, ionic, and $[NH_2R'R'']^+[Cl]^-$ salts are shown in **Table 3.1** and **Table 3.2**.

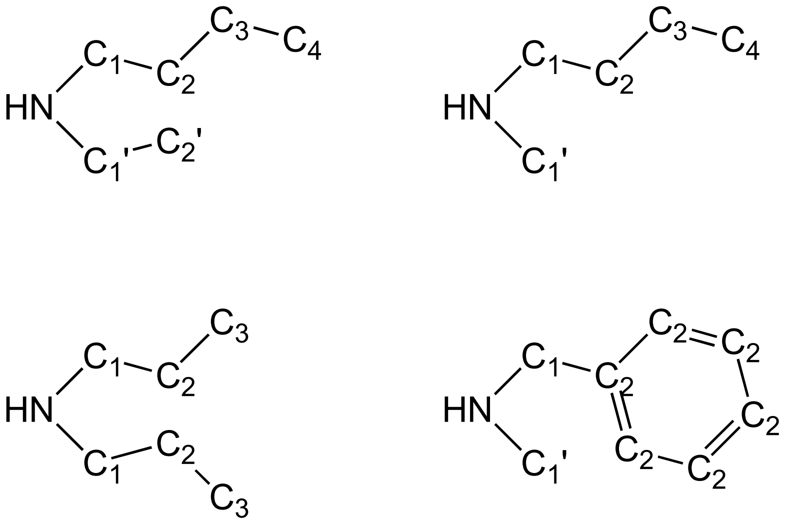


Figure 3.4 Numbering scheme used for ^1H and ^{13}C NMR assignments of the secondary amines.

Table 3.1 ^{1}H NMR spectroscopic data for amines and their carbamate salts relative to $CDCl_3$ at 7.25 ppm.

Species	C1	C2	C3	C4	C1’	C2’	C3’
NHBuEt	2.55 t 7.6 Hz	1.42 qn 7.5 Hz	1.28 sx 7.5 Hz	0.86 t 7.4 Hz	2.59 q 7.0 Hz	1.05 t 7.2 Hz	-
NHBuEt carbamate	3.15 br 2.68 br	1.44 br 1.98 br	1.26 br	0.84 t 7.4 Hz	3.15 br 2.78 br	1.02 br 1.18 br	-
$[NH_2BuEt][Cl]$	2.85 t 7.8 Hz	1.82 qn 7.8 Hz	1.36 sx 7.6 Hz	0.88 t 7.4 Hz	2.97 q 6.8 Hz	1.42 t 7.4 Hz	-
NHBuMe neutral	2.50 t 7.0 Hz	1.40 qn 7.3 Hz	1.27 sx 7.2 Hz	0.85 t 7.2 Hz	2.36 s	-	-
NHBuMe carbamate	2.94 br 2.54 br	1.32 br 1.20 br	1.04 br	0.62 t 7.4 Hz	2.54 br 2.27 br	-	-
$[NH_2BuMe]^+[Cl]^-$	2.95 t 7.8 Hz	1.87 qn 7.8 Hz	1.46 sx 7.5 Hz	0.98 t 7.4 Hz	2.70 s	-	-
$NHPr_2$	2.49 t 7.2 Hz	1.44 sx 7.2 Hz	0.84 t 7.4 Hz	-	-	-	-
$NHPr_2$ carbamate	2.73 br 3.17 br	1.70 br 1.54 br	0.89 br	-	-	-	-
$[NH_2Pr_2]^+[Cl]^-$	2.91 br	1.96 sx 7.9 Hz	1.03 t 7.4 Hz	-	-	-	-
NHBzMe	3.68 s	7.1-7.3	-	-	2.39 s	-	-
NHBzMe carbamate	4.43 s 3.78 s	7.1-7.4	-	-	2.80 s 2.27 s	-	-
$[NH_2MeBz]^+[Cl]^-$	3.96 s	7.4-7.6	-	-	2.42 s	-	-

Abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet or apparent quintet, sx = sextet or apparent sextet.

Table 3.2 ^{13}C NMR spectroscopic data for amines and their carbamate and HCl salts in $CDCl_3$, with all chemical shifts relative to $CDCl_3$ at 77.0 ppm.

Species	C1	C2	C3	C4	C1’	C2’	CO
NHBuEt	49.4	32.1	20.4	13.9	44.0	15.1	-
NHBuEt carbamate	46.6 45.7	30.6 28.5	19.8	13.4	41.8 40.8	11.6	161.5
$[NH_2BuEt]^+[Cl]^-$	47.1	27.9	20.1	13.5	42.7	11.1	-
NHBuMe	51.9	32.1	20.4	14.0	36.5	-	-
NHBuMe carbamate	48.1	29.6 27.6	19.5	13.2	33.4 32.3	-	161.9
$[NH_2BuMe]^+[Cl]^-$	49.2	27.8	20.0	13.5	32.8	-	-
$NHPr_2$	51.9	23.2	11.7	-	-	-	-
$NHPr_2$ carbamate	48.9 48.1	21.2 19.7	10.8	-	-	-	161.2
$[NH_2Pr_2]^+[Cl]^-$	49.3	19.4	11.3	-	-	-	-
NHMeBz	56.1	140.4 128.4 128.1 126.9	-	-	36.1	-	-
NHMeBz carbamate	51.8 39.8	138.8 132.6 125-132	-	-	33.5 31.0	-	161.7
$[NH_2MeBz]^+[Cl]^-$	52.1	130.3 129.8 129.6 129.2	-	-	31.2	-	-

3.3.2 ^{1}H NMR spectroscopy of $NHPr_2$

Another method to study the switchability and the formation of the ions in our secondary amines was to do ^{1}H NMR spectroscopy studies as the amine is being turned into its ionic form. $NHPr_2$ was chosen for this study because of its symmetrical structure. **Figure 3.5** is a stacked plot of the ^{1}H NMR spectra over the period of CO_2 exposure. The non-ionic form of $NHPr_2$ has three sets of peaks, a triplet at 2.49 ppm, a sextet at 1.44 ppm, and another triplet at 0.84 ppm.

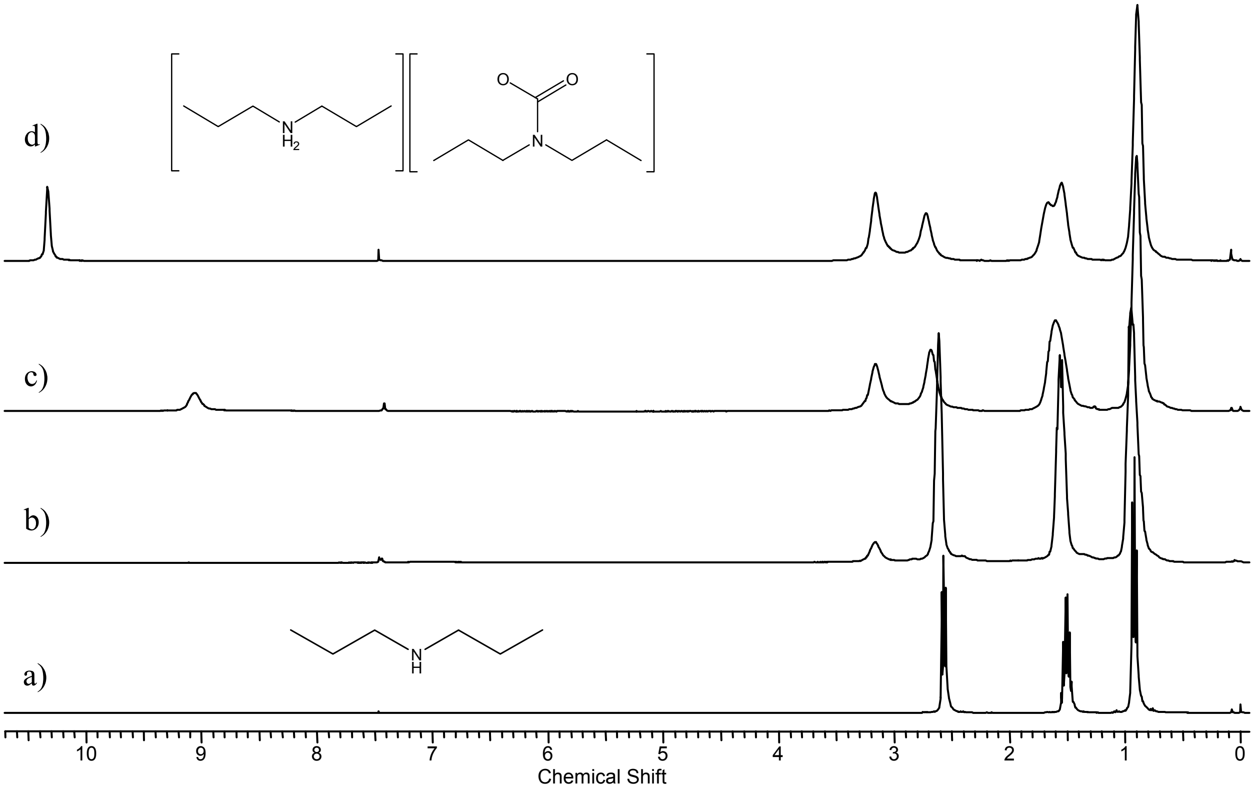


Figure 3.5 Stacked ^{1}H NMR spectra of $NHPr_2$ during treatment with CO_2. a) neutral $NHPr_2$ before CO_2 exposure; b) after 1 min of CO_2 exposure; c) after 2 min of CO_2 exposure; c) after 3 min of CO_2 exposure; d) after 4 min of CO_2 exposure.

As CO_2 is being added, we can see the growth of two new peaks at 3.17 ppm and 1.54 ppm. These two new peaks are fully formed after 2 min of CO_2 treatment. These peaks can be assigned as the anion and cation because the integrations of these peaks are roughly in a 1:1 ratio. The ^{13}C NMR peak of the carbonyl at 161.2 ppm is comparable to the δ(C=O) at 158 ppm of i-PrNHCOOH,[60] and the peak at 21.2 ppm is similar to the carbamic acid of isopropylamine at 21 ppm.[60]

Our detection methods were all done at room temperature, so when comparing our results to that of the literature, we can see that there are times when we could not detect the presence of one of the species, hence, we had to use results from many techniques. The ^{1}H NMR spectrum of the ionic form of $NHPr_2$ (**Figure 3.5d**) shows a singlet at 10.4 ppm, and two sets of equal intensity propyl resonances, suggesting the presence of two different species. The 10.4 ppm peak is higher than that of the $[NH_2Pr_2]^+[Cl]^-$ signal at 9.43 ppm, but this could be due to the presence of mixture of acidic protons of both the carbamate acid and cation.[62] We have experimentally confirmed that mixtures of NHBuEt and $[NH_2EtBut]^+[Cl]^-$ in $CDCl_3$ give rise to only one set of resonance. This result also agreed with the analyses done by George and Weiss[72] where they show that the detection of carbamate anion is concentration-dependent, while the cation is independent.

There are three possible explanations for these spectrum characteristics. a) the reaction of the secondary amines could have proceeded to complete conversion to the carbamate salt, giving signals for the cation, $[NH_2Pr_2]^+$, and for the anion, $[O_2CNPr_2]^-$. b) the second explanation is that half of the amine is converted to the carbamic acid, which is hydrogen bonding (R'R"NH•••$HO_2CNR'R"$) to unreacted amine molecules (akin to a carbamic dimer), thus giving one set of signal for the neutral amine, and the other set for HO_2CNPr_2. c) The third and most probable explanation, is that these signals come from a mixture of R'R"NH•••$HO_2CNR'R"$ and $[R_2NH_2]^+[O_2CNR_2]^-$ if the proton transfer did not go to completion.

One analytical technique alone will not clearly identify which species are present in the ionic form, thus we must combined individual verification from many analysis to clearly identify the composition of the ionic form. Carbamic acid peaks are identifiable by FTIR at low temperatures.[73] The IR spectrum of the ionic form of $NHPr_2$ showed new bands at 1618 and 1537 cm^{-1}. The 1537 cm^{-1} band is consistent with the carbamate anion[74] at 1545 cm^{-1} or while the band at 1618 cm^{-1} is not too far off from the carbamic acid observed for $(PhCH_2)_2NCO_2H$[73] at 1640 cm^{-1}. Works done by Dijkstra have shown the detection of the carbamic acid δ(O-H) (6.2 ppm in CDCl3, and at 9.2 ppm in DMSO) after isopropyl amine is reacted with CO_2,[60] (this indicates that the detection of the acid is solvent dependent) Dijkstra et al. also detected bands at 1575 and 1650 cm^{-1} which verify the presence of the carbamate anion and carbamic acid, respectively. Another influential factor is temperature at which the analysis is done, at higher temperatures there is fewer carbamic acid presence because of its instability, the detection of the acidic protons are more profound below 236 K.[62] Higher pressures also favour the formation of the carbamic acid.[60] The presence of carbamic acid was also proven by Radeglia when he formed the methylester of DIMCARB with diazomethane.[62] The carbamic acid of dimethylamine and dimethylamine were always found in a 1:1 ratio by hydrogen bonding to each other.[63] Although our amines are different from those in the literature, there are many similar spectroscopic results, therefore it does suggest the presence of both carbamic acid and carbamate salts, supporting our third interpretation.

Being a mixture of carbamic acid and carbamate salt can have significant effects in terms of applications of this system. Firstly, their melting points will be lower, because of its impure state. Secondly, it concludes that these amines do not react with CO_2 to completion, which will affect the polarity of its ionic form, this is case, and it will always be lower because of the presence of the unreacted amines will decrease the polarity of the ionic form. The formation of carbamates is temperature dependent as shown by Dibenedetto et al. (in their study of primary amines),[61] at low temperatures (273K) the salt slowly converts to carbamic acid dimers.

3.3.3 FTIR analysis and the melting points of $[NH_2R'R'']^+[Cl]^-$ salts

FTIR spectrum of non-ionic and ionic forms also proved the switchability of these amines, their signals are shown below (s = strong; m = medium; w = weak signals).

a) NHBuMe:

Before CO_2 treatment: 2961 s, 2921 s, 2867 m, 2787 w, 1464 w, 1380 w, 1147 w, 1124 w

After CO_2 treatment: 2961 s, 2928 s, 2867 s, 2464 w, 1626 m, 1552 m, 1474 s, 1377 s, 1306 s, 1255 m, 1056 w, 1032 w.

b) NHBzMe:

Before CO_2 treatment: 3027 s, 2967 s, 2932 m, 2843 m, 2789 s, 1495 s, 1474 m, 1453 s, 1356 w, 1104 w, 1073 w.

After CO_2 treatment: 3029 m, 2840 m, 2787 m, 1622 m, 1555 m, 1494 s, 1447 s, 1380 s, 1261 m, 1023 m.

c) $NHPr_2$:

Before CO_2 treatment: 2961 s, 2928 m, 2867 m, 2800 m, 1457 m, 1360 w, 1130 m

After CO_2 treatment: 2955 s, 2930 s, 2868 s, 1618 m, 1537 m, 1465 s, 1403 s, 1311 m, 1260 m, 1060 w.

d) NHBuEt:

Before CO_2 treatment: 2956 s, 2927 s, 2871 m, 2810 m, 1462 w, 1375 w, 1128 w

After CO_2 treatment: 2954 s, 2927 s, 2874 m, 2356 w, 1615 m, 1548 m, 1467 s, 1410 s, 1370 m, 1296 s, 1063 w.

