Designing the Head Group of Switchable Surfactants

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Abstract

This thesis is an investigation into the development of amidine and guanidine based compounds to be employed as switchable surfactants. The surface activity of these molecules can be triggered by reaction with a benign gas, CO_2. The ultimate application of these surfactants was to be used as emulsifying and demulsifying agents of crude oil and water emulsions. Synthesis and characterization of the following desired bases: *N'*-octyl-*N,N*-dimethylacetamidine (1), 2-octyl-2-imidazoline (2), 1-methyl-2-octyl-2-imidiazoline (3), *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidine (4), *N'*-(4-(octyloxy)phenyl)-*N,N*-dimethylacetamidine (5), *N'*-(4-(methyloxy)phenyl)-*N,N*-dimethylacetamidine (6), and *N*-octyl-*N',N',N'',N''*-tetramethylguanidine (7) was carried out. Their solubility in water was quantified with NMR spectroscopy. All bases were reacted with CO_2 and H_2O to form bicarbonate salts, of which *in situ* characterization was achieved by IR and NMR spectroscopy. Percent conversion to the protonated forms at elevated temperatures was determined using NMR spectroscopy. A direct correlation between switchability and basicity was observed, as the strongest bases possessed the largest conversions to the protonated species, even at higher temperatures. The enthalpy of protonation was determined for each base through calorimetry experiments. These compounds were tested as demulsifying surfactants of crude oil and water emulsions. Demulsifying ability was determined to differ greatly with the head group structure of the various surfactants.

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List of Abbreviations

ADM	*N′,N′*-dimethylacetamidine
CMC	Critical micelle concentration
DBU	1,8-diazabicylo-[5.4.0]-undec-7-ene
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EOR	Enhanced oil recovery
FDM	*N′,N′*-dimethylformamidines
FTMA	11-ferrocenylundecyl trimethylammonium bromide
HLB	Hydrophile-lipophile balance
NMR	Nuclear magnetic resonance
O/W	Oil in water
PVC	Polyvinyl chloride
SBR	Styrene-butadiene rubber
SDS	Sodium dodecyl sulfate
TGA	Thermogravimetric analysis
T_k	Krafft temperature
W/O	Water in oil

1. Introduction

1.1 General Overview

Surfactants have found use in a plethora of products and applications including: detergents, paints, adhesives, and emulsifiers in chemical processing. As a result of the wide utilization of surfactants, an environmental concern has developed due to the large amount of waste surfactant that is being expelled into the environment. This issue becomes much more problematic if the surfactant is environmentally persistent, toxic, or can bioaccumulate causing unwanted physical effects in our sewage systems and waterways.[1] The development of surfactants that are more easily recovered and reused can help alleviate the environmental stresses created by their use.

Uses for surfactants in the chemical industry involve stabilizing emulsions in certain stages of manufacturing, cleaning, and are particularly important in the petrochemical industry for oil recovery and transport. Commonly for these applications, an emulsion is desired for one part of the process and then hinders the separation of components later in the process cycle. The use of a temporary emulsifier, also known as a **switchable surfactant***,* is therefore desirable as it can convert between an active and inactive form, allowing for the formation of a temporary emulsion that can then be broken at a later stage through the application of a specific trigger. The “inactive” form may in fact be surface active, but significantly less active than the other form, or it may be active as a demulsifier. This reversibility of switchable surfactants could result in a

large reduction of waste being generated for these processes through the facile separation of materials and reusability of the surfactant.

The switchable surfactants developed by Jessop and co-workers to date use benign gases (CO_2 and air) as triggers to switch between the active ("On") and inactive ("Off") forms of the molecule. These switchable surfactants were found to stabilize alkane/water and crude oil/water emulsions in the "On" form, and then destabilize the emulsion of the "Off" form after removal of the trigger.[2] To this end, switchable surfactants can be employed as either emulsifers or demulsifiers, however, further development was required to improve the use of such compounds as demulsifiers for heavier crude oil/water emulsions and for other potential applications.

This project resulted in a variety of novel switchable surfactants and compared their ability to readily convert between the "On" and "Off" forms of the molecule. The extent of conversion of each new surfactant was monitored by nuclear magnetic resonance (NMR) and calorimetry experiments and was compared against switchable surfactants previously reported in our group.[2] It was found that the switchability of these surfactants was dependent on the basicity of the proton acceptor, which is part of the head group of the surfactant. Some switchable surfactant structures are more versatile and can be used in varied applications, while other structures are optimal for a specific application.

1.2 Surfactants

1.2.1 Definition of Surfactants

The term surfactant is a technical term referring to surface-active agents, which have the tendency to gather at surfaces or interfaces between immiscible phases.[4] Surfactants alter the properties of the surface or interface, as they aggregate there due to different parts of the molecule possessing a greater affinity for one of the two phases. Their presence often reduces the surface or interfacial tension that exists between the two phases. Surfactant molecules are composed of a hydrophobic (or lipophilic) "tail" and a hydrophilic (or lipophobic) "head", where the "tail" is commonly a linear or branched hydrocarbon chain and the "head" is a polar or ionic moiety. The hydrophobic "tail" does not interact strongly with water molecules, while the hydrophilic "head" does causing the molecule to be solvated in aqueous solution (Figure 1.1).[3] This phenomenon leads to the self-assembly of surfactants into aggregates known as micelles.[4]

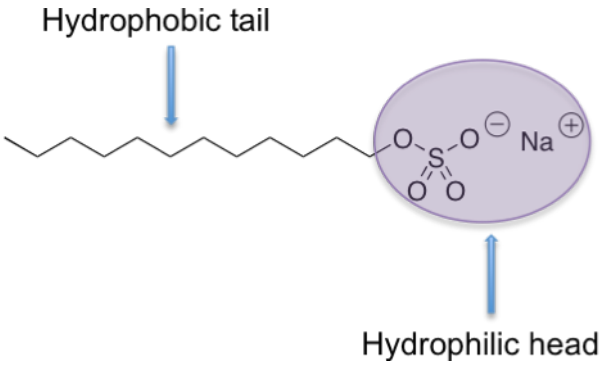
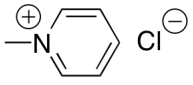


Figure 1.1 Sodium dodecyl sulfate (SDS) a commonly used surfactant.

1.2.2 Types of Surfactants

The chemical composition of surfactants can vary greatly as alterations can be made to either the hydrophobic "tail" or hydrophilic "head" depending on the desired application. Surfactants are generally classified by the nature of their head group and the main classes include: anionic, cationic, zwitterionic (amphoteric), non-ionic, and combinations of the above. A summary of the main classes, some examples, and their uses can be seen in Table 1.1. It should be noted that the incorporation of multiple head groups, the most common being the alkyl ethoxy sulphates group ($R(OCH_2CH_2)_nOSO_3^-$), into the same molecule produces surfactants with very advantageous properties and have found applications in dishwashing liquids and shampoos as they are mild on the skin.[5]

Table 1.1 Summary of main classes of surfactants.[5]