The salts were synthesized to locate the appropriate shifts in the ^1H NMR spectra, data in **Table 3.1**. The melting points of $[NH_2EtBu]^+[Cl]^-$ (197 °C, lit[75] 197 °C), $[NH_2MeBz]^+[Cl]^-$ (178-180 °C, lit[76] 178-179 °C), $[NH_2Pr_2]^+[Cl]^-$ (sealed tube 263-265 °C, lit[77] 268-269 °C) and $[NH_2BuMe]^+[Cl]^-$ (174 °C, lit[78] 174-175 °C) match closely or exactly those reported in the literature. There was no literature precedent for the melting point of $[NH_2{}^{sec}BuPr]^+[Cl]^-$, which we found to melt at 182 °C.

3.3.4 UV/Visible spectroscopy of NR in secondary amines SPS

A solvent's polarity can be measured using a solvatochromic dye by UV/Visible spectroscopy. The UV/Visible spectra of a dye in the two forms of the SPS can be used to measure the polarity change after the reaction with CO_2. The solvatochromic dye, Nile Red (NR), was used in these sets of experiments to obtain the λ_{max} of the dye in the amine solution. Reichardt's "$E_T(30)$" dye is not compatible with these systems because the carbamic acids can bleach the dye, and results in unreliable measurements. The λ_{max} of

NR in neutral amines was measured, before and after its reaction with CO_2. The liquid was heated to 60 °C with N_2 bubbling for 1 h, the absorbance was again measured to see if the amine was able to be reversed back to the original value. These NR λ_{max} values are presented in **Table 3.3.**

Table 3.3 Solvatochromic data for Nile Red in the chosen secondary amines and other liquids for comparison.

Liquid	λ_{max} of non-ionic	λ_{max} of ionic	λ_{max} of non-ionic[a]
NHBuEt	517 nm	531 nm	519 nm
$NHPr_2$	518 nm	530 nm	521 nm
NHBuMe	519 nm	536 nm	530 nm
NHBzMe	532 nm	542 nm	536 nm
NHBuPr	516 nm	523 nm	516 nm
NHMePr	525 nm	537 nm	536 nm
Diethyl ether	504 nm[52]	-	-
Ethyl acetate	520 nm[52]	-	-
Acetone	530 nm[52]	-	-
DBU/HexOH	536 nm	543 nm	-
DMF	541 nm[52]	-	-
Methanol	550 nm[52]	-	-
$[bmim]^+[BF_4]^-$	-	551 nm[79]	-
$[PMeDec_3]^+[Br]^-$	-	525 nm[80]	-

[a] After N_2 was bubbled through the ionic form for 2.5 h at 60 °C.

In all cases where the secondary amine remains a liquid in its ionic form, there was a change in NR λ_{max}. NHBuEt, $NHPr_2$, NHBuMe, NHBzMe, NHBuPr, and NHMePr were all liquids in their ionic forms and showed an increase in NR λ_{max}. Note that NHBuMe and NHMePr were not able to be reversed back to the original NR λ_{max} value.

Compared to the NR λ_{max} value of $[bmim]^+[BF_4]^-$, all the NR λ_{max} values of our carbamate salt liquids are lower. Although model calculations of methyltridecylphosphonium bromide have been reported to have a λ_{max} of 525 nm,[80] no other ionic liquids exhibit NR λ_{max} in such low values. These secondary amine switchable solvents may be the first SPS ionic liquids to exhibit such a low NR λ_{max} value. Their low NR λ_{max} values can be attributed to the fact that this SPS is a mixture of carbamic acids, carbamate salts, and unreacted amines. As previously discussed, the reaction of this SPS does not go to completion, and the presence of the neutral amine could decrease the overall polarity of the ionic form.

One benefit of this set of secondary amines is that they have different ranges of polarity. This can be useful in cases where a reaction or chemical process requires a solvent to be at a specific polarity for a specific purpose, thus, one can just pick out the amine that possesses the desire polarity range. When compared to conventional solvents, our amines can have the polarity range from ethyl acetate (NR λ_{max} = 520 nm) up to that of DMF (NR λ_{max} = 541 nm). When compared to the first SPS discussed in Chapter 2, the NR λ_{max} of DBU/ROH, ranged from 536 nm to 543 nm,[37] which is similar to the range exhibited by NHBzMe.

It should be noted that not all of the NR λ_{max} of secondary amine amines were able to be switched back to the neutral form. Repeated trials with NHMePr and NHBuMe did not give the same reversibility in polarity as the other amines. Possible reasons for this behaviour could be that these two amines are more volatile[81] than the rest, and also their ionic forms are more thermodynamically favourable, thus it takes a longer time for them to reverse back to their non-ionic form.

3.3.5 Viscosity measurements

All the secondary amines have drastically higher viscosity in their ionic forms than their non-ionic forms, this high viscosity is a common characteristic that all ionic liquids possess.[82] The viscosity values are reported in **Table 3.4**.

Table 3.4 Viscosities of various secondary amines in the neutral and ionic forms.

	Viscosity (cP)	
Amine	Non-ionic form	Ionic Form
NHBuEt	0.57	59.3
$NHPr_2$	0.52	33.5
NHBuMe	0.48	55.7
NHBzMe	1.70	4.00×10^3

Generally, all the secondary amines show an increase in viscosity when they are in their ionic forms, which is one indication of the formation of an ionic liquid.[83] The first three amines: NHBuEt, $NHPr_2$, and NHBuMe all have viscosities in the neutral form comparable to that of methanol (from Aldrich) at 0.55 cP. In their ionic forms, their viscosities are comparable to that of most vegetable oils. NHBzMe is the exceptional case, where the viscosity is similar to water in its non-ionic form and is drastically increased after exposure to CO_2 to a value that is higher than honey (3000 cP)[84] and maple syrup (3200 cP).[29]

3.3.6 Conductivity measurement of NHBuEt

The neutral forms of the amines contain no ions; therefore, we would expect this form to have no conductance. After exposure to CO_2, the ionic forms contain ions and therefore should have conductivity. The starting conductivity of the neat sample of NHBuEt is 0.00 μS/cm (**Figure 3.6**). As CO_2 was bubbled through the vial, the conductance was recorded at 5-min intervals. Initially, there was a steady increase in conductivity because this is the onset of the reaction. After about 50 min, the rise is slower, indicating that the reaction was nearing completion. The conductivity reached a maximum value of 92 μS/cm, and this level was maintained even after an extended period of CO_2 exposure. After 60 min, the vial was heated to 60 ^{o}C and bubbled through with N_2. Even though the profile of the reversing process was not tracked, a final conductivity of 0.00 μS/cm was reached. The readings from 85 to 95 min were done after the solution had been sufficiently reversed to its neutral form. Normally, pure ionic liquids have very high conductance; for example, 1-ethyl-3-methylimidazolium ethylsulfate[85] is 398 μS/cm, butyltrimethylammonium bis(trifluoromethylsulfonyl)imide[86] is 0.21 μS/cm. Since the ionic forms of our amines are mixtures of its carbamic acid, neutral amine and carbamate salts, the low values in the conductance of the ionic form are plausible.

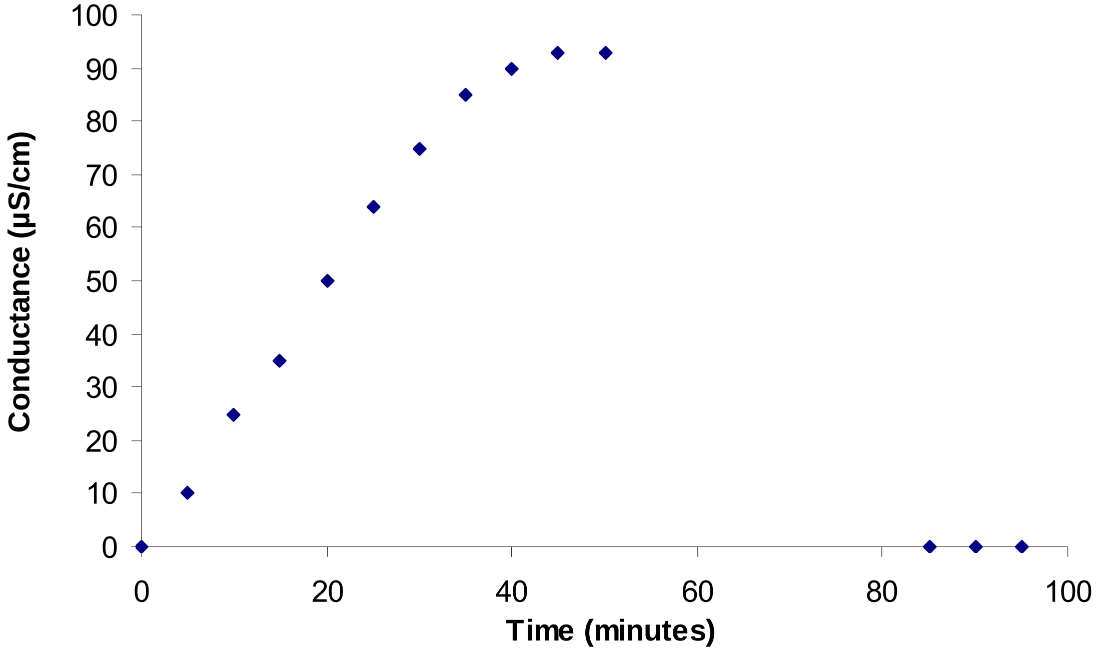


Figure 3.6 Conductivity profile of neat NHBuEt done at room temperature. From time 0 to 60, the amine is being turned into the ionic form. From 60 min, the ionic form is being reversed back to the non-ionic form.

Viscosity plays an important role in the ability of a liquid to conduct an electrical current. To alleviate the viscosity factor, it was decided to study the conductance of NHBuEt in a non-conducting solvent. The conductivity of a solution of neat NHBuEt carbamate is 92 µS/cm, but in anhydrous DMSO, the conductivity rises to 334 µS/cm. We have observed that the ionic form is a viscous mixture composed of neutral amine, carbamic acid, and carbamate salt; all of these factors contribute to the overall low conductivity of this solvent. The greater conductivity in DMSO is because the presence of a solvent increases the mobility of the ions by lowering the viscosity of the solution.

Another purpose of this experiment was to demonstrate the equilibrium position between the non-ionic form and the ionic form. If the two forms are similar in energy, then the equilibrium position should depend on the ratio of gases used. In such a case, amines exposed to 80 % CO_2 : 20 % N_2 would favour the ionic form when compared to a gas mixture of 20 % CO_2 : 80 % N_2. The results (**Figure 3.7**) do not agree with this prediction, in fact, it can be concluded that the ionic form is the preferred form, as each trial tends to settle out at the same conductivity regardless of the composition of the gas mixture. A closer look at the 80 % CO_2 : 20 % N_2 trial showed a spike very early in the run, reasons for this spike is unknown. For cases where the CO_2 concentration is lower than that of N_2, the rise is slower and more gradual. When DMSO is used as the solvent, the final equilibrium conductance is around 283 µS/cm for every trial

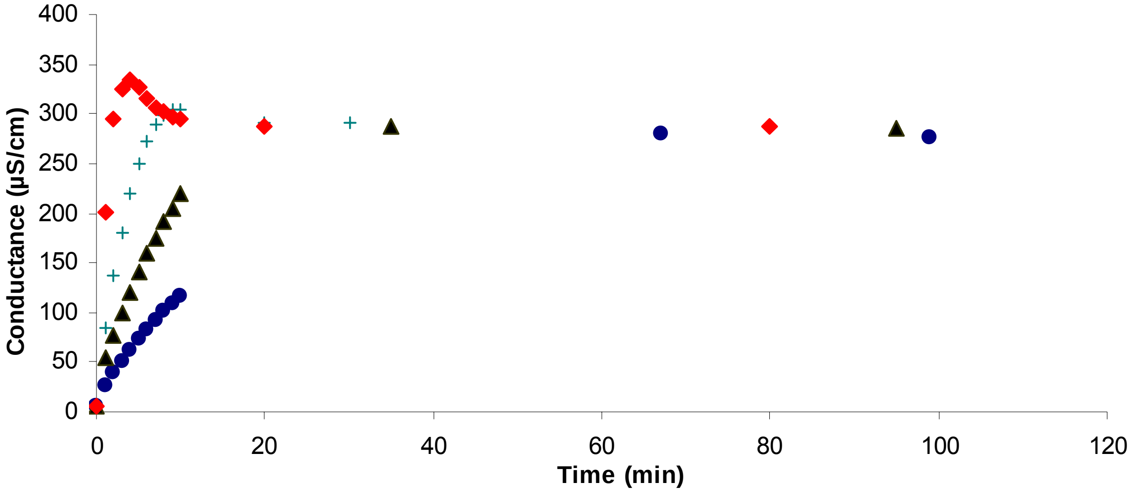


Figure 3.7 Conductivity profile of NHBuEt in DMSO (1:5 by moles) at room temperature. (♦) 80 % CO_2 : 20 % N_2; (+) 60 % CO_2 : 40 % N_2; (▲) 40 % CO_2 : 60 % N_2 (●) 20 % CO_2 : 80 % N_2.

3.3.7 Solubility and miscibility tests

The change in the polarity of a solvent can drastically affect its ability to dissolve certain chemicals. For example, a polar solvent would dissolve a polar solute, while a non-polar solvent would dissolve a non-polar substance. We have already seen that secondary amines can go from a lower polarity liquid to a higher polarity liquid after exposure to CO_2, therefore, it can be envisioned that a certain substance would be soluble in one form and not the other. Various substances were qualitatively tested for their solubility in the non-ionic form, after which CO_2 was added to convert the amine to the ionic form, and the solubility of the substance was tested again.

All solubility and miscibility tests were done using NHBuEt. There seems to be a few general trends that can predict whether a substance will be soluble or insoluble in any of the two forms (**Table 3.5** and **Table 3.6**). Low polarity solids such as polystyrene (both MW = 2,000 and 100,000) and tetracosane dissolved in the non-ionic form, and precipitated out of solution in the ionic form. Polar solids such as polyacrylic acid sodium salt and poly(sodium-4-styrene sulfonate) were insoluble in both forms, while cellulose, benzyltriethylammonium chloride, (vinylbenzyl)trimethylammonium chloride were insoluble in both forms. Both the sodium toluenesulfonate and tetraethylammonium-p-toluene sulfonate, along with glucose were insoluble in the non-ionic form, while they were solubilized in the ionic form. Many other substrates showed solubility in both forms, notably ibuprofen, which is capable of protonating amines, was soluble in both forms. This explanation can also be used to explain the behaviour of glucose, which only dissolves in the ionic form, as the presence of the acid may react with the sugar. A dehydration reaction between the sugar and carbamic acid is the most probable case, as the final solution was black when left over a long period of time.

Table 3.5 Dissolution results of 0.5 g various solids in both forms of NHBuEt.