Class	Head Group	Main applications
Anionic	$-CO_2^- Na^+$	Soaps
	$-SO_3^- Na^+$	Synthetic detergents
	$-O-SO_3^- Na^+$	Detergents, personal care products
	$-O-PO_3^- Na^+$	Corrosion inhibitors, emulsifiers
	$-(OCH_2CH_2)_n-O-SO_3^- Na^+$	Liquid detergents, toiletries, emulsifiers
Cationic	$-N(CH_3)_3^+ Cl^-$	Bitumen emulsions
		Bactericides, antistatic agents
	$>N(CH_3)_2^+ Cl^-$	Fabric and hair conditioners
Zwitterionic	$-N^+(CH_3)_2-CH_2-CO_2^-$	Shampoos, cosmetics
	$-N^+(CH_3)-CH_2-SO_3^-$	
Non-ionic	$-(OCH_2CH_2)_nOH$	Detergents, emulsifiers

1.2.3 Micelles

As mentioned previously, surfactant molecules can assemble into micellular structures in the right environment. Generally, the formation of micelles involves the arrangement of the hydrophobic "tails" into the interior of the micelle in order to reduce their interaction with the surrounding aqueous solution, while the hydrophilic "head" is directed toward the water interface. This is an alternative organization of surfactants to the adsorption at the phase interface, which also reduces contact of the hydrophobic portion of the molecule from water. Micelles form to reduce the free energy of the system, however, this is a dynamic process as surfactant monomers are rapidly leaving and joining the micelle (Figure 1.2).[6,7,8]

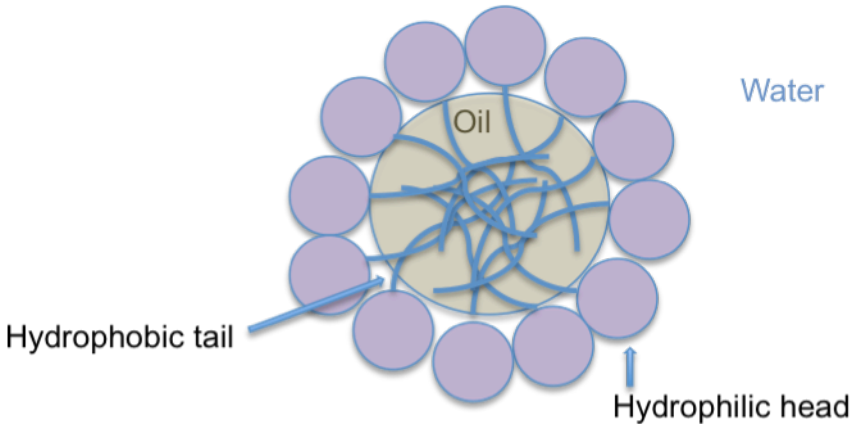


Figure 1.2 Schematic representation of the structure of a micelle and solubilization of oil in water.

1.2.3.1 Critical Micelle Concentration

The critical micelle concentration (CMC) is the concentration of a surfactant solution above which micelle formation occurs spontaneously.[7] The CMC is unique to each surfactant and the bulk properties of surfactant solutions dramatically change above this concentration. Since such properties as electrical conductivity, surface tension, light scattering ability and solubility are altered once the CMC is reached, measurement of such properties allow for the determination of the CMC for different surfactants. CMC's are influenced by the structural features of the surfactant such that a CMC will increase when the hydrophilicity of the "head" is increased or when the hydrophobicity of the "tail" is decreased. The CMC is an important parameter in characterizing surfactants as it relates to the control of emulsification, solubilization, and dispersion of otherwise immiscible materials.[7,8]

1.2.4 Emulsions

An emulsion is a heterogeneous system in which at least one immiscible liquid is dispersed (dispersed phase) in another (continuous phase) as small droplets (**Figure 1.3**).[9] Emulsions are usually classified as either oil-in-water O/W or water-in-oil W/O. In an O/W emulsion the organic liquid phase is dispersed in the water phase. Conversely in a W/O emulsion, the water phase is dispersed in the organic liquid continuous phase. Two immiscible liquids will try to separate to minimize the surface area between them, which causes emulsions to be kinetically unstable without the addition of an emulsifier (surfactant). Many types of emulsifiers can be employed to stabilize an emulsion as

they reduce the rate of coalescence of the droplets in the dispersed phase. The stabilization provided by an emulsifier can occur through several different mechanisms including: (1) the reduction of the interfacial tension, (2) the formation of a steric barrier between the two phases, (3) the formation of electrostatic repulsion between the two phases (provided by an ionic surfactant), and (4) an increase in the viscosity of the continuous phase. The type of emulsion that is formed can depend strongly on the type of emulsifier that is used.[9]

Figure 1.3 Hexadecane/water emulsion.[2]

1.2.4.1 Hydrophile-Lipophile Balance

The type of emulsion that will form is related to the ratio between the hydrophilicity of the "head" and the hydrophobicity of the "tail", which is known as the hydrophile-lipophile balance (HLB). The HLB can be determined either theoretically or empirically and these values are used to classify surfactants into categories related to what type of emulsion will be formed and what they are best used for (Table 1.2). A low HLB value signifies that the molecule is more hydrophobic and will likely form W/O emulsions, where a surfactant with a high HLB value is more hydrophilic and will likely form O/W emulsions. The HLB value is used qualitatively when selecting a surfactant because it only approximates the type of emulsion that will form and not the efficiency of

the emulsion. Furthermore, the type of emulsion formed can be altered by such solution parameters as: temperature, shear rate, concentration ratio of surfactant to oil, and relative phase-volume of oil and water.[10,11]

Table 1.2 Classification of emulsifiers according to HLB.[10]

Range of HLB Values	Application
3-6	W/O emulsifier
7-9	Wetting agent
8-18	O/W emulsifier
12-15	Detergent
15-18	Solubilizing agent

1.2.5 Surfactant Solubility

1.2.5.1 Bancroft Rule

An older method for predicting what type of emulsion will be formed is through determination of the surfactant's solubility in each phase. The phase in which the surfactant is most soluble defines the continuous phase of the emulsion. This technique is known as Bancroft's rule and even though it is not as good of an approximation as the HLB scale, it is still used as a rough guideline for emulsion classification.[10] The solubility in water of some surfactant compounds that are related to this thesis are shown in Table 1.3.

Table 1.3 Solubility of various organic compounds in water.

Compound	Solubility in Water (g/L)	Ref
C_{10} - C_{34} n-alkanes	< 2.0×10^{-4}	12
C_9 - C_{30} n-alkanoic and n-alkenoic acids and their esters	< 2.6×10^{-3}	12
C_{10} - C_{35} n-alkanols	< 3.7×10^{-4}	12
n-butylamine	1.00×10^{3}	13
n-hexylamine	1.20×10^{1}	13
n-heptylamine	6.79	13
n-octylamine	2.00×10^{-1}	13
Triethylamine	7.37×10^{1}	13
Arginine	1.5	12
DBU	miscible	12

1.2.5.2 Krafft Point

The solubility of a surfactant is not linearly related to solvent temperature, but rather a temperature exists at which there is a sharp increase in the solubility of a surfactant. At this temperature, the concentration of the surfactant becomes equal to the CMC and is defined as the Krafft temperature or point (T_k), which varies for each surfactant. Most surfactants are used above this temperature to ensure the maximum surface tension reduction by overcoming the CMC.[14,15]