Solute	Non-ionic form	Ionic form
Benzyltriethylammonium chloride	X	X
Poly(sodium-4-styrene sulfonate)	X	X
Polyacrylic acid sodium salt	X	X
(Vinylbenzyl) trimethylammonium chloride	X	X
Cellulose	X	X
Tetraethylammonium-p-toluene sulfonate	X	√
Sodium toluene sulfonate	X	√
Glucose	X	√
Tetracosane	√	X
Polystyrene MW 2,000	√	X
Polystyrene MW 100,000	√	X
Stilbene	√	X
Mesitylene	√	√
Ibuprofen	√	√
Benzylbenzamide	√	√
Cholesterol	√	√

√: totally dissolved; X: insoluble or has some undissolved solids remaining.

Table 3.6 Miscibility of 0.5 mL various liquids in both forms of NHBuEt.

Solute	Non-ionic form	Ionic form
Toluene	√	√
Decane	√	√
Hexadecane	√	√
Styrene	√	√
5-trans-decene	√	√
Propylene carbonate	√	√

√: miscible; X: immiscible

3.3.8 NHBuEt as a solvent for polymer/catalyst separation

This switchable polarity solvent system was applied in the alternating polymerization of cyclohexene oxide with CO_2 (**Figure 3.8**). The theoretical recycling of the amine solvent is possible because itsthe polarity switching that causes the polymer product and catalyst to separate (**Figure 3.9**) The polymerization was done without solvent in a pressure vessel at 35 bar CO_2, with the catalyst as Cr(salen)Cl, and $[PPN]N_3$ as co-catalyst.[87] The crude product was dissolved in distilled NHBuEt. After CO_2 was bubbled through the solution to get the ionic form, the polymer precipitated out of solution.

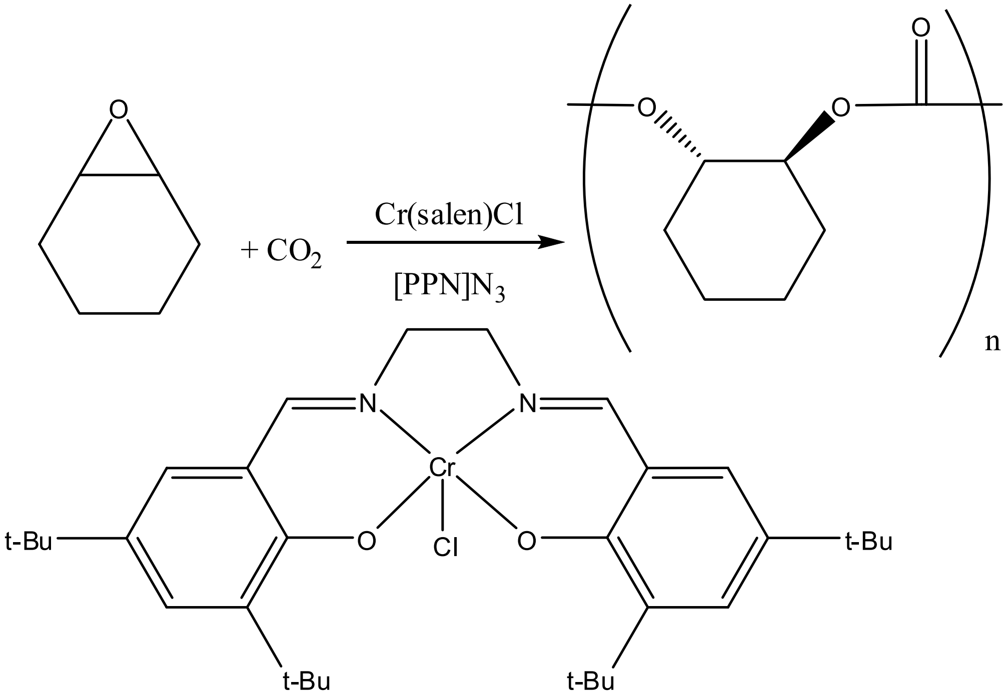


Figure 3.8 Reaction scheme for copolymerization of CO_2 and cyclohexene oxide.

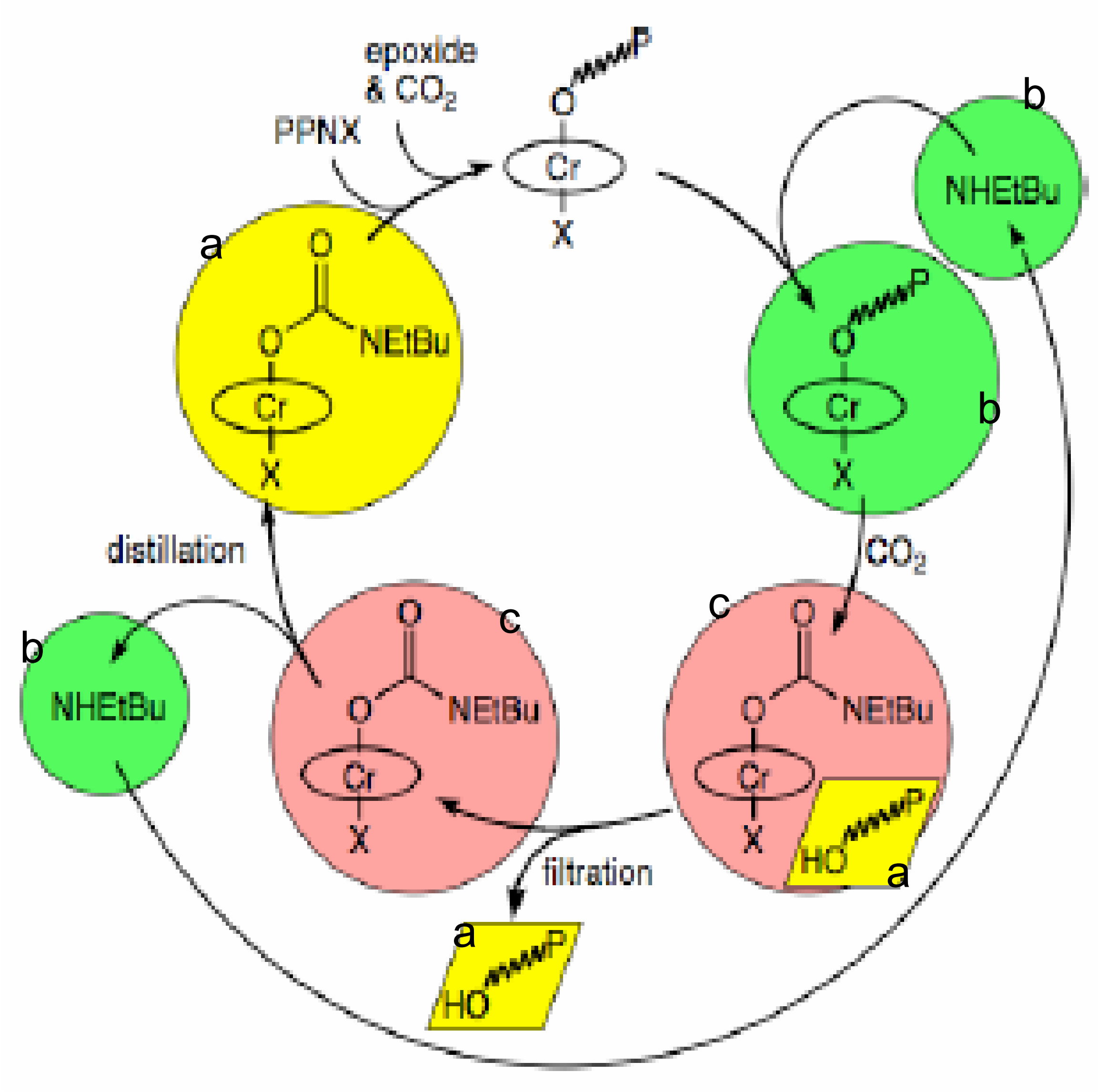


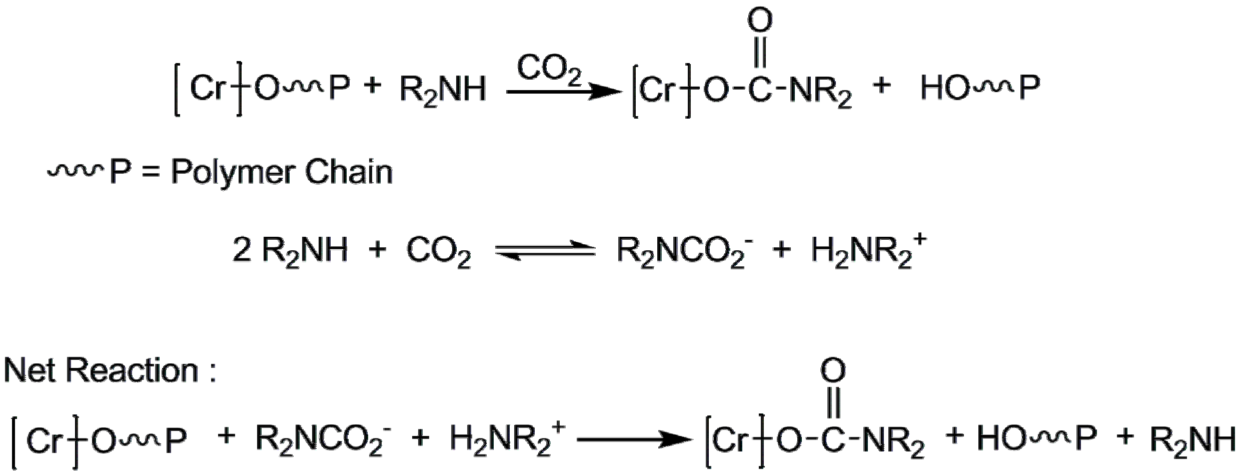
Figure 3.9 Recyclable schematic using NHBuEt in the copolymerization of CO_2 and cyclohexene oxide. [a] polymer attached; [b] solvent in non-ionic form; [c] solvent in ionic form

The separated polymer was easily filtered and gave a whitish solid ($M_n = 23000$ Daltons, PDI = 1.13) and left orange-brown solution of catalyst in ionic NHBuEt. There was still some traces of the catalyst in the polymer because of its slightly off-white colour (pure polymer is white.) The separated polymer can be further treated with more washes using the ionic form of NHBuEt to remove the remaining traces of catalyst. Samples of the polymer after the first treatment with ionic ethylbutylamine and the final product were submitted to GPC analysis to ascertain any effects of the separation process on the molecular weight of the polycarbonate (**Table 3.7**).

Table 3.7 Polymer degradation changes after first wash and final wash.

Sample	M_n (Daltons)	M_w (Daltons)	PDI
First	23,106	26,145	1.132
Final	23,335	25,751	1.104

A comparison of the data obtained implies that the separation process does not degrade the polymer in any way. The molecular weight values for the isolated polymers were also similar to the polymer obtained from washing with a typical acidified methanol method; a 1M HCl solution in methanol is added to the polymer-catalyst mixture to promote the precipitation of the polymer, because the acid will cleave the catalyst from the polymer. In both separation techniques, the presence of an acid is required to cleave the Cr catalyst from the polymer chain. When NHBuEt is used as the extraction solvent, after its reaction with CO_2, the formation of the carbamic acid could act in the same manner as the HCl, where it cleaves off the polymer and leave the catalyst remaining in the ionic liquid medium. The reaction scheme for this catalyst cleavage is shown in **Figure 3.10**. Note that there is no experimental evidence confirming that the carbamic acid performs this role or that a carbamate ligand ends up with the Cr atom.



$$[Cr]\text{-}O\sim P + R_2NH \xrightarrow{CO_2} [Cr]\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NR_2 + HO\sim P$$

$\sim P$ = Polymer Chain

$$2\,R_2NH + CO_2 \rightleftharpoons R_2NCO_2^- + H_2NR_2^+$$

Net Reaction :

$$[Cr]\text{-}O\sim P + R_2NCO_2^- + H_2NR_2^+ \longrightarrow [Cr]\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NR_2 + HO\sim P + R_2NH$$

Figure 3.10 Extraction reaction of the carbamate of NHBuEt in polymer separation procedures.

The catalyst contained in the carbamate salt eluent was recovered by distilling off the CO_2 and NHBuEt. The catalyst was then re-used for the next solventless copolymerization run, with a fresh batch of cyclohexene oxide and CO_2. Copolymer yield (17 g compared to 21 g in the first run) and M_n (15,300) decreased, while the PDI is 1.10. This showed that catalytic activity had decreased, but this can be improved if a better catalyst recovery method is found. A visual comparison of the three polymer samples is shown in **Figure 3.11**.

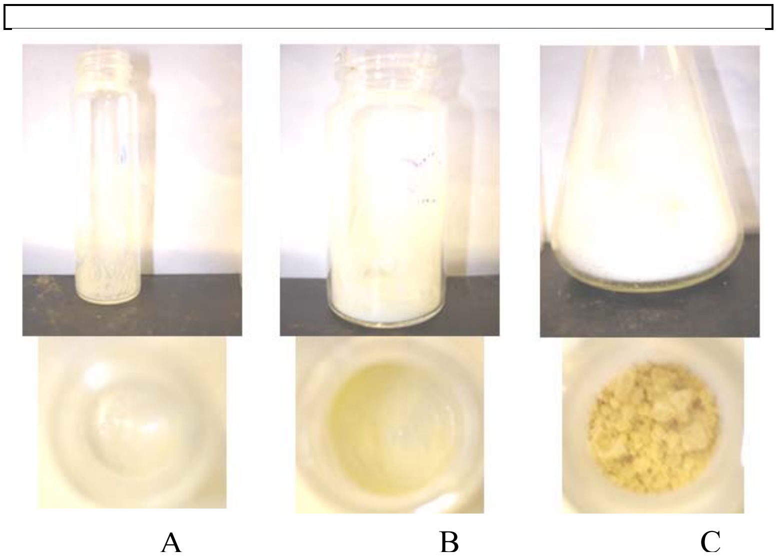


Figure 3.11 Separated polymer samples: A) White polymer isolated by acidified methanol wash, b) Lightly yellow polymer isolated after first carbamate wash with ethylbutylamine, c) Intense yellow polymer isolated after second carbamate salt wash with NHBuEt. The gradient bar above is representative of the intensity of the colours of the polymers obtained.

3.4 Conclusions and Future Work

These carbamate salt ionic liquid SPS systems have many potential uses in chemical processes. They have clear advantages over the DBU/ROH SPS system in terms of water sensitivity, polarity range and being a single component solvent. Yet no system is perfect for every chemical process. The disadvantage in using amines as solvents is that no acidic or alkylating reactions can be used, and that certain amines can be toxic. For example, the LD_{50} of NHBuEt is 310 mg/kg in rats, which is about rated as moderately toxic according to the Canadian Centre for Occupational Health and Safety. Nevertheless, the same benign trigger of CO_2 is used to activate, while heat and N_2 can reverse the system, and the solvent switchability and recyclability are major advantages when considering the costs of solvents in any chemical work, and these amine SPS have been shown to be recyclable over many reaction cycles.

There will likely be numerous secondary amines that give liquid carbamate salts. There is likely to be a wide range of polarity available. All the chemical application done during this thesis work has been with NHBuEt, and some procedures were unsuccessful because of the polarity range of NHBuEt. Further work should be done with the more polar amines, such as NHBzMe.

Chapter 4: Soybean Oil Separation

4.1 Introduction

4.1.1 Properties and uses of soybeans

Soybean, *Glycine max*, is a legume native to eastern Asia. It can grow as high as 2 m. The leaves contain three to five leaflets. The seed, small and round, is stored in the leaf. When matured, the soybean can take on many colours, ranging from yellow to dark brown. The soybean contains 40 % protein, 20 % oil, 35 % carbohydrates and 5 % ash.[88] Soybeans are used in the food industry as soy meal and soy oil. The former is used as meal feed for animals. The latter is used as vegetable oils for cooking purposes, or substitutes for cheese and margarine. Other industrial uses of soybean are: biodiesel, plastics, inks, soaps, resins and clothing additives.

In 2004, soybeans were planted on 30.4 million hectares in the U.S., with a total market value greater than $17.7 billion. The United States produce roughly 40 % of the soybeans in the world, with exports to Canada, China, Japan, Mexico and countries in the European Union.

Significant advantages of soybean oil over other vegetable oils include that it:[88] (a) has higher levels of unsaturation, (b) remains liquid over a wide range of temperatures, (c) is easy to selectively hydrogenate, (d) contains antioxidants such as tocopherol that are not easily removed during processing.

4.1.2 Industrial methods of soybean processing

One historical extraction method for soybean oil is the hydraulic pressing method. As the name suggest, this method uses a hydraulic ram to compress the seeds together to release the oil. This method is quite labour intensive, hence has been abandoned in favour of more feasible processes.

The current extraction method for today's oil industry is solvent extraction as a "batch process". The first industrial scale implementation of this solvent-extraction process was introduced in the United States in 1930.[88] This large-scale extraction process involves a counter-current flow of hexanes and soybean flakes, (a saturated solution of oil in hexanes is called the miscella). The best continuous soybean extraction has a solvent-to-bean ratio of 1.0 or less by mass, which is equivalent to a solvent-oil mass ratio of 5. Oil seeds arriving at the plant must be pretreated before exposure to hexanes. The seeds are cracked and crushed into paper-thin flakes, then soy oil is extracted and purified.

The solvent currently being used for soybean extraction is hexanes, although it poses some environmental and flammability issues. For a general industrial extraction, up to 7.6 L of hexane is lost per ton of seed processed.[88]

4.1.3 Our strategy for separating soy oil

The Jessop group has been collaborating with researchers at Pacific Northwest National Lab (PNNL) to devise new methods for soy oil extraction and separation. Their research team is determining which solvents would give the maximum soy oil extraction from the flakes. We will investigate different methods to separate the oil from extracting solvent. We currently have six separate strategies for separation.

The first is to use an upper critical solution temperature (UCST), which is defined by IUPAC[89] as the temperature at which two immiscible liquids become miscible. We will test a series of solvents. The soy oil extraction would be done with the solvent above its UCST, and the separation will occur by lowering the temperature below the UCST. If this solvent is immiscible with soy oil at room temperature, then its UCST will be identified. On the other hand, if this solvent is miscible with soy oil at room temperature, meaning that its UCST is below room temperature, the temperature must be lowered to cause immiscibility. The figure below explains the concept of this strategy.

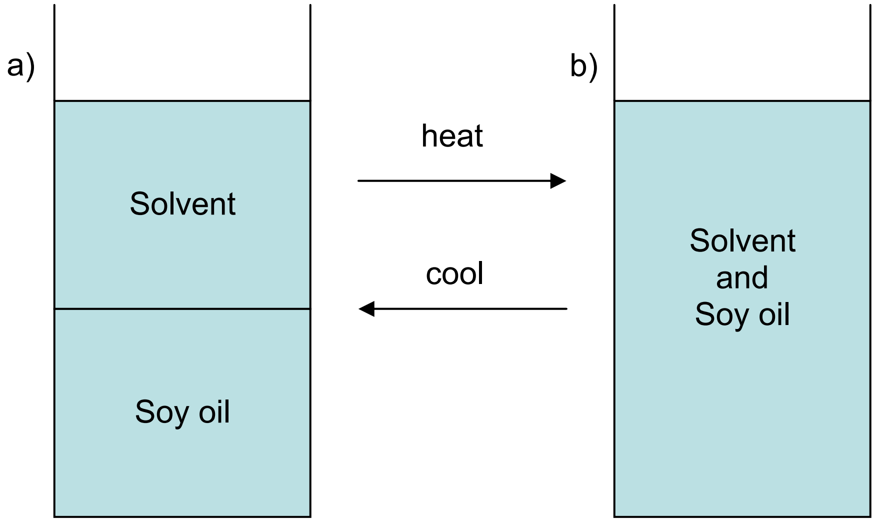


Figure 4.1 Soy oil separation using the UCST strategy. a) soy oil and solvents (immiscible) will need to be heated to its UCST to induce miscibility; b) miscible mixture of solvent and soy oil at or above its UCST.

The second strategy is to use CO_2-expanded solvents[90] to induce a polarity change to cause the oil to separate from or merge with the solvent. When a solvent and soy oil are contained in a vessel that has been pressurized with CO_2, the solvent will absorb CO_2 and expand, increasing its volume and decreasing its polarity. We hope that the change in polarity is sufficient and that it could be low enough for the solvent to become miscible with the oil. The soy oil extraction step will be done using the expanded solvent, after which the release of pressure will cause the soy oil to separate out. A set up of the apparatus is shown in **Figure 4.2**.

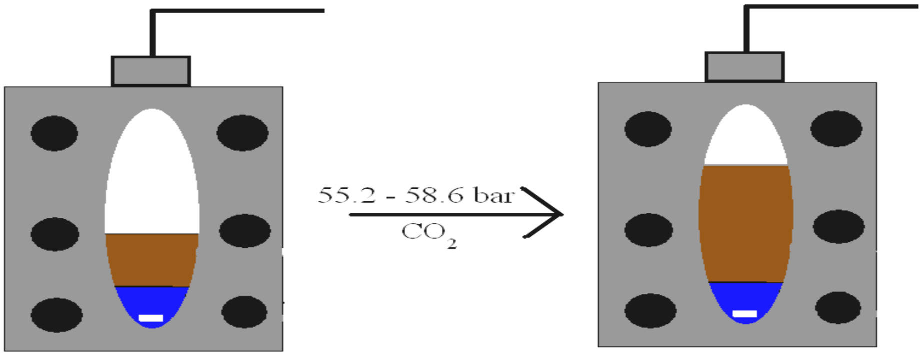


Figure 4.2 Using CO_2-expanded solvents as a strategy for soy oil extraction and separation.

The third strategy is to use an amidine-based switchable polarity solvents (SPS).[37, 38] When a trigger is applied to cause a polarity switch in the solvents, the change in polarity is sufficient to cause the soy oil to separate out (**Figure 4.3**).

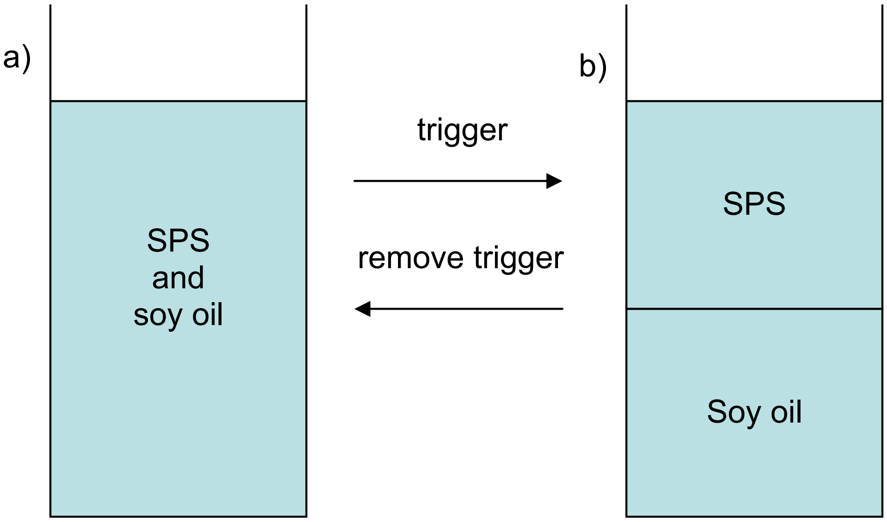


Figure 4.3 Schematic for oil separation using switchable polarity solvents. a) SPS and soy oil are miscible before the trigger is applied; b) the SPS and soy oil are immiscible after the trigger is applied.

The fourth strategy, similar to the third, uses a secondary amine-based SPS[91] that also exhibits a polarity increase after a trigger is applied. The same schematic (**Figure 4.3**) can be used to explain this strategy.

The fifth strategy is to use a surfactant to obtain an emulsion of the immiscible mixture soy oil and a solvent. This surfactant contains an amidine moiety,[17] which allows it to be turned "ON" when we need an emulsion, after which the surfactant can be turned "OFF" to allow the solvent and soy oil to separate. The diagram below explains how this strategy works.

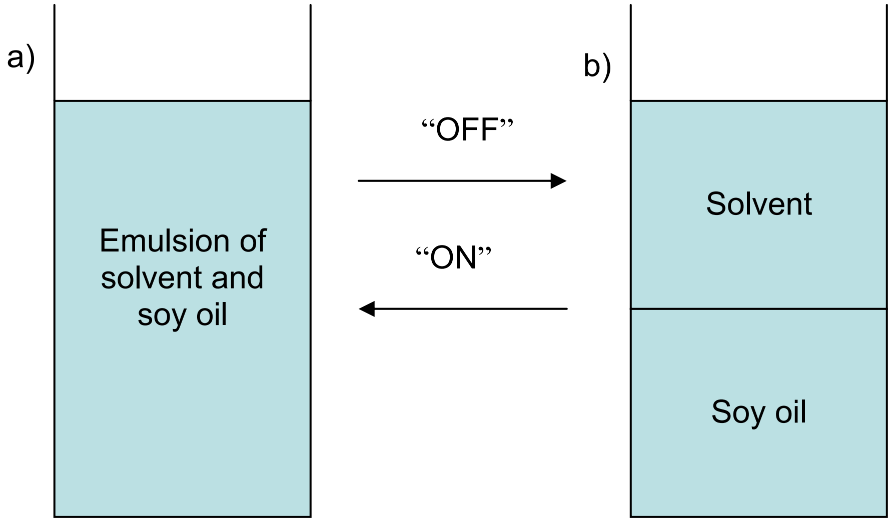


Figure 4.4 Using surfactants to separate soy oil. a) an emulsion is formed between soy oil and an immiscible solvent with the surfactant[17] in its "ON" form; b) when the surfactant is turned "OFF", the emulsion crashes out into two separate phase of soy oil and solvent.

All these strategies will be compared in terms of their ability to give the highest amount and purest soy oil. The soy oil was analyzed by ^{1}H NMR spectroscopy for any traces of the solvents that still remain after separation; these traces will be referred to as contamination level.

4.2 Experimental Methods

Soy oil was used as received from Bunge. DBU (Aldrich, 98% grade) was dried according to the methods in Chapter 2. Supercritical grade CO_2 (99.999%, H_2O < 0.5 ppm), nitrogen (99.998%, H_2O < 3 ppm) and argon (99.998%, H_2O < 5 ppm) were used as received from Praxair. NMR spectra were acquired at 400 MHz and referenced to TMS at 0 ppm unless specified otherwise. All other solvents were used as received from Aldrich or Fisher.

4.2.1 Miscibility tests

A vial containing 4.0 mL of solvent and 2.0 mL of soybean oil was stirred for 10 minutes and left to settle for 20 min, then the miscibility of the soy oil and solvent was visually observed.

4.2.2 Quantitative analysis of solvent/soy oil mixtures by ^{1}H NMR spectroscopy

A calibration curve was prepared in the following manner. Different masses of oil and solvents were charged into sealed vials. The contents of each vial were stirred and then allowed to settle. If required, the contents were heated to an appropriate temperature to achieve miscibility (UCST). The ^{1}H NMR spectrum of a portion of the mixture in $CDCl_3$ was acquired and selected peaks from 4.1 to 4.2 ppm associated with the oil were compared to selected peaks of the solvent that did not have any overlap (**Figure 4.5**). Their integration ratio was graphed against the mass % of solvent in the solvent and oil mixture (mass percentages ranged from 1 to 10 %). Such calibration curves were prepared for mixtures of soy oil with: n-PrOH, i-PrOH, EtOH, DBU, and NHBzMe.

The scan time for ^{1}H NMR analysis was 4 s, with a delay time of 1 s. Detection limits were as low as 0.01 wt. % of the solvent. When an unknown mixture of soy oil and solvent is analyzed, its peak integration ratio can be used to calculate the contamination level of that solvent in the soy oil. In order to calculate a contamination level of an unknown, a mathematical equation was then derived for each mixture.

4.2.3 Temperature-dependence on separation of soy oil and solvents

In a septum-capped vial, 4.0 mL of n-PrOH and 2.0 mL of soy oil were combined and stirred. The vial was cooled to the desired temperature (-15 to 15 ^{o}C). The vial was allowed to settle until two clear phases were observed, after which the soy oil layer was analyzed as described in Section 4.2.2.

In a septum-capped vial, 4.0 ml of EtOH and 2 mL of soy oil were combined and stirred. The vial was heated to 67 ^{o}C with strong stirring so that the contents became miscible, and then was cooled to different temperatures (-5 to 10 ^{o}C.) The vial was allowed to settle until two clear phases were observed, and the soy oil layer was analyzed as described in Section 4.2.2.

4.2.4 Time-lapse study on separation at -10 ^{o}C

A vial containing 4.0 mL of n-PrOH and 2.0 mL of soy oil was stirred and cooled to -10 ^{o}C. The vial was allowed to settle at different time intervals before the oil layer was analyzed at room temperature as described in Section 4.2.2.

4.2.5 Water effect on contamination of i-PrOH and soy oil

To a septum-capped vial containing a stir bar, 4.0 mL of i-PrOH (containing 5, 10 or 15 wt. % water) and 2.0 mL of soy oil were added. The mixture was heated to the UCST, until the two phases merged, after which the homogeneous mixture was allowed to cool to room temperature and the oil layer was analyzed as described in Section 4.2.2.

4.2.6 Liquid expansion of EtOH and soy oil

A liquid level flat gauge containing 4.0 mL of EtOH and 2.0 mL of soy oil and a magnetic stir bar was flushed with CO_2 three times. The gauge was filled with CO_2 to 58 bar at room temperature, and the contents were vigorously stirred for 10 minutes, the miscibility of soy oil and EtOH was recorded.

4.2.7 Separation of soy oil using switchable polarity solvents: amidine-base

CO_2 was bubbled through a mixture of 3.0 mL of DBU, 1.6 mL of EtOH, and 4 mL of soy oil in a septum-capped vial for 1 h with stirring. The contents were left to settle over night. The oil layer was analyzed as described in Section 4.2.2.

Similar procedures were done using different amounts of EtOH, MeOH, and water.