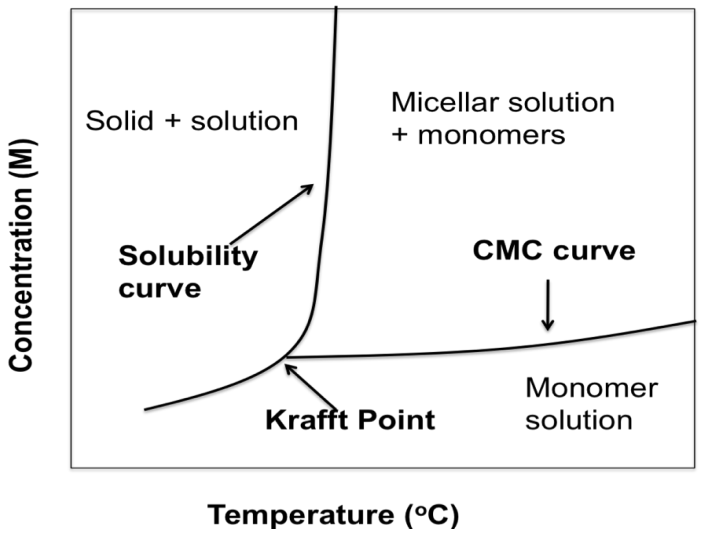


Figure 1.4 Schematic of CMC and Krafft temperature of a surfactant in an aqueous solution.[16]

1.2.6 Uses of Surfactants

Surfactants are used in numerous applications to form stable emulsions, including:

a) Emulsion polymerizations[17]

Surfactants are used in some polymerizations to allow for emulsification and stabilization of the polymer particles. They are used for exothermic polymerization reactions, as the heat released during chain propagation is absorbed by the aqueous phase reducing product decomposition. The most common polymerization that uses emulsion technology is radical catalyzed processes as high-molecular-weight products are produced with higher reaction rates than with other polymerization methods. The emulsion allows the propagation step to be more efficient as the macroradicals are

isolated from one another, decreasing the likelihood of two radicals coming into contact, ultimately reducing the frequency of termination reactions. Specifically, emulsion polymerizations are used to make large amounts of styrene-butadiene rubbers (SBR), latex paints, latex adhesives, PVC paste polymers, among many other products.

b) Viscous oil transportation through pipelines[18,19]

Heavy crude oil often needs to be transported from where it is produced to where it is refined by pipeline. This transportation can be very expensive and is sometimes not reasonable due to the high viscosity of the material. There are several methods used to increase the mobility of heavy crudes including: heating, diluting with lighter fractions of oil and creating oil-in-water O/W emulsions using surfactants. The formation of an O/W emulsion is the most advantageous strategy in terms of cost effectiveness; however, this process suffers as additional energy is required to remove the aqueous solvent and ultimately decreases the net value and amount of energy obtained from the oil.

c) Enhanced oil-recovery[20,21,22]

The formation of emulsions and foams using surfactants is also employed in the petroleum industry for enhanced oil-recovery (EOR) processes. Oil can be trapped in the pores of rock and can be extracted by employing a gas flood, however, this method can be relatively ineffective. Another example of an EOR technique involves the injection of a foam (emulsion) into a highly permeable oil field in order to achieve increased levels of oil recovery by reducing the interfacial tensions and solubilizing the oil.

d) Separation of oil sand constituents[23]

Oil sands are loosely arranged sand deposits containing bitumen, a highly viscous petroleum. The largest deposit of oil sands in the world is located in north-eastern Alberta. Using current technologies, it is estimated that 300 billion barrels of oil can be recovered from Canada's oil sands. There are many natural surfactants in the oil, meaning compounds that can be converted into surfactants when activated by NaOH. However, it has been found that commercial surfactants decrease the amount of NaOH required for maximum bitumen recovery by enhancing the oil detachment from the solid surfaces. Surfactants are also used in other steps of the oil sands separation and processing. The major challenges associated with oil sands recovery is to improve the efficiency, affordability, and environmental impact of the oil separation, in which the development of more productive surfactants can play an important role.

e) Cosmetic emulsions[24]

Emulsions are used extensively in cosmetic formulations due to their amphiphilic nature. Water and surfactants are very common ingredients in these products and allow for the solubilization and delivery of the active ingredients. They also play an important role in controlling the penetration into the skin or target area. Most cosmetic emulsions are intended to break upon application, and when used as moisturizers the emulsion disperses to create a uniform layer that makes the skin hydrophobic, preventing moisture loss from the skin. Surfactants have been used to date in barrier, cleansing, sunscreen, and splash-on lotions, among other cosmetic products.

1.2.7 Demulsifiers

Formation of emulsions can be unfavourable in some chemical processes, especially within the petroleum industry as crude oil contains natural emulsifiers that can cause stable emulsions with water. Separation of the oil-water emulsions require the addition of surfactant compounds, known as demulsifiers, which reduce the stability of the emulsion by encouraging the coalescence of the droplets of the dispersed phase. Breaking of the emulsion can have a crude oil layer forming on the top (creaming) as well as the settling out of the water forming a layer at the bottom (sedimentation). Because the chemical composition of crude oil is so diverse, a mixture of demulsifiers is often needed to achieve complete separation of the various phases. Furthermore, the demulsifiers employed can be customized to compliment the composition of the petroleum.[25] Surfactants that have an HLB value higher than 15 are the most effective for W/O emulsions and some basic types of mixtures that are used contain sodium salts of sulfosuccinates and polypropylene/polyethylene glycol block copolymers.[26] The use of amidines and guanidines as successful demulsifers of crude oil and water emulsions has also been previously reported (Figure 1.5).[27, 28, 29, 30, 31, 32]

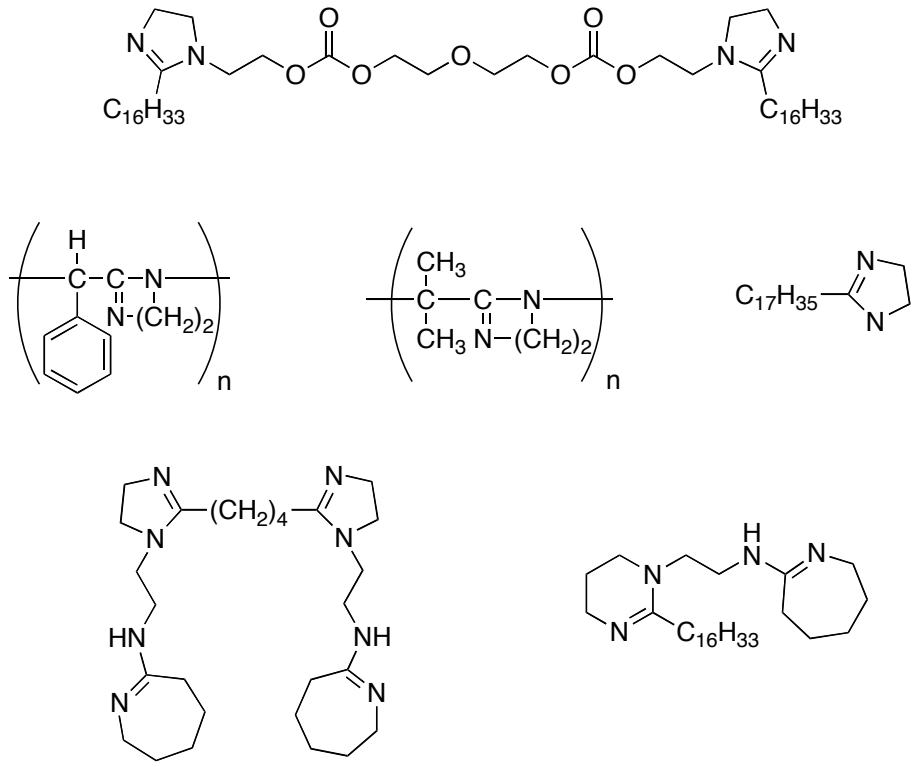


Figure 1.5 Amidines with the ability to demulsify crude oil and water emulsions.

1.3 Environmental Impact

As it can be seen from previous sections, there are a myriad of applications in which surfactants are used. This leads to the consumption of millions of tons of synthetic surfactants annually worldwide, with annual increases in use of 2-5%.[33] When surfactants enter aquatic environments, they can have acute effects on plants, animals and microorganisms but also a long-term effect on entire ecosystems. For example, even low surfactant concentrations decrease plankton populations, an important food source for many aquatic species. Furthermore, under certain conditions the presence of surfactants can stimulate algae growth. It can therefore be seen that the

anthropogenic effects of surfactants can cause major imbalances in the trophic chain. There is a wide range of biological effects that occur due to surfactants and their degradation products because both are persistent and have large potentials for bioaccumulation.[33]

1.3.1 Biodegradability, Toxicity and Bioaccumulation

Biodegradability is an important consideration when choosing a surfactant for an industrial application. To this end, some general relationships between biodegradability and the structure of a surfactant have been identified: (1) biodegradability decreases with more branching in the hydrophobic "tail," (2) biodegradation decreases with increasing amounts of oxyalkylene units in non-ionic polyoxyalkylene surfactants, (3) biodegradability of ammonium surfactants decreases with the introduction of two or more alkyl or benzyl groups, and (4) imidazolinium surfactants biodegrade more quickly than ammonium compounds, while pyridinium surfactants biodegrade more slowly. Many of the structural changes that increase the biodegradability of surfactants, such as decreasing branching and oxyethylene content, results in an increase in toxicity and bioaccumulation of the surfactant.[34] The data available on the effects of surfactants should be taken into account when designing new surfactants so that they have increased biodegradability along with decreased toxicity and reduced ability to bioaccumulate.

1.4 Temporary Emulsions

For many of the applications employing surfactants, the emulsion is only required for one part of the process and then the presence of the surfactant hinders the subsequent separation of components later in the product cycle, thus making temporary emulsions desirable. Emulsions can be broken by the addition of triggers such as: acids, bases, oxidants, and reductants. These types of triggers often require a stoichiometric addition. There are drawbacks to these large additions including: the economic and environmental costs, as well as contamination and modification of the product. Both cleavable and switchable surfactants have the ability of forming temporary emulsions, making them two possible candidates for preventing the aforementioned difficulties of permanent emulsions often encountered in the chemical industry.[2]

1.5 Cleavable Surfactants

A cleavable surfactant typically has a sensitive functional group located between the “head” and “tail” moieties, such as an ester group (Figure 1.6), which, upon the application of a trigger, cleaves the molecule in two. Once the surfactant is cleaved, the surface activity of the molecule is lost and separation of the emulsion occurs. The disadvantages of cleavable surfactants are: (1) irreversible conversion to the surface inactive form, (2) the cleavage step occurs slowly, and (3) use of non-environmentally friendly triggers such as an acid or base.[35]

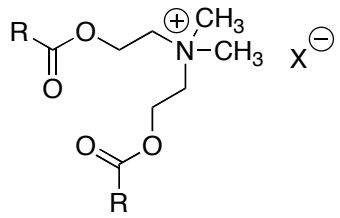


Figure 1.6 Molecular structure of an ester-containing, cleavable surfactant.[35]

1.6 Switchable Surfactants

1.6.1 Switchable Surfactant Definition

There are very few switchable surfactants reported in the literature, although, they are preferred over their cleavable counterparts since they do not decompose upon the application of a trigger. As such, they can be recovered and recycled after separation from the reaction mixture. Most triggers for switchable surfactants require redox or photochemical reactions, however, our group was the first to employ the environmental benign CO_2 as a trigger for switchable surfactants.

1.6.2 Redox Switchable Surfactants

An example of a redox switchable surfactant was reported by Saji *et al.*[36] using 11-ferrocenylundecyl trimethylammonium bromide (FTMA) and involves the functionalization of the ferrocenyl group (Figure 1.7). In its reduced form, the ferrocenyl group is hydrophobic, and upon the application of an electrochemical or chemical trigger, the group is oxidized into a hydrophilic cation. This change greatly alters the surface activity of the molecule, where the reduced form is capable of forming micelles

and the oxidized form is not, thus acting as a demulsifier.[36] The drawbacks of these switchable surfactants include their high cost, oxygen sensitivity, and high toxicity, which all limit their application.

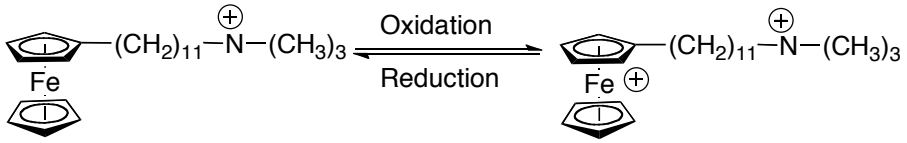


Figure 1.7 Molecular structure of a FTMA redox switchable surfactant.[36]

1.6.3 Photochemical Switchable Surfactants

One reported example of a photochemically switchable surfactant involves use of azobenzenes (Figure 1.8).[37] Upon irradiation with UV and visible light, these molecules can reversibly undergo a *trans-cis* isomerization where the length of the molecule increases slightly with the *trans* molecule. This transformation increases the hydrophobicity of the molecule, and the ability of the *trans* compound to form micelles in comparison with the *cis* isomer. The major drawback to these surfactants is the opacity of most of these emulsions, which hinders the use of light for the switch.

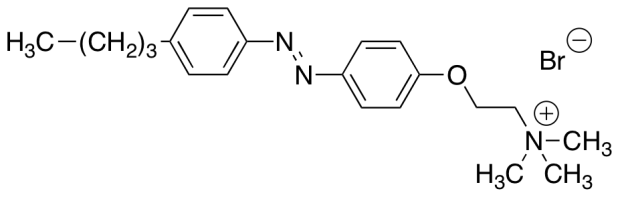


Figure 1.8 Chemical structure of an azobenzene-based switchable surfactant in its *trans* isomer.[37]

1.7 CO_2 Induced Switchability

Carbon dioxide, CO_2, is a molecule that is produced in large quantities from fossil fuel combustion, and as such, is considered one of the most threatening causes of climate change. For this reason, CO_2 has gained a negative reputation, however, it has the potential to be a feedstock that is readily available, cheap, and chemically stable. CO_2 does possess some chemical reactivity; some of the best examples are with bases such as amidines and guanidines. They have been shown to promote hydrogenation, carboxylation and coupling reactions to occur with CO_2 with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) being the most frequently used amidine.[38]

1.7.1 DBU

Amidines and guanidines have such efficiency with promoting CO_2 fixation that there was speculation in the literature that a zwitterionic adduct was being formed;[38] however, further studies have shown that such an adduct, as shown in Figure 1.9, was not the product of this reaction. Rather, it was verified that the creation of a bicarbonate salt of DBU was produced in the presence of H_2O (Figure 1.10). No reaction occurs in the absence of H_2O, thus eliminating the possibility of the formation of a zwitterionic species.[38] It was during that work that the concept of using this chemistry for switchable systems was developed.