4.2.8 Separation of soy oil using secondary amine SPS

CO_2 was bubbled through a mixture of 4.0 ml of NHBzMe and 2.0 mL soy oil in a stirred and septum-capped vial for at least 1 h or until the heat from the reaction subsided. The contents were left to settle over night. The oil layer was analyzed as described in Section 4.2.2.

4.2.9 Emulsions between soy oil and water

The surfactants used were synthesized as outlined by Jessop et al.[17] 3.0 mg of the surfactant salt was added into a septum-sealed vial containing 4.0 mL of water and 2.0 mL of soy oil. CO_2 was bubbled into the mixture for 20 min with stirring. The contents were sonicated for 10 min, and left over night to test the stability of the emulsion.

4.2.10 Polymer-supported amidine as a solvent trapping agent

In a septum-sealed vial containing 2 ml of n-PrOH and 1 mL of soy oil, 0.5 g of polystyrene bound to DBU (available from Aldrich) was added. CO_2 was bubbled through the solution for 30 min, and then allowed to settle.

4.3 Results and Discussion

4.3.1 Miscibility results

Soybean oil is miscible with many organic solvents, especially those which are apolar and aprotic.[88] Beckel et al.[92] did extensive research in finding which solvents could be used as extractants. Of the seven solvents they studied (EtOH, i-PrOH, isobutyl alcohol, ethylene dichloride, trichloroethylene, carbon tetrachloride and hexane) EtOH gave the best extraction but the recovered oil was still not good enough for practical application, because it still has high levels of EtOH contamination.

The solvents chosen in this experiment (**Table 4.1**) have a wide range of physical characteristics such as dielectric constant and Hildebrand Parameter. Dielectric constant is a measure of the ability of a material to store a charge from an applied electromagnetic field and then transmit that energy, and the Hildebrand parameter is a measurement of the cohesion of a solvent, energy required to create a cavity in the solvent.[93]

Table 4.1 Solvent and soy oil miscibility at room temperature.

Solvent	Hildebrand Parameter	[a]Dielectric constant[94]	Miscible	Reference
i-Propylamine	--	--	yes	this work
Tripropylamine	--	--	yes	this work
DBU	--	--	yes	this work
Et_3N	7.4	2.4	yes	this work
Acetone	10.0	20.7	yes	[88]
Acetic acid	10.1	6.2	no	this work
Pyridine	10.7	12.9	yes	this work
i-PrOH	11.5	18.3	no	[88]
n-PrOH	11.9	20.1	yes	[88]
Acetonitrile	11.9	37.5	no	this work
DMF	12.1	36.7	no	this work
DMSO	13.0	46.6	no	this work
Ethanol	13.4	22.4	no	[88]
Methanol	14.5	32.6	no	[88]
Water	23.5	79.7	no	[88]

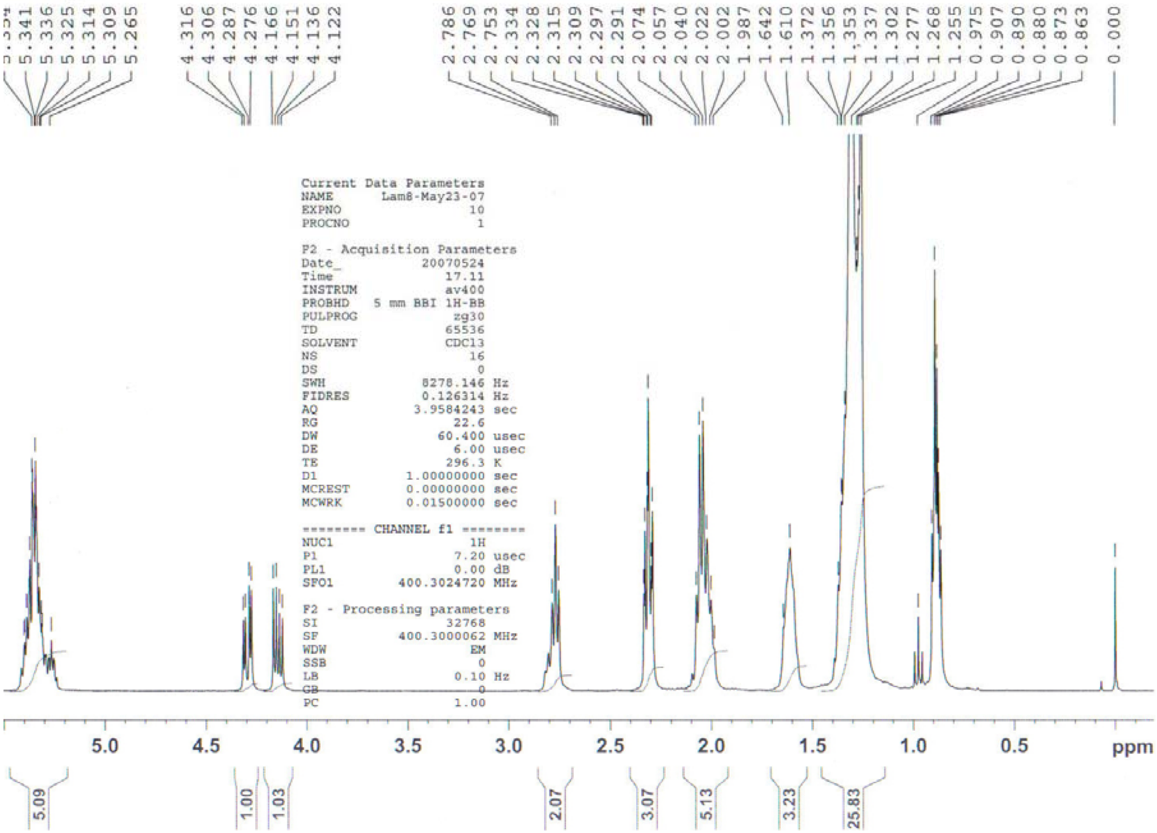
[a] Dielectric constant reported at 20 °C.

The dielectric constant of most vegetable oils is 3.0-3.2,[88] therefore it is not surprising to see that the solvents with high dielectric constant are immiscible with soy oil. The solvents that have a dielectric constant of 21 or higher are all immiscible with soy oil, while the dielectric constant below 21 seems to contain both miscible and immiscible solvents. The acidic solvent acetic acid is immiscible with soy oil while the basic solvent pyridine is miscible with soy oil. When we tested the other basic solvents, pyridine (pKa of its conjugate acid is 12.53 in acetonitrile[95]) showed miscibility with soy oil. Recent tests with DBU (pKa of its conjugate acid is 24.34 in acetonitrile[95]), which is a stronger base than pyridine, also showed miscibility with soy oil at room temperature. Triethylamine, tripropylamine and isopropylamine were all miscible with soy oil. Chlorinated solvents, like trichloroethylene and ethylene dichloride have been shown by Johnstone et al.[96] to be miscible, but due to their toxicity they are not suitable as extraction solvents.

The results from our miscibility tests identified the solvents that could be further investigated. The first strategy of using a UCST was tested for a set of selected solvents. A series of calibration graphs were prepared, and an equation was used to calculate contamination levels. Factors such as temperature, settling time, and excess water were studied for their effects on contamination levels.

4.3.2 Development of an analytical method

The purpose for generating these series of graphs is to use them as calibration curves to calculate the contamination of the soy oil. One set of peaks in the ^{1}H NMR spectrum of soy oil (**Figure 4.5**) and the solvent are integrated and compared. The set of peaks for oil is 4.2 to 4.3 ppm, 3.6 ppm for n-PrOH, 4.0 ppm for i-PrOH, 3.6 to 3.8 ppm for EtOH, 3.1 to 3.4 ppm for DBU, and 3.7 ppm for NHBzMe. The integration ratio of the oil:solvent and the wt. % of solvent was used to generate a mathematical formula that can be used to calculate the contamination level of an unknown mixture of that solvent in the soy oil.



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MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.20 usec
PL1                   0.00 dB
SFO1           400.3024720 MHz