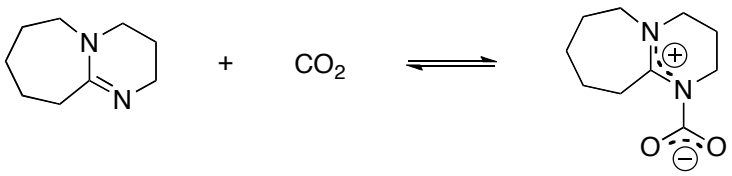


Figure 1.9 The proposed zwitterionic adduct formed between DBU and CO_2.[38]

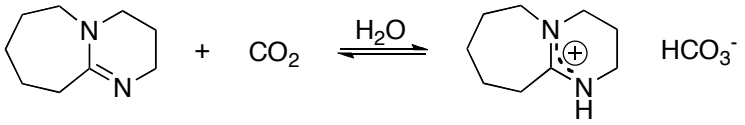


Figure 1.10 The reaction of CO_2 and DBU forming of a bicarbonate salt.

1.7.1.1 Switchable Solvents

The reaction between DBU and CO_2 in the presence of water was first investigated as a switchable solvent system.[39] Organic syntheses in industry often require multiple step reactions that need one type of solvent for one step and a different type needed for each subsequent reaction. A multiple step reaction therefore requires the solvent to be removed and replaced many times, which leads to a large amount of waste. The concept of a switchable solvent involves the application of a trigger, which alters the properties of the solvent, allowing one solvent to be used for multiple steps as the trigger can be applied and removed to control the solvent properties as desired. The use of a switchable solvent would dramatically reduce the amount of solvent waste created in a chemical process. When a 1:1 mixture of DBU and 1-hexanol, a low polarity solvent mixture, is exposed to CO_2, it is converted into an ionic liquid, which causes a dramatic increase in the solvent polarity similar to that of dimethylformamide (DMF). Upon application of $N_{2(g)}$ the ionic liquid is converted back to its low polarity

form by forcing the equilibrium back to release CO_2. The polarity switch was demonstrated by dissolving decane in a DBU-hexanol (low polarity) mixture where it is miscible but upon exposure to CO_2, the decane became immiscible due to the increase in polarity (Figure 1.11).[39] Along with switchable solvents, CO_2 and amidines have been proven to be useful for other switchable applications including: switchable catalysts,[40] switching the hydrophilicity of a solute,[41] CO_2 capture agents,[42] and switchable surfactants.[2]

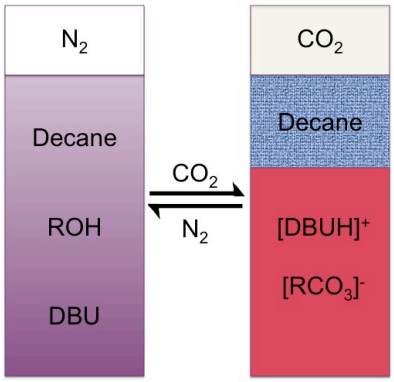
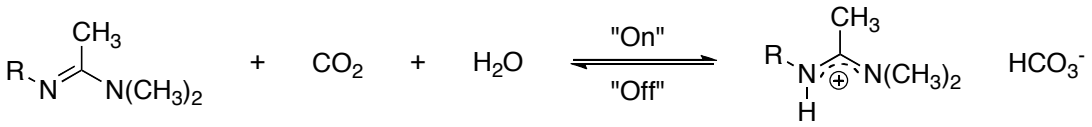


Figure 1.11 The switchable solvent showing the miscibility of decane with the nonpolar form of the ROH/DBU switchable solvent under N_2 (left) change to immiscibility upon the application of CO_2 to the polar form (right).[39]

1.7.2 CO_2 Switchable Surfactants

The development of switchable surfactants using benign gases (i.e. CO_2 and air) as the triggers to switch them "On" and "Off" has been previously reported by the Jessop group.[2] A long-chain amidine in water can be exothermically converted to a bicarbonate salt when exposed to atmospheric CO_2 gas, effectively turning the

surfactant “On” (Figure 1.12). The process can be reversed to turn the surfactant “Off” by bubbling an inert gas (N_2, Ar, or air) through the solution.[2]



Amidine A, R = $C_{16}H_{33}$
Amidine B, R = $C_{12}H_{25}$

Figure 1.12 Reaction of amidine to form amidinium bicarbonate salt.[2]

The switchability of the amidine surfactants was tested using conductivity experiments. The conductivity of a solution of **Amidine A** in wet dimethyl sulfoxide (DMSO) was monitored over three cycles while CO_2 and argon were alternatively bubbled through the solution. It was found that the conductivity increased when CO_2 was introduced into the solution, while a decrease was observed when the mixture was bubbled with argon (Figure 1.13).[2]

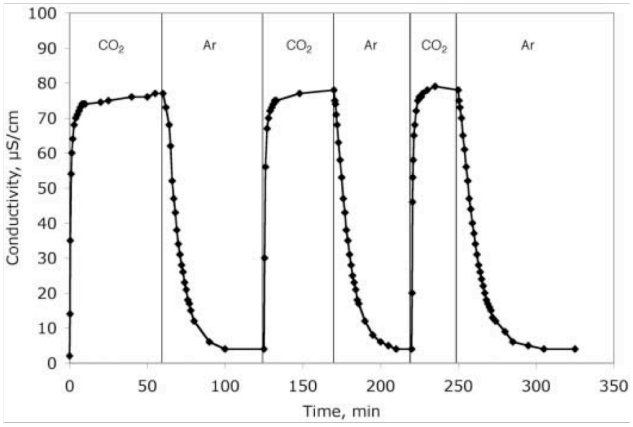


Figure 1.13 Conductivity of a DMSO solution of **Amidine A** at 23°C as a function of time during three cycles of treatment with CO_2, followed by argon. Reprinted with permission from Ref. (2). Copyright © Science 2006.

The ability of the amidinium bicarbonate salt to stabilize emulsions was tested by shaking a mixture of two parts hexadecane and one part water with **Amidine A**. An emulsion formed, but separated within 5 min; however, when CO_2 was bubbled through the solution, the "On" form of the surfactant provided a stable emulsion for > 30 min (Figure 1.14). The ability to turn the surfactant "Off" was also demonstrated by bubbling argon at 65 to 70°C for two hours (Photograph D, Figure 1.14).[2]

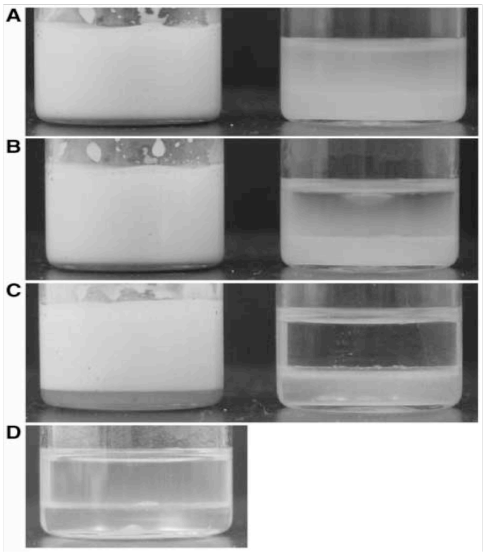


Figure 1.14 Photographs of 2:1 (v/v) hexadecane/water mixtures containing **Amidine A** and CO_2(left) or argon (right) after 10 min of shaking followed by a waiting period of (A) 5 min, (B) 30 min, (C) 24 hours, (D) bubbled with argon for 2 hours at 65 °C. Reprinted with permission from Ref. (2). Copyright © Science 2006.

Similar experiments were done to test the demulsifying ability of **Amidine A** in crude oil and water emulsions. Light crude oil and water form an emulsion due to natural surfactants found in oil. Stable emulsions are also formed when the "On" surfactant is added to the oil and water. Under an argon atmosphere, the "Off" **Amidine A** will demulsify the emulsion into two separate layers of oil and water in < 30 min

(Figure 1.15).[2] When similar experiments were performed using heavy crude oil, more stable emulsions were formed and only partial separation was achieved after 16 h once the surfactant was turned "Off". Optimization of these switchable surfactants would enable the demulsification of heavy crude for possible industrial applications such as breaking emulsions in enhanced-oil recovery, oil-sands separation, and equipment cleaning processes.[43]

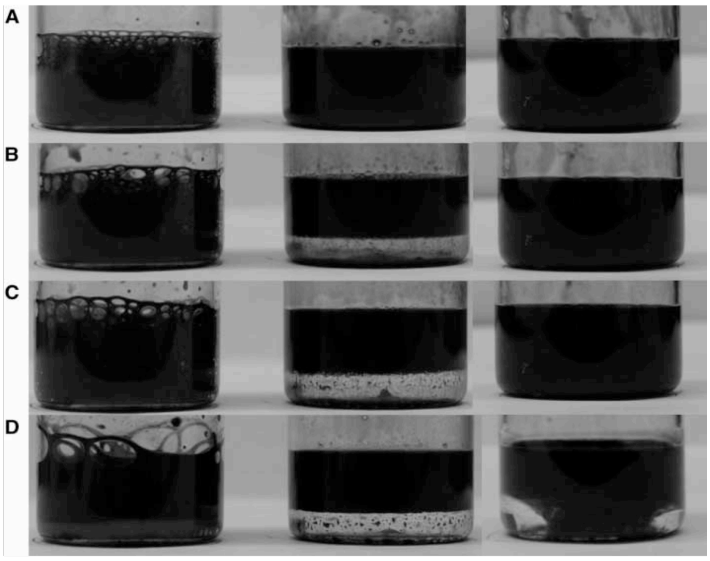


Figure 1.15 Photographs of 2:1 (v/v) crude oil/water mixtures that also contain argon (right), **Amidine A** and argon (center), or amidine and CO_2 (left) after 10 min of shaking followed by a waiting period of (A) 5 min, (B) 30 min, (C) 60 min, and (D) 15.5 h. Reprinted with permission from Ref. (2). Copyright © Science 2006.

1.8 Basicity

1.8.1 Structure Effects

A base is an electron pair donor that will donate its electrons to an electron pair acceptor, or acid.[44] There are many factors that influence the basicity of a molecule including: the stability of the conjugate acid, existing charge on the molecule, solvent, electronegativity, hybridization at the basic site, and the accessibility of the electrons. Nitrogen bases are among the strongest neutral bases because of their readily available lone pair. The electron density on the nitrogen is dependent on the substitution of the molecule, which has the most significant effect on the basicity. Electron-donating groups increase the basicity at the nitrogen and electron-withdrawing groups decrease the basicity at the nitrogen. In the gas phase, the basicities of the following amines increase with the increase of the electron donating ability of the attached alkyl groups: $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$. The basicity increase arises from the inductive effect provided by the alkyl groups, but also from the increased stabilization of the forming positive charge in the conjugate acid. Basicity is further influenced by solvent as the basicity of common amine bases in aqueous solution becomes: $NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$. The tertiary amine is much less basic in H_2O due to an increase in the stability of the ammonium ion of the conjugate acid through solvation effects of those containing an NH bond. Furthermore, $(CH_3)_3N$ is more basic than NH_3 due to electron donation from the alkyl groups. As mentioned above, basicity of a molecule can be reduced by decreasing the electron density (availability of the lone pair on the

nitrogen donor) which can occur when the nitrogen atom is directly bonded to or conjugated with an electron withdrawing group, the lone pair is in an sp or sp^2 hybridized orbital, or if the lone pair is involved in maintaining aromaticity of the molecule. Basicities of different molecules can be quantitatively compared by looking at their pK_{aH} values.[44]

1.8.2 pK_{aH}

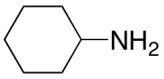
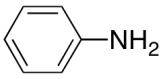
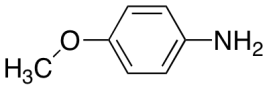
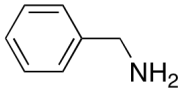
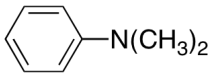
K_a is an equilibrium constant, more specifically an acid dissociation constant that is a quantitative measure of the acidity of a molecule in solution. This value is most often expressed as the negative logarithm, or the pK_a. The larger the pK_a value of a molecule the less acidic, or more basic it is. For basic molecules, the pK_a values of their conjugate acids (protonated forms) are used, expressed as pK_{aH}. It is important to note that the solvent can have a large effect on pK_{aH}, making it difficult to compare values in different solvents. Below are the pK_a values of the oxygen-containing molecules that are important to this thesis (Table 1.4).

Table 1.4 pK_a values of related oxygen containing compounds.

Molecule	pK_a (H_2O Scale)	Ref
H_3O^+	-1.74	45
H_2O	15.7	46
H_2CO_3	6.35	45
HCO_3^-	10.2	45

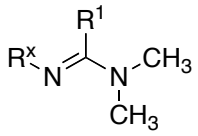
There are trends that can be elucidated between structure and basicity of amines (Table 1.5). When the length of the alkyl chain increases on the nitrogen of an amine, the basicity also increases slightly. The presence of a phenyl group in a nitrogen base will decrease the pK_{aH} value as can be seen with cyclohexylamine and aniline. As well if the phenyl group is not directly attached to the nitrogen the basicity is not as affected. This can be seen with aniline, which has a much larger basicity decrease than benzylamine whose nitrogen is not directly attached to the phenyl electron-withdrawing group. A basicity increase can be seen with the addition of an electron-donating group in 4-methoxyaniline as compared to aniline. The solvent can be seen to affect the basicity of a molecule as well.

Table 1.5 pK_{aH} values of selected amines.

Molecule	pK_{aH} (H_2O scale)	Ref	pK_{aH} (DMSO scale)	Ref
NH_3	9.2	45	10.5	47
NH_2^-	38	45	41	48
CH_3NH_2	10.64	45	--	--
$CH_3CH_2NH_2$	10.75	45	--	--
	10.64	45	--	--
	4.58	45	3.7	55
	5.08	45	--	--
	5.30	45	--	--
	9.3	49	4.15	49
	5.07	50	2.51	49
$(CH_2CH_3)_2NH$	10.98	45	--	--
$(CH_2CH_3)_3N$	10.76	45	9.0	55

Trends in basicity and structure can also be seen in amidines (Table 1.6). The presence of a methyl group on the middle carbon, which forms an acetamidine, increases the basicity compared to an unsubstituted derivative, a formamidine (Figure

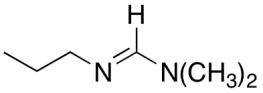
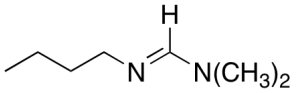
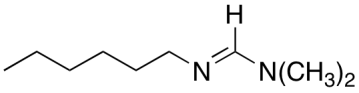
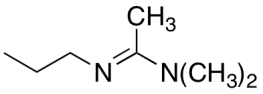
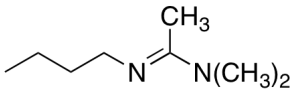
1.16). The introduction of a phenyl group at the imino nitrogen greatly decreases the basicity and a slight basicity increase can be seen with the addition of an electron-donating group at the para position of the phenyl group.