F2 - Processing parameters
SI                   32768
SF             400.3000062 MHz
WDW                     EM
SSB                      0
LB                    0.10 Hz
GB                       0
PC                    1.00
```

Figure 4.5 ^{1}H NMR spectrum of soy oil in $CDCl_3$ at room temperature.

To derive the mathematical equation to use for all solvents and soy oil, we need to make some assumptions. The integration of the soy oil peak is compared to that of the solvent peak, and this ratio is correlated to the wt. % of solvent in the oil and solvent mixture. For an arbitrary 100 g sample, we would have:

$$W_{\text{oil}} + W_{\text{sol}} = 100 \text{ g} \qquad (1)$$

$$I_{\text{oil}} = W_{\text{oil}} \text{ x B} \qquad (2)$$

$$I_{\mathrm{sol}} = W_{\mathrm{sol}} \text{ x A} \qquad (3)$$

where "W_{oil}" is the wt. % of the oil and "W_{sol}" is the wt. % of the solvent, "I_{oil}" is the integration of the oil peak, and "I_{sol}" is the integration of the solvent peak. "B" and "A" are response factors that is inherit to the integration peak of the soy oil and solvent, respectively.

By rearranging "A/B" we actually are calculating for the integration ratio (IR).

$$IR = \frac{A}{B}\left(\frac{W_{Sol}}{100 - W_{sol}}\right) \qquad (4)$$

Therefore, after we obtain a series IR from the ^{1}H NMR spectra of the oil and solvent mixtures, we can plot IR vs. the $W_{\mathrm{sol}}/(100-W_{\mathrm{sol}})$, which will result in a linear graph, with the slope of that line being "A/B".

We can then use this general equation to calculate the contamination level of any unknown in a sample of oil, and the corresponding "A/B" will be strictly for a certain solvent.

$$W_{sol} = \frac{100IR}{\frac{A}{B} + IR} \qquad (5)$$

Table 4.2 Selected ^{1}H NMR spectra peaks and "A/B" values for the solvents used in deriving contamination formula.

Solvent	Peak (ppm)	"A/B"	H_{sol}	$(A/B)\bullet M_{sol}/H_{sol}$
NHBzMe	3.7	6.97	2	422
i-PrOH	4.0	7.03	1	423
n-PrOH	3.6	13.77	2	414
EtOH	3.6 to 3.8	15.22	2	351
DBU	3.1 to 3.4	17.27	6	438

The value of A/B is best determined experimentally, but it can also be predicted for other solvents using equation 5. The ratio of response factors A/B is the same as the ratio of factors that determine the peak intensity, because peak IR is proportional to H/M, where "H" is the number of H atoms responsible for that peak per molecule and "M" is molar mass, then we have:

$$\frac{A}{B} = \frac{H_{sol} \bullet M_{oil}}{H_{oil} \bullet M_{sol}} \qquad (6)$$

$$\frac{A}{B} \bullet \frac{M_{sol}}{H_{sol}} = \frac{M_{oil}}{H_{oil}} \qquad (7)$$

Therefore (A/B)•M_{sol}/H_{sol} should be independent of the choice of solvent. This is shown in the last column of **Table 4.2**. The value for ethanol is a bit low for unknown reasons. The average value of (A/B)•M_{sol}/H_{sol}, neglecting the value for ethanol, is 424. To check the accuracy of this number we can use equation 7 to calculate M_{oil}; because H_{oil} is 2, we can calculate that the average molar mass of the soy oil sample is approximately 848 g/mol. The most common acid in soy oil is linoleic, so the molar mass of oil should be roughly the same as trilinolein, which is 880 g/mol. This is within experimental error and therefore confirms the validity of this method. Therefore, for any new solvent, one can predict that the value of A/B should be approximately 424•H_{sol}/M_{sol}.

Tables for the wt. % of solvent to oil, and their corresponding integration ratio for benzylmethylamine, i-PrOH, n-PrOH, EtOH and DBU are show in **Table 4.3**, **Table 4.4**, **Table 4.5**, **Table 4.6**, and **Table 4.7**, respectively.

Table 4.3 Wt. % of benzylmethylamine in soy oil used to obtain "A/B."

Soy Oil (mg)	NHBzMe (mg)	wt. % of NHBzMe	IR[a]
4957	60	1.20	0.08
4905	102	2.04	0.14
4751	259	5.17	0.38
4506	501	10.01	0.77

[a] IR: integration ratio of the soy oil peak to the solvent peak

Table 4.4 Wt. % of i-PrOH in soy oil used to obtain "A/B."

Soy Oil (mg)	i-PrOH (mg)	wt. % of i-PrOH	IR
4952	50	1.00	0.10
4910	101	2.02	0.18
4856	154	3.07	0.24
4798	202	4.04	0.35
4756	249	4.98	0.40
4703	299	5.98	0.48
4655	353	7.05	0.57
4601	399	7.98	0.65
4557	453	9.04	0.72
4506	500	9.99	0.75

[a] IR: integration ratio of the soy oil peak to the solvent peak

Table 4.5 Wt. % of n-PrOH in soy oil used to obtain "A/B."

Soy Oil (mg)	n-PrOH (mg)	wt. % of n-PrOH	IR
4910	100	2.0	0.22
4850	150	3.0	0.43
4790	200	4.0	0.56
4700	300	6.0	0.84
4650	350	7.0	1.00
4600	400	8.0	1.08
4550	460	9.2	1.45
4500	500	10.0	1.53
4500	520	10.4	1.52
4010	1020	20.3	3.47
3550	1500	29.7	5.91
3000	1990	39.9	9.07
2500	2500	50.0	13.59
2010	3000	59.9	20.60
1500	3490	69.9	31.45
1010	4000	79.8	42.22

[a] IR: integration ratio of the soy oil peak to the solvent peak

Table 4.6 Wt. % of EtOH in soy oil used to obtain "A/B."

Soy Oil (mg)	EtOH (mg)	wt. % of EtOH	IR
92.5	55	37.29	8.93
107.8	32.3	23.05	5.06
117.5	17.6	13.03	2.42
121.2	9.7	7.41	1.32
126.0	5	3.82	0.68
128.0	2.6	1.99	0.33
135.6	1.35	0.99	0.16

[a] IR: integration ratio of the soy oil peak to the solvent peak

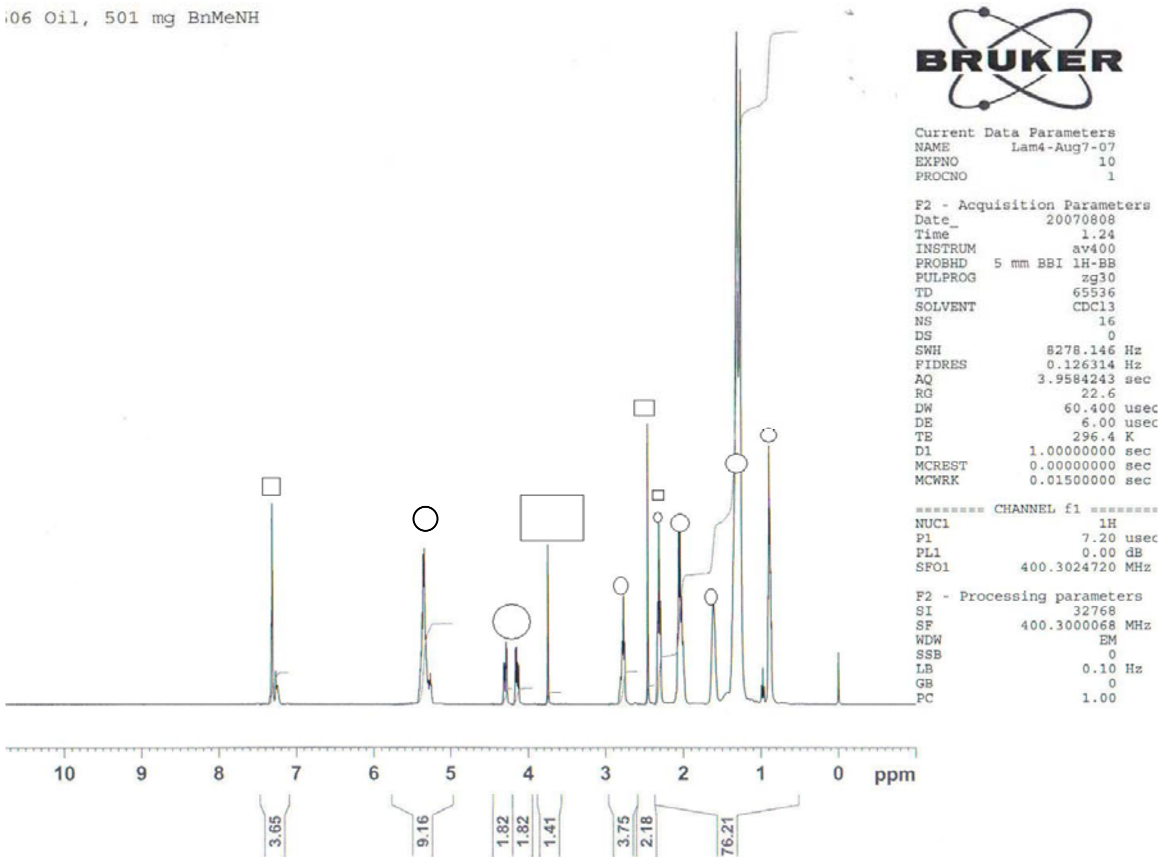
Table 4.7 Wt. % of DBU in soy oil used to obtain "A/B."

Soy Oil (mg)	DBU (mg)	wt. % of DBU	IR

4950	50	1.00	0.20
4900	108	2.16	0.35
4754	253	5.05	0.91
4501	510	10.18	1.96

[a]IR: integration ratio of the soy oil peak to the solvent peak

^{1}H NMR spectra of each mixture of solvent and soy oil are shown in **Figure 4.6**, **Figure 4.7**, **Figure 4.8**, **Figure 4.9**, **Figure 4.10** for NHBzMe, i-PrOH, n-PrOH, EtOH and DBU, respectively.



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FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   22.6
DW                 60.400 usec
DE                   6.00 usec
TE                  296.4 K
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MCWRK          0.01500000 sec

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PL1                  0.00 dB
SFO1          400.3024720 MHz

F2 - Processing parameters
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SF            400.3000068 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00
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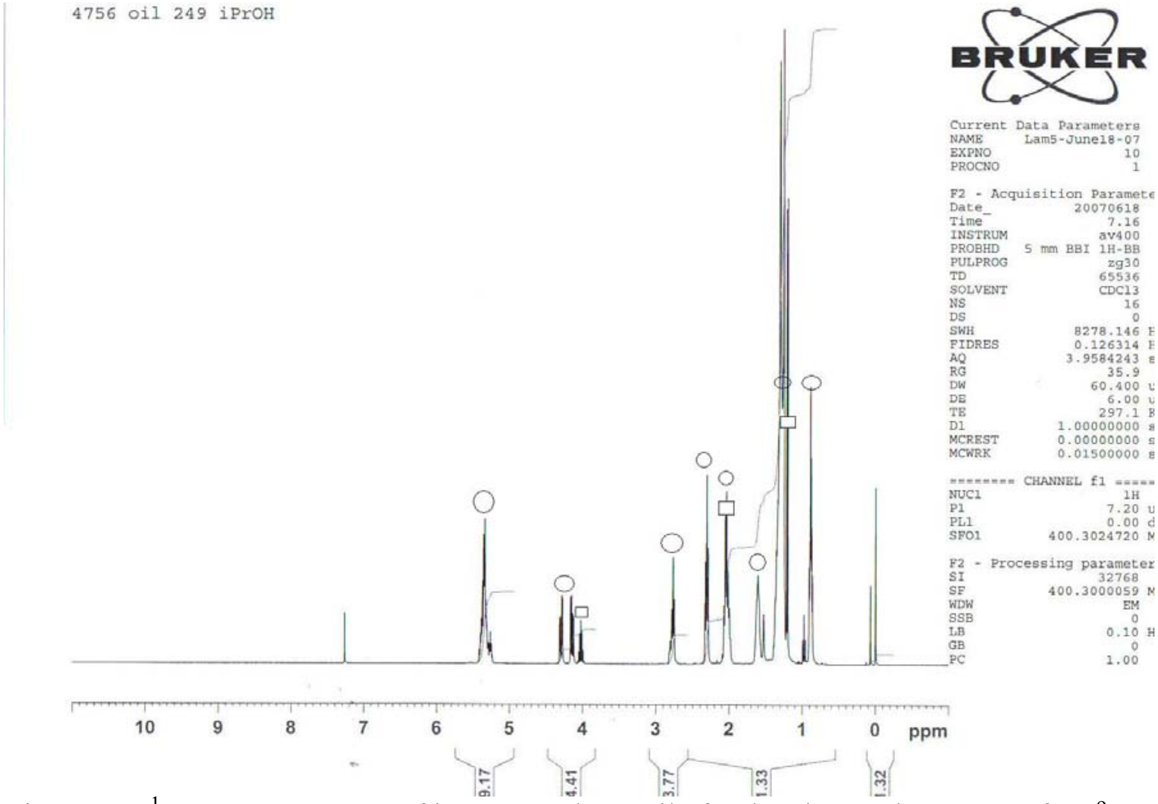
Figure 4.6 ^{1}H NMR spectrum of soy oil and neutral NHBzMe, in $CDCl_3$, used for generating “A/B”. Circles represent peaks of soy oil, boxed represent that of NHBzMe. There are some overlapping peaks.



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PULPROG             zg30
TD                 65536
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NS                    16
DS                     0
SWH             8278.146
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AQ             3.9584243
RG                  35.9
DW                60.400
DE                  6.00
TE                 297.1
D1            1.00000000
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MCWRK         0.01500000

======== CHANNEL f1 =====
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PL1                 0.00
SFO1         400.3024720

F2 - Processing parameter
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WDW                   EM
SSB                    0
LB                  0.10
GB                     0
PC                  1.00
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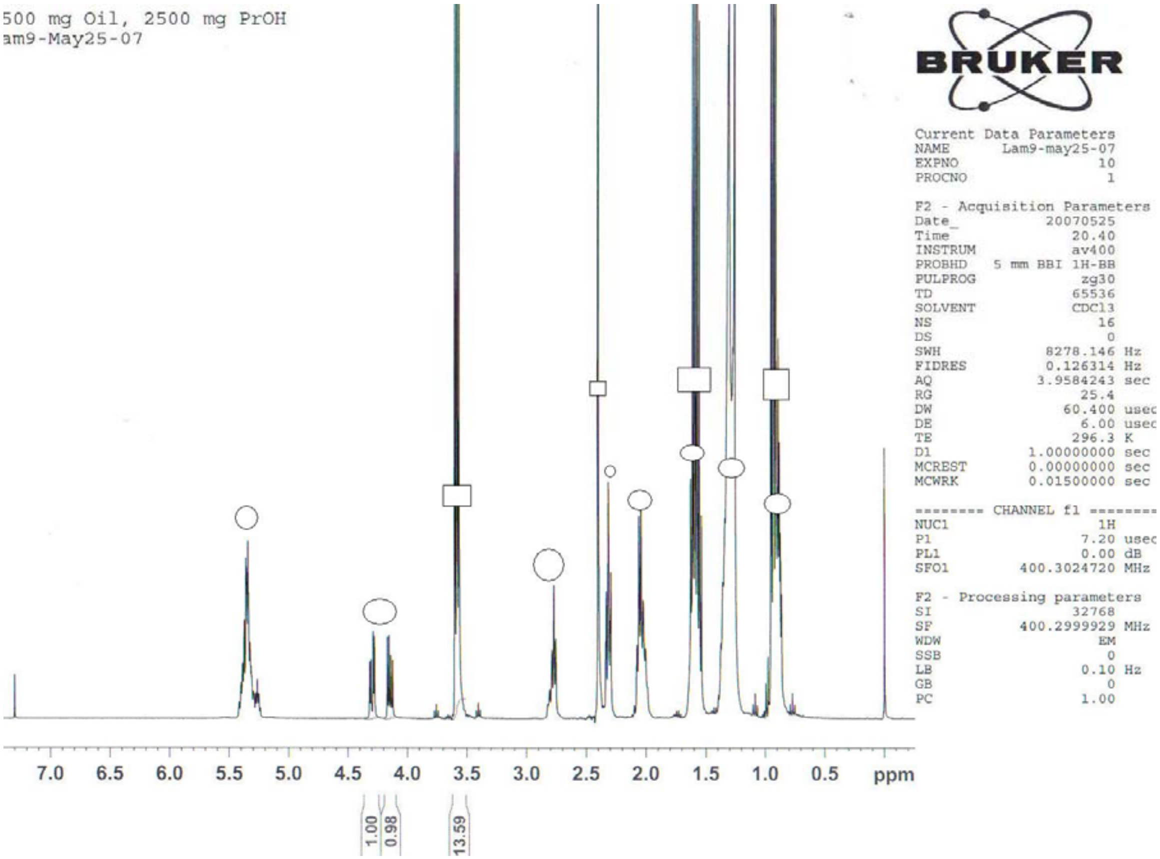
Figure 4.7 ^{1}H NMR spectrum of i-PrOH and soy oil after heating to the UCST of 40 ^{o}C used for generating “A/B”. Circles represent peaks of soy oil, boxed represent that of i-PrOH. There are some overlapping peaks.



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PROCNO                 1

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SOLVENT            CDCl3
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SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  25.4
DW                60.400 usec
DE                  6.00 usec
TE                 296.3 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
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P1                  7.20 usec
PL1                 0.00 dB
SFO1         400.3024720 MHz

F2 - Processing parameters
SI                 32768
SF           400.2999929 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
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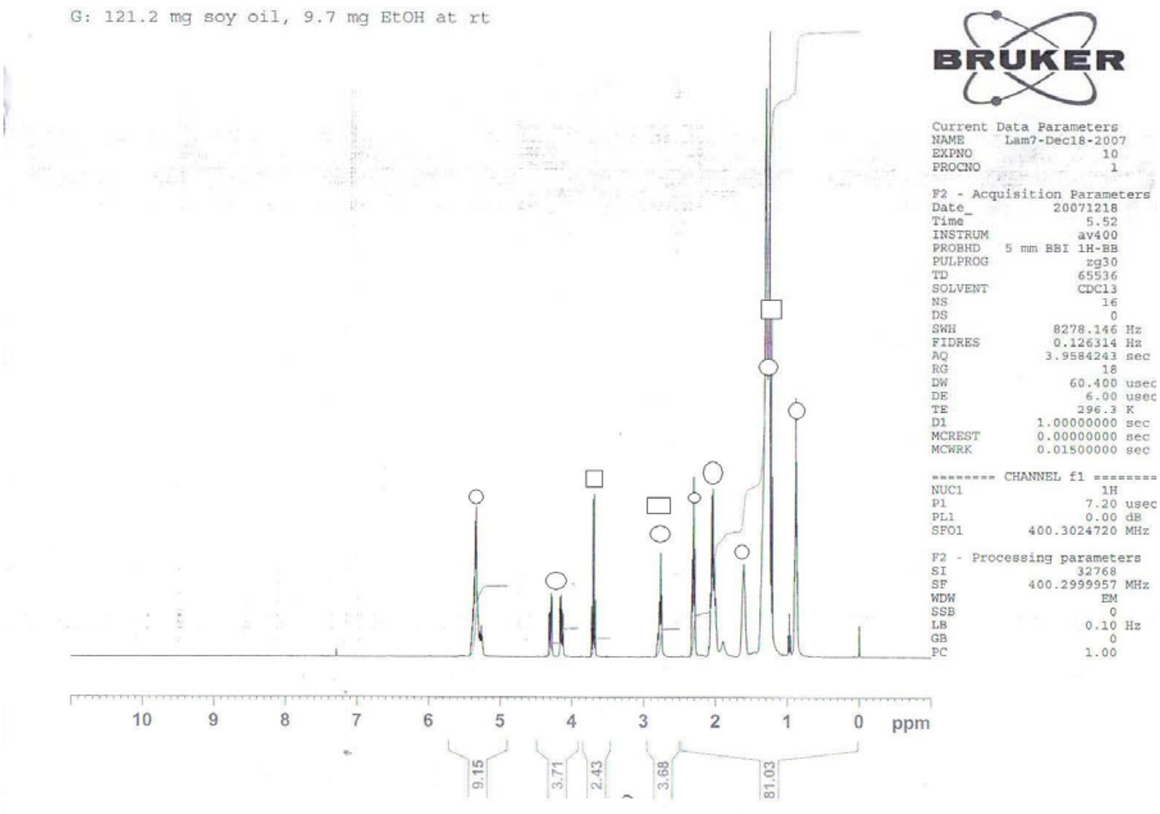
Figure 4.8 ^{1}H NMR spectrum of n-PrOH and soy oil used for generating "A/B" in $CDCl_3$ at room temperature. Circles represent peaks of soy oil, boxed represent that of n-PrOH. There may be overlapping peaks.



G: 121.2 mg soy oil, 9.7 mg EtOH at rt

```
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PROCNO                  1

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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                     18
DW                 60.400 usec
DE                   6.00 usec
TE                  296.3 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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PL1                  0.00 dB
SFO1          400.3024720 MHz