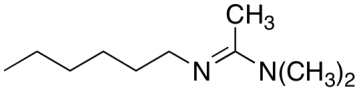
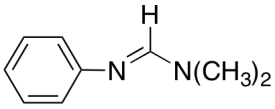
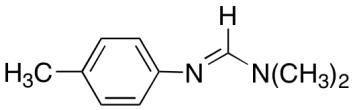
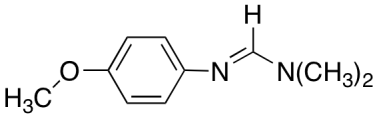
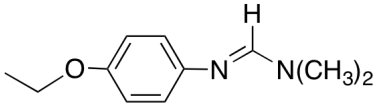
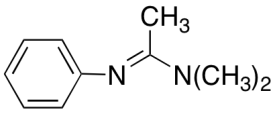
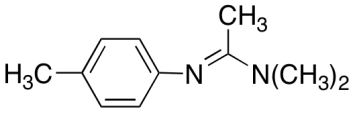
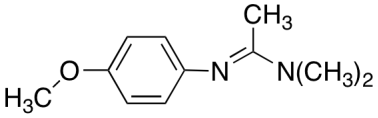
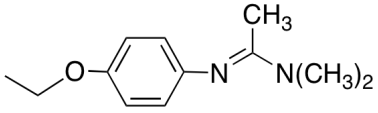


R^1	Amidines	Series
H	*N′,N′*-dimethylformamidines	**FDM**
CH_3	*N′,N′*-dimethylacetamidines	**ADM**

Figure 1.16 Schematic of the difference between FDM and ADM series where R^x can be any substituent.

Table 1.6 pK_{aH} values of selected amidines.

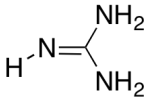
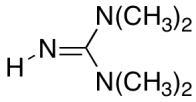
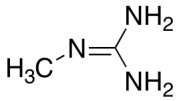
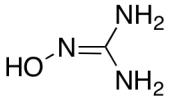
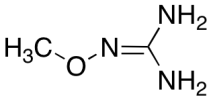
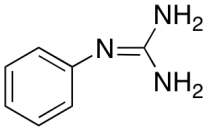
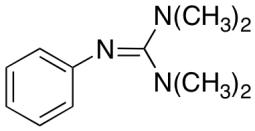
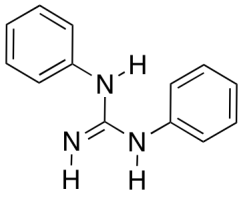
Molecule	pK_{aH} (95.6% EtOH scale)	Ref	pK_{aH} (DMSO scale)	Ref
DBU	--	--	13.9	51
	10.84	52	--	--
	10.80	52	--	--
	10.75	52	--	--
	12.46	53	--	--
	12.34	53	--	--

	12.37	53	--	--
	7.45	52	--	--
	7.75	52	--	--
	7.91	52	--	--
	7.83	52	--	--
	8.32	53	--	--
	8.65	53	--	--
	8.96	53	--	--
	8.90	53	--	--

Trends in basicity and structure are also present in guanidines (Table 1.7). A hydrogen on the imino nitrogen makes the molecule less basic than a methyl group on that same nitrogen. The presence of an electron-withdrawing group on the imino

nitrogen causes a decrease in basicity and two phenyl groups bonded to the guanidine moiety results in a much less basic molecule than the unsubstituted guanidine.

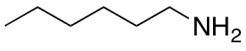
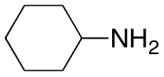
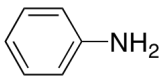
Table 1.7 pK_{aH} values of selected guanidines.

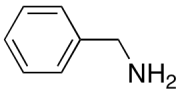
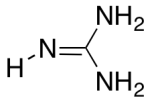
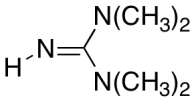
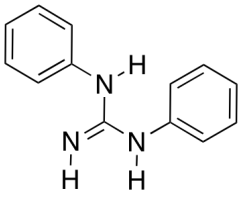
Molecule	pK_{aH} (H_2O scale)	Ref	pK_{aH} (DMSO scale)	Ref
	14.46	54	--	--
	13.6	49	13.2	55
	14.1	56	--	--
	7.96	56	--	--
	7.46	54	--	--
	10.77	54	--	--
	12.18	57	--	--
	--	--	8.6	55

1.8.3 Enthalpy of Protonation (∆H)

Another method of quantitatively comparing the basicity of molecules is through the enthalpy of protonation, ∆H. The amount of energy that is released during protonation has been shown to vary directly with the basicity of the molecule. The larger the enthalpy (heat) of protonation, the more basic the compound. The same relationships between structure and basicity outlined above are evidenced by enthalpy of protonation experiments. The ∆H increases with increasing alkyl chain length of a primary amine, correlating to the increase in basicity; the introduction of a phenyl group in a molecule greatly decreases the ∆H value correlating to the decrease in basicity.

Table 1.8 Enthalpy of protonation values of selected molecules.

Molecule	∆H in H_2O (kJ/mol)	Ref	∆H in DMSO (kJ/mol)	Ref
OH^-	56	58	--	--
CO_3^{2-}	15	58	--	--
NH_3	52.4 ± 0.2	59	--	--
CH_3NH_2	55.6 ± 0.5	59	--	--
$CH_3CH_2NH_2$	57.4 ± 0.2	59	--	--
	59.0 ± 0.1	60	--	--
	60.2 ± 0.5	59	--	--
	30.1	61	31	55

	54.3 ± 0.3	59	--	--
$(CH_3CH_2)_2NH$	53.3 ± 0.3	59	--	--
$(CH_3CH_2)_3N$	43.2 ± 0.2	59	63.7	55
	76	58	--	--
	87.8	--	87.8	55
	--	--	58.4	55

1.8.4 Basicity and Switchability

As discussed above, the structure and substituents of a nitrogenous base can greatly affect its basicity. This is an important factor when a base is being employed as a CO_2 switchable surfactant as the process involves protonation of the nitrogen donor to form a bicarbonate salt. More basic compounds than the first generation switchable surfactants can be designed which will cause the “On” form to be more stable at higher temperatures and therefore to be usable in a wider variety of processes. At the same time, if the surfactant is too basic, the switch to the “Off” form may be so difficult that it cannot be practically achieved. Switchable surfactants that are less basic than the first

generation will cause the “On” form to be less stable, even at lower temperatures making them easier to turn “Off”.

Similar basicity considerations were found to be important in a study of the use of switchable solvents for reversible CO_2 and SO_2 capture (Figure 1.17). Even though the process was reversible with CO_2, the solvent did not release SO_2, which is a stronger acid. To solve this problem a weaker base was needed to maintain good switchability for SO_2.[62] This example emphasizes the balance required between the basic switchable surfactant and the acidic trigger used to switch the system between the “On” and “Off” forms. As such, switchable surfactants can be modified and potentially tuned for an intended application depending on the parameters (i.e. acidic species, temperature).