F2 - Processing parameters
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SF            400.2999957 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00
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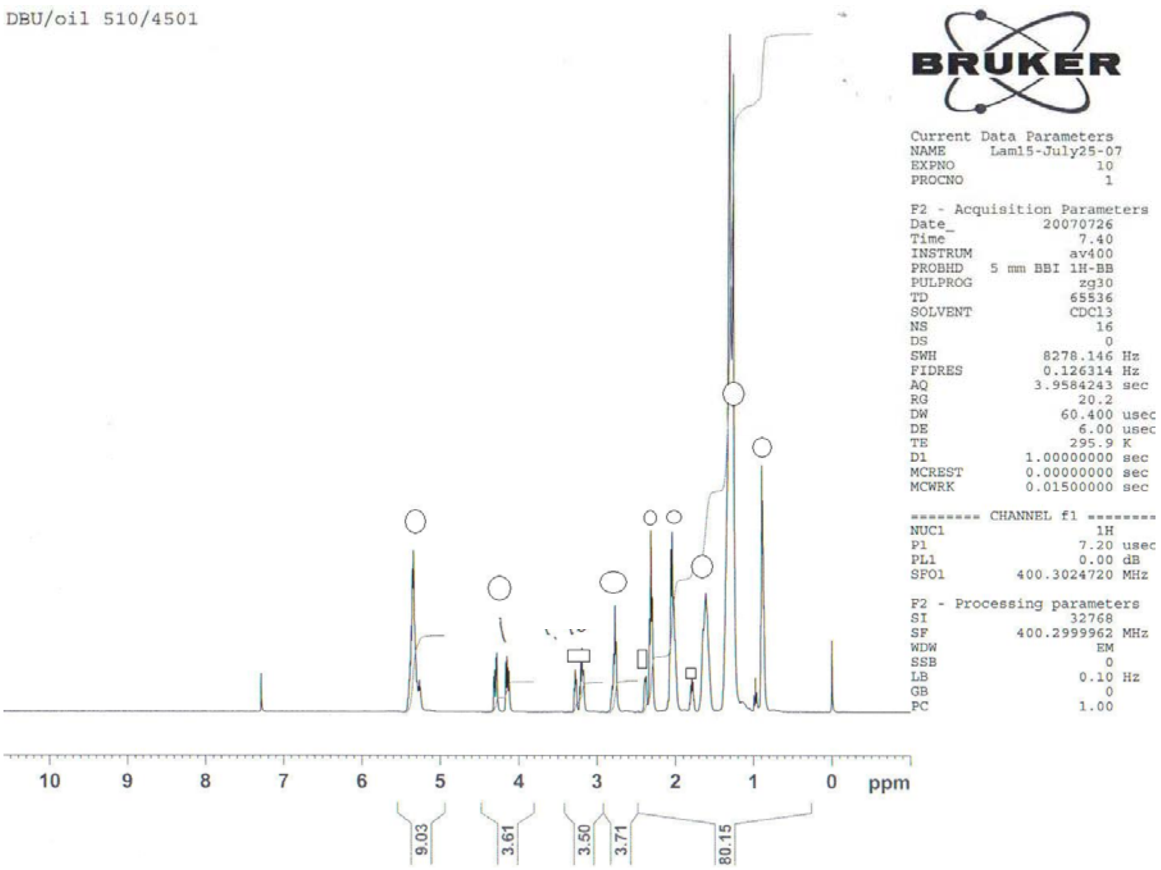
Figure 4.9 ^{1}H NMR spectrum of soy oil and EtOH in $CDCl_3$ at room temperature for generating "A/B". Circles represent peaks of soy oil, boxed represent that of EtOH. There are some overlapping peaks.



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PROCNO                   1

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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                    20.2
DW                  60.400 usec
DE                    6.00 usec
TE                   295.9 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.20 usec
PL1                   0.00 dB
SFO1           400.3024720 MHz

F2 - Processing parameters
SI                   32768
SF             400.2999962 MHz
WDW                     EM
SSB                      0
LB                    0.10 Hz
GB                       0
PC                    1.00
```

Figure 4.10 ^{1}H NMR spectrum of DBU and soy oil, in $CDCl_3$ at room temperature used for generating “A/B”. Circles represent peaks of soy oil, boxed represent that of DBU.

4.3.3 Evaluation of UCST strategy

Solvents chosen for the soy oil separation exhibit different UCST points, for example, n-PrOH and soy oil has a UCST below 15 °C, i-PrOH and soy oil has a UCST at 40 °C, and the UCST of soy oil and EtOH mixture is 67 °C.[88] We wanted to test how far can we go below the UCST before it showed any effects on contamination levels.

n-PrOH was chosen for this test because it is miscible with soy oil at room temperature, so we can lower the temperature and analyze the oil sample as described in

Section 4.2.2, and see if the IR showed any changes. The density of soy oil is greater than that of n-PrOH, so to only sample from the bottom phase required a special vial with a plastic seal. When the liquids in the vial were cooled to the desired temperature, the vial was inverted and allowed to settle until the two phases showed a clear separation. A needle was carefully inserted from below the vial and only the oil layer was sampled, thus avoiding any contact of the needle with the alcohol layer above. The resulting integration ratio is plotted vs. temperature in **Figure 4.11** below.

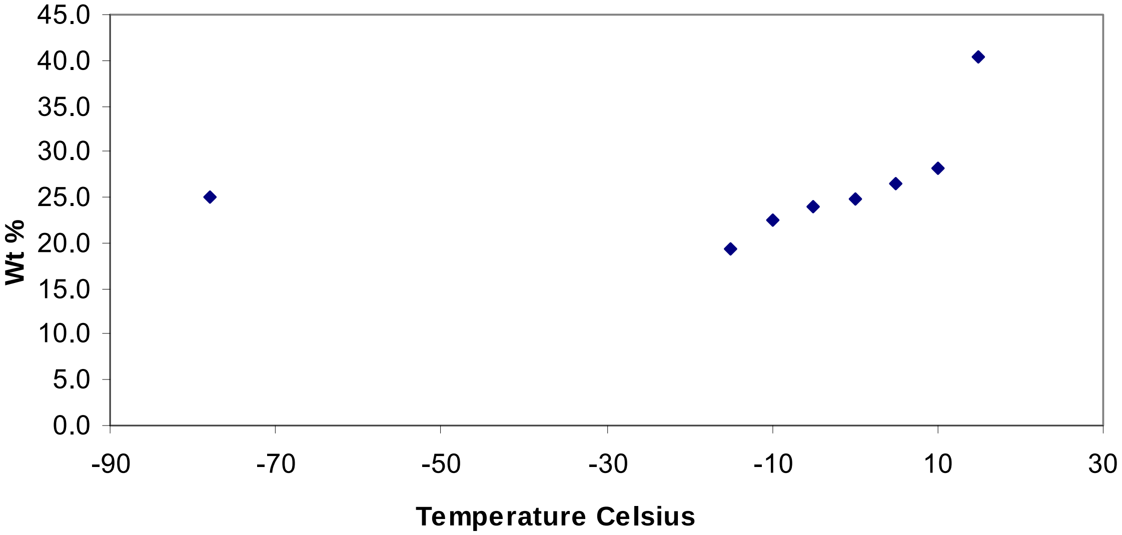


Figure 4.11 IR values of n-PrOH and soy oil at different temperatures below the UCST.

For n-PrOH and soy oil, separation was done at temperatures ranging from -78 ^{o}C to 15 ^{o}C. The wt. % of n-PrOH in the soy oil layer was calculated using equation (5), with “A/B” of 13.77. The temperature that yielded the lowest contamination is from -15 ^{o}C to -10 ^{o}C , giving the final contamination of 19.4 to 22.6 %. Even at the extreme temperature of -78 ^{o}C, the contamination level was 25.0 %. On the other side of our temperature scale, a contamination of 40.4 % was observed at 15 ^{o}C.

Similar experiments were done using EtOH. A mixture of 4 ml of EtOH and 2 mL of soy oil was heated to 70 ^{o}C then cooled to different temperatures and analyzed for contamination resulted in 13.2 % at -5 ^{o}C, 12.3 % at 0 ^{o}C, and 13.5 % at 10 ^{o}C. A controlled sample that was not heated to its UCST had contamination of 15.5 %.

To use this cooling technique as a separation strategy on a large scale could be unfeasible, because the energy required to cool the solvents to -10 ^{o}C would be high. Another disappointing fact is that the overall contamination is still quite high. All the contamination is based on only one separation cycle, if there are further separation procedures, such as column chromatography, and then the final contamination level could decrease. But in order to obtain highly pure soy oil with just one separation run, then we must find other strategies that give a lower degree of contamination %.

4.3.4 Study on settling time on affecting contamination levels

The temperature dependence experiments only analyzed the oil layer once the oil and n-PrOH showed clear separation; it took no account as to how long the liquids were left to settle. The reason for this time-lapse experiment was to determine if there was a relationship between the settling times to contamination levels. Since we have already determined that separation at between -15 ^{o}C to -10 ^{o}C results in the least contamination, these trials were all carried out at -10 ^{o}C. The liquids mixtures were left to settle for durations of 10 min, 1 h and 2 h. All three samples revealed that there is no strong correlation between the times of settling to the contamination percentages because the contamination is around 21 % (**Table 4.8**). Since the integration ratio turned out to be independent of settling time, we can conclude that the oil is sufficiently separated from n-PrOH within 10 min.

Table 4.8 Time lapse on separation at -10 ^{o}C of n-PrOH and soy oil.

Time allowed to settle	Integration Ratio	Contamination %
10 minutes	3.68	21.1
1 hour	3.59	20.7
2 hours	3.62	20.8

4.3.5 Water effects on UCST and contamination levels

Experiments that were done up to this point have been with solvents provided by Aldrich, without any further purification. Water is totally immiscible with soy oil, so it was questioned that if our solvents contain small traces of water, that make for better separation and lower contamination, because the water would make the overall solvent more polar, therefore, less likely to be miscible with the soy oil.

The purpose of combining i-PrOH and small amounts of water is to test whether or not water will have an effect on the contamination after the oil is separated. It has already been established that i-PrOH and soy oil are immiscible at room temperature, but the mixture has a UCST at 40 ^{o}C. The results of the UCST change and final calculated contamination (at room temperature) are presented in **Table 4.9**.

Table 4.9 Calculated contamination with different amounts of water in i-PrOH.

Wt. % of Water Added	Temperature of miscibility (^{o}C)	Contamination %
5	50	14.0
10	73	12.6
15	> 90	N/A

i-PrOH initially contained 495 ppm of water, as measured by a Karl-Fischer Coulometer. After adding small amounts of water to i-PrOH and soy oil mixture, we saw an increased in the UCST of the mixture. Our results showed that the added water results in a decrease in the level of contamination. With 5 wt. % of water added, the contamination was 14.0 %, the corresponding contamination number for 10 wt. % of water added was 12.6 %. The UCST for the mixture with 15 wt. % water added was too high, greater than 90 °C, almost reaching that of boiling point of water; hence no further data was collected.

This simple experiment does offer a possible strategy to use water-containing solvents to lower the contamination. One concern of this strategy is how to remove this added water after the soy oil has been separated, and does the excess water have any adverse effect on subsequent soy oil extraction steps. To answer this question, researchers at PNNL are currently testing the ability of different solvents containing excess water to extract soy oil.

4.3.6 Strategy two: using CO_2-expanded liquids

We tested strategy two and used EtOH as our solvent. The purpose of using expanded EtOH as a separation solvent is because CO_2-expanded liquids tend to be less polar than their normal state.[88] The decrease in the solvent polarity turns the solvent into more a favourable medium to dissolve oil. The strategy would be to use CO_2-expanded

EtOH to extract the soy oil out of the flakes, after which the CO_2 pressure would be released so that the soy oil would separate from the EtOH.

Unfortunately, even when the soy oil and EtOH mixture in the pressure gauge were pressurized to 58 bar of CO_2 at room temperature, so that the EtOH layer had greatly increased in volume, the oil still remained immiscible. Even after the mixture was stirred vigorously for 10 min, and the contents allowed to settle, there were still two distinct phases; the oil at the bottom, and the expanded EtOH on top. This result showed that we can not achieve separation under these conditions. Further work can be done at elevated temperatures, because higher temperature would affect the overall polarity of the solvent.

4.3.7 Strategy three: DBU/ROH SPS

This DBU/ROH SPS system was able to separate the oil after its reaction with CO_2 because of the change in the solvent polarity. It has been shown that DBU/n-PrOH has a starting polarity[38] similar to that of DMF, but after exposure to CO_2, the polarity increases greater than that of MeOH. Although we have seen that DMF is immiscible with soy oil, while the non-ionic form of DBU/n-PrOH is actually miscible with soy oil. This can be attributed to the fact that the mixture contains the non-polar DBU, and polar and miscible PrOH. The actual reaction scheme of the switchable solvent can be seen in **Figure 4.12** below.

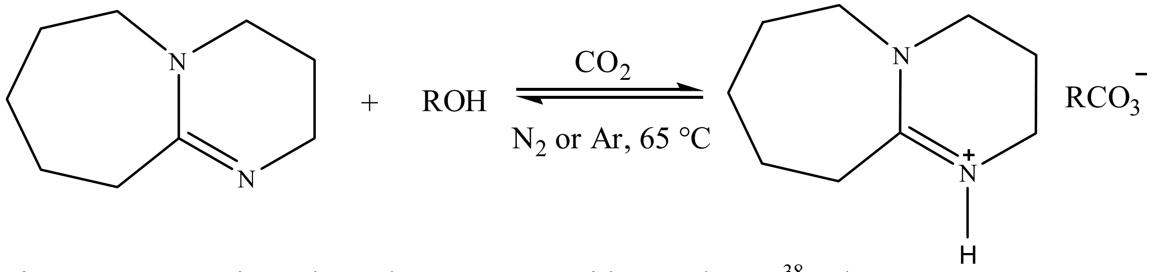


Figure 4.12 Reaction scheme between CO$_2$ with DBU/ROH.[38] When R = H, CH$_3$, C$_2$H$_5$, the corresponding salts are solids at room temperature; when R = C$_3$H$_7$ or longer, the corresponding salts are liquids at room temperature.

The polar forms of these switchable polarity solvents are only liquid if the alcohol chains are propyl- or longer, we used the three shortest alcohols because their $[\mathrm{DBUH}]^+[\mathrm{OCO_2R}]^-$ salts are liquid when mixed with soy oil.

Table 4.10 Contamination levels of soy oil for DBU and water, MeOH, or EtOH mixtures.

		Volumes (ml)			
Trial	DBU	H$_2$O	MeOH	EtOH	% Contamination
1	3[a]		0.6		Poor separation
2	3[a]	0.4			DBU:6.19[c], 1.76[d]
3	2[b]	1			DBU: 2.10
4	2[b]	2			DBU: 1.14
5	2[b]	2			DBU: 1.23
6	2[b]	2			DBU: 0.11
7	2[b]	2			DBU: undetectable
8	2[b]	2			DBU: undetectable
9	3[a]			1.6	DBU: 2.10[c], 0.75[d] EtOH: 0.52[c], 0.26[d]
10	2[b]			2	DBU: 2.10 EtOH: 3.05
11	2[b]			5	DBU: 1.31 EtOH: 7.08

---

[a]: 4 mL of soy oil was used
[b]: 2 mL of soy oil was used
[c]: 1st separation
[d]: 2nd separation using the oil from 1st separation

In trial 9, equimolar amounts of EtOH and DBU were used, with 4 mL of soy oil. When all three liquids were mixed, the mixture was one phase. After treatment with

CO_2, the reaction between DBU/EtOH and CO_2 causes the soy oil to slowly separate and rise to the top. The oil was drawn out via syringe and analyzed by ^1H NMR spectroscopy, showing that the soy oil still contains 2.10 wt. % DBU and 0.52 wt. % EtOH. In order to remove these small traces of contamination, a second separation cycle was done by bubbling more CO_2 into the drawn out soy oil. ^1H NMR analysis of the oil phase showed only 0.75 wt. % of DBU and 0.26 wt. % of EtOH remained in the oil. When excess EtOH was used (trials 10 and 11), contamination of DBU was low (2.10 wt. % and 1.31 %, respectively), and the contamination of EtOH were 3.05 wt. % and 7.08 wt. %, respectively. For trials 7 and 8, the ^1H NMR spectra of the oil layer showed no signal for any traces of DBU: this is because the DBU amounts were too low to be detectable by our ^1H NMR method (detection limit was 0.1 wt. %).

Similar steps were carried out using MeOH instead of EtOH. Surprisingly, after exposure to CO_2, a slurry mixture of oil, solids and solvents appeared, because the DBU/methylcarbonate salt is a solid;[50, 51] resulting in poor separation (**Table 4.10**, entry 1). Separation techniques proved to be ineffective; hence, no further trials were done with this DBU/MeOH system.

The best results were obtained using DBU/H_2O, (**Table 4.10**, and entrees 3 to 8). The best ratio of DBU:H_2O was 1:1 by volume. After CO_2 exposure, the entire mixture remained a liquid. This is because the $[DBUH]^+[OCO_2H]^-$ is soluble in water. This turned out to be one of the best strategies for separation of soy oil as the contamination levels were extremely low. One could use DBU as the extracting solvent from the flakes, after which equal volumes of water could be added to the system, and CO_2 would be bubbled through. The reaction between DBU/H_2O and CO_2 would cause the oil to separate out, and any amounts of remaining water, unreacted DBU, bicarbonate salt would all partition into the aqueous layer. The floating soy oil could then be separated by decantation.

One potential problem with this system is the recovery and recycling of the DBU. Once the aqueous phase is removed from the oil, the DBU must be recovered from the aqueous phase. The only successful method found in our tests was to distill out the water to leave DBU. This method is feasible on a lab scale, but to carry this out on an industrial scale could require too much energy.

Another alternative to solve the recyclability issue of this SPS is to find an amidine or guanidine that is immiscible with water under ambient conditions. In its non-ionic form, this amidine should be immiscible with water, but after the reaction with CO_2, the ionic form would be soluble in water. If the ionic form of this amidine can adequately separate the soy oil, the oil can be removed, and the reversing of the ionic form would give us back the biphasic mixture of water and neutral amidine.

4.3.8 Strategy four: secondary amine SPS

The fourth strategy, similar to the third, uses a SPS. Secondary amines react with CO_2 to form carbamate salts,[38] which were found to be immiscible with the soy oil (**Figure 4.13**).

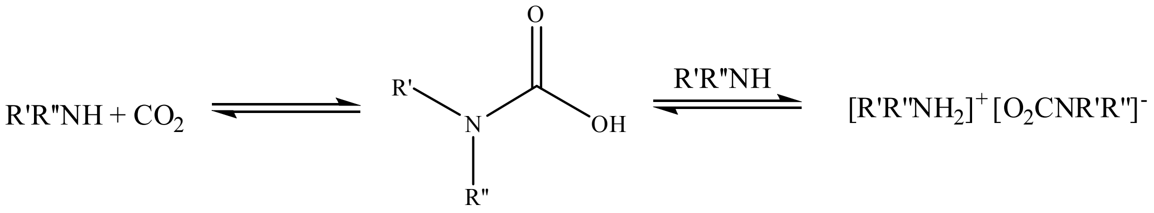


Figure 4.13 Reaction of a secondary amine with CO_2 to form carbamate salts. The neutral form of NHBzMe (far left) is miscible with soy oil, while the ionic form (far right) is immiscible.[38]

These secondary amines behave similar to the DBU/ROH SPS, where the amines can react with CO_2 to form a carbamate salt that is liquid at room temperature. In their non-ionic form, the amines would be miscible with the soy oil, but after reaction with CO_2, the carbamate salt liquid that is formed is more polar[38] hence the separation of soy oil is possible.

The non-ionic form of NHBzMe and soy oil are miscible at room temperature, but after exposure to CO_2 and allowed to settle, the two liquids slowly separated. Analysis of the oil layer showed a contamination of 12.2 % by wt. of the carbamate salt mixtures. If further reduction in contamination is desired, a separation by column or mild wash in acidic water could remove the amine. One major concern of using NHBzMe is its inherent toxicity. The MSDS of NHBzMe from Aldrich states that it is dangerous to skin, can potentially causing burns, combustible and is corrosive.

Another secondary amine, NHBuEt (a less toxic compared to NHBzMe) was also tested. Soy oil is miscible with this base in its non-ionic form, but unfortunately, CO_2 exposure failed to cause any separation between the ionic form and soy oil even after allowed to settle over several days.

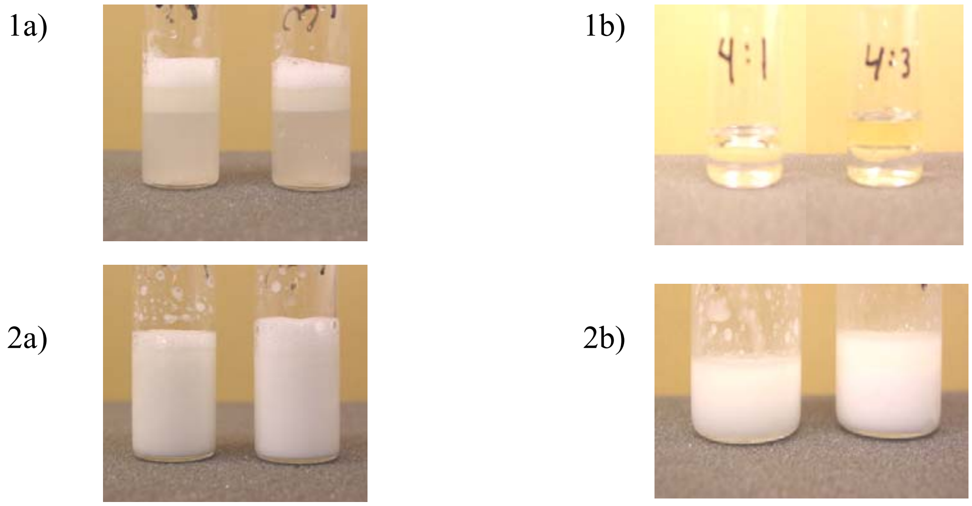
As we have seen in Chapter 3, the polarity of certain secondary amines increases when reacted with CO_2. For example, NHBzMe's polarity goes from a NR λ_{max} of 531 nm (non-ionic form) to 541 nm (ionic form), while the respective NR λ_{max} numbers for NHBuEt are 517 nm and 530 nm.[38] Therefore, one possible reason why soy oil separates from NHBzMe mixture and not from NHBuEt mixture is because NHBzMe is more polar in its ionic form than NHBuEt's ionic form.

Tests using i-propylamine, tripropylamine and triethylamine gave interesting results. All of these three amines are miscible with soy oil, but when water is added, the mixture becomes a biphasic liquid, with the water at the bottom, and the amine/soy oil portion on top. The best result was from using the 2.0 mL of soy oil and 2.0 mL of i-propylamine, then adding 2 mL of water. After bubbling CO_2 into the liquids for 30 min, the aqueous layer was seen to increase and the top layer shrunk in volume. This indicated that the amine has partitioned into the aqueous layer after its reaction with CO_2, indicating that it has been effectively removed from the soy oil layer. ^{1}H NMR analysis of the separated oil layer shoed no traces of the amine. Although the recycling steps have not been done, it can be imagined that the water and i-propylamine can be separated by distillation.

4.3.9 Strategy five: switchable surfactants

Jessop et al.[17] have demonstrated a surfactant that can be turned "ON" to stabilize an emulsion, and can be turned "OFF" to break the emulsion. They called this surfactant a switchable surfactant, which is similar to the SPS concept. This surfactant can be turned "ON" when exposed to CO_2, and is turned "OFF" by bubbling N_2 or heating the emulsion.

Our test of this strategy used different lengths of the surfactant salts. Pictures of their emulsion are shown below.


1a) 1b)

2a) 2b)

Figure 4.14 Emulsions of soy oil and water formed by various switchable surfactants. a) before CO_2 exposure; b) after CO_2 exposure and sonication; 1) N'-hexadecyl-N,N-dimethylacetamidine bicarbonate salt; 2) N'-octyl-N,N-dimethylacetamidine.

A stable emulsion was formed between 4 mL of water and 2 mL of soy oil with 5 or 3 mg of the N'-hexadecyl-N,N-dimethylacetamidine bicarbonate salt (**Figure 4.14**, **1a** and **2a**). This emulsion was stable over a 12 h period, after which we can see some separation of the two liquids. The N'-octyl-N,N-dimethylacetamidine was not used in its salt form, but in the neutral amidine form (**Figure 4.14**, **1b** and **2b**). With water as the media, the corresponding surfactant can be generated *in situ* when CO_2 is added.

Nonetheless, a stable emulsion was formed with just 12 mg of the N’-octyl-N,N-dimethylacetamidine, but this emulsion showed signs of instability when left over night.

The strategy of using this surfactant is similar to how washing your hands with soap and water to remove oils and dirt. The flakes would be exposed to water that contains the surfactant salt or the neutral amidine. Then CO_2 and shear force would be applied, as the oil is extracted from the flakes, an emulsion will form between the soy oil and water. The flakes are then physically separated from the emulsion through filtration. Then emulsion of water and soy oil would be broken to give a liquid mixture of soy oil on top and aqueous lower layer. The reuse of the aqueous layer and surfactant is theoretically possible.

4.3.10 Strategy six: polymer-bound as a trapping agent for solvent

Commercially available polystyrene-bound DBU has a loading of 1 mmol of amidine sites per gram of polymer. At this loading, 1 g of polymer can trap 60 mg (75 μL) of n-PrOH. If the polymer was to be used to remove n-PrOH from soy oil after the n-PrOH had been used to extract the oil at a 5:1 (solvent:oil by volume), then 1 g of polymer would can only remove 15 μL of n-PrOH. In other words, to clean up 1 L of soy oil would require 67 kg of polymer. This is obviously unsatisfactory, even if the polymer is recycled. Due to the small loading, this polymer-bound amidine can never be used to remove bulk solvent from soy oil.

However, such a polymer could be used to remove small traces of alcohol contaminants from soy oil (**Figure 4.15**). For example, if either the UCST or DBU/EtOH switchable solvent method is adopted as the method for separating the oil from the solvent, then the residual traces of alcohol could be removed from the oil by amidine-supported polymer. If the separated oil contains 5 % of propanol by volume, then it would only require 3.5 kg of the amidine-bound polymer to clean up 1 L of oil. This may still be too expensive, but is closer to practicality. Therefore the polymer-supported amidine strategy can only be used to clean up small amounts of contaminants as a second stage of a process. For this reason, work in this direction was not performed.

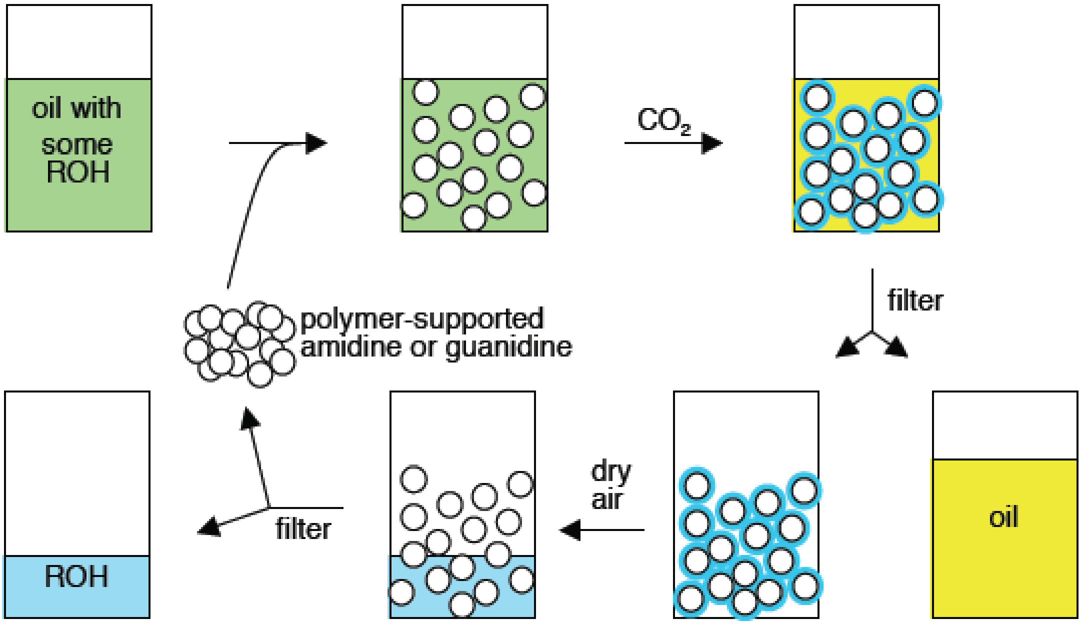


Figure 4.15 Schematics for using polymer-bound amidine to remove small traces of alcohols or water from the soy oil.

4.4 Conclusions and Future Work

We have seen that each strategy of the six strategies was tested for its ability to separate and give the lowest contaminated soy oil. The strategy that turned out to be a failure was the CO_2-expanded EtOH, because the soy oil remained immiscible with EtOH even after it has been expanded with CO_2, but it should be noted that this test was done at room temperature, therefore, we can not predict the behaviour of the mixture at higher temperatures. The strategy using UCST showed mild success, with the lowest contamination level being 12.8 % when using i-PrOH containing excess amounts of water. For the use of DBU/ROH SPS, the best results were obtained using equal volumes of DBU and water. The other SPS using secondary amines was also tested, but this time the final contamination level of 12.2 % was obtained when NHBzMe was used. There are major disadvantages of using amines are their toxicity and unpleasant to work with. The strategy of using surfactant to separate the soy oil via emulsion showed us that immiscible mixtures of soy oil and water could be temporarily emulsified with small amounts of surfactants. Steps to break the emulsion and recover the soy oil are yet to be done. The surfactants or neutral amidine used in this strategy were all oil soluble, so it may be difficult to remove the surfactant after the soy oil is separated. What we need is then a water-soluble surfactant, which means that the surfactants always partition into the aqueous layer, and the recycling of water and surfactant would be then possible. Tests using amidine-bound polymer showed that this strategy can only be used as a secondary removal step, as it amount of polymer required for total separation is too high to be practical.

Similar to the goals in the 1970's, the search of that elusive solvent to replace hexanes is still underway. This solvent must be safe for the processing workers, safe for the consumers and able to provide high purity oil. Chlorinated solvents are unsuitable because of toxicity, while simple solvents like EtOH and i-PrOH are also unfeasible because of the difficulty in removing the solvent from the soy oil and gave only moderately pure soy oil.

Amidine or guanidine base have been shown to be able to give high-quality oil, but there is still much more work to find the best base. The optimum base should be miscible with the oil, immiscible with water, have low toxicity, show recyclability and give high purity soybean oil. Intensive work is currently underway to find this base.

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$wR_2 = \{\sum [w\,(Fo^2 - Fc^2)^2] / \sum [w(Fo^2)^2]\}^{1/2}$

$(w = 1 / [\sigma^2(Fo^2) + (0.0291P)^2\ ]$, where $P = [\mathrm{Max}\,(Fo^2, 0) + 2Fc^2] / 3)$
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