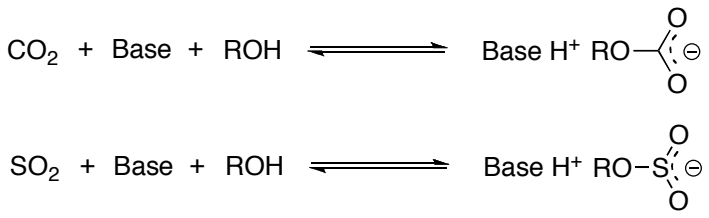


Figure 1.17 Schematic of switchable solvents for reversible uptake of CO_2 and SO_2.

1.9 Goals of this Study

The goal of this project was the further development and optimization of neutral amidines or guanidines to be employed as switchable surfactants/demulsifiers for such processes as separation of heavy crude oil and water emulsions. By varying the head

group of the surfactants, the properties are modified to improve the ability of the “Off” form to demulsify O/W emulsions. This research project explored the synthesis and characterization of a series of amidine and guanidine compounds to be employed as demulsifiers. Their solubility in both oil and water was determined. Important to this project was the characterization of the “On” form of the surfactants, which was achieved employing NMR and IR spectroscopy.

A series of amidine and guanidine compounds were tested to determine the thermodynamics of the switching process. NMR spectroscopy under an atmosphere of CO_2 provided the percent conversion between the “Off” and “On” form at various temperatures. Calorimetry experiments were used to determine the basicity of these compounds in order to evaluate how they relate to the structural differences of the head group. Lastly, TGA was used to determine the enthalpy and temperature required for CO_2 loss from the “On” form of the compounds.

Demulsifying of crude oil and water emulsion experiments were performed with the compounds using a cathetometer to measure the height of water separation over time.

This research provided the necessary data to determine the effect of altering the head group of amidine and guanidine-based surfactants, and whether these compounds have improved demulsifying capabilities over those that have been previously studied. The long-range goal of the project is the discovery of widely applicable, recyclable, switchable surfactants to be used in the chemical industry.

2 Experimental

2.1 Source of Reagents

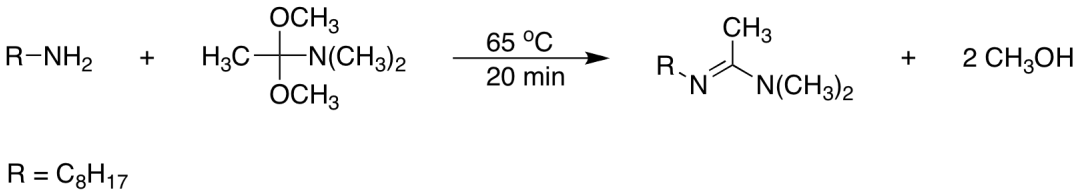
CO_2 (Praxair, 99.998%), nitrogen (Praxair, 99.998%), and argon (Praxair, 99.998%) were used as received. CRC59017-18-41 North Sea crude oil was obtained from Chevron and used for the demulsification experiments. Dimethylacetamide dimethyl acetal (90.0%) was received from TCI. All other reagents were received from Aldrich Chemical Company. All standard reagents and solvents were used without additional purification, unless otherwise noted.

2.2 Instrumentation

Infrared spectra were recorded for all liquid samples neat on an Avatar 360 FT-IR spectrometer. Solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer. Thermogravimetric analyses were performed with a STA 1500 instrument. All heats of protonation were recorded using an isothermal mixing and reaction calorimeter, model superCRC 208-110. All height measurements for crude oil demulsifying experiments were performed using an Eberbach Cathetometer.

2.3 Synthesis of Amidines

2.3.1 *N'*-octyl-*N,N*-dimethylacetamidine (1a)

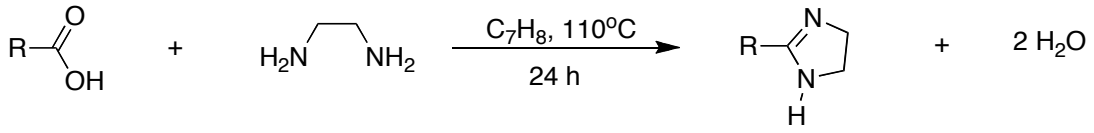


R = C_8H_{17}

Figure 2.1 Synthesis of *N'*-octyl-*N,N*-dimethylacetamidine.

The synthesis of the first generation switchable surfactant, **1a**, was produced by a modified procedure to that reported by Scoggins' and co-workers[63] as well as previous work performed in the Jessop lab.[2] Octyl amine (8.34 mL, 50.4 mmol) and *N,N*-dimethylacetamide dimethyl acetal (6.69 g, 50.2 mol) were combined together. The clear yellowish liquid mixture was heated at 65°C for 20 min and then the methanol by-product was removed by rotary evaporation. The clear orange crude product was purified by vacuum distillation to produce a clear liquid (7.57 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.28 (m, 10H, C_5H_{10}), 1.47 (m, 2H, CH_2CH_2N), 1.84 (s, 3H, CCH_3), 2.84 (s, 6H, $N(CH_3)_2$), 3.14 (t, *J* = 7.2 Hz, 2H, $C_5H_{10}CH_2N$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.3, 14.1, 22.7, 27.6, 29.3, 29.6, 31.9, 32.4. 37.9, 50.2, 158.6. IR (neat, cm^{-1}): 1008 (m), 1184 (m), 1259 (w), 1343 (m), 1455 (s), 1629 (s, υ (C=N)), 2853 (m), 2925 (s). HRMS (EI^+) m/z calc. for $[C_{12}H_{27}N_2]^+$ 199.2168, observed 199.2161.

2.3.2 2-octyl-2-imidazoline (2a)



R = C_8H_{17}

Figure 2.2 Synthesis of 2-octyl-2-imidazoline.

Shi *et al.* synthetic method was used in the preparation of cyclic amidines, which are also known as imidazolines; however, the purification method was modified.[64] Nonanoic acid (1.44 mL, 8.23 mmol) and ethylene diamine (0.66 mL, 9.88 mmol) were added to a round bottom flask containing toluene (50 mL). The reaction mixture was refluxed for 24 h employing a Dean-Stark trap apparatus to remove the water by-product. Toluene was removed by rotary evaporation leaving a yellow powder. The crude product was purified by vacuum distillation to yield a white crystalline powder (0.27 g, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H, CH_2CH_3), 1.27 (m, 10H, C_5H_{10}), 1.61 (m, 2H, $CH_2CH_2CH_2C$), 2.24 (t, J = 7.8 Hz, 2H, CH_2CH_2C), 3.39 (s, 4H, NCH_2CH_2NH), 5.51 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 26.7, 29.1, 29.3, 29.4, 31.8, 49.4, 168.3. IR (KBr, cm^{-1}): 723 (m), 817 (m), 1051 (m), 1117 (m), 1223 (m), 1351 (m), 1466 (m), 1647 (s, υ (C=N)), 2853 (s), 2924 (s), 3301 (w). HRMS (EI$^+$) m/z calc. for $[C_{11}H_{23}N_2]^+$ 183.1861, observed 183.1901.

2.3.3 1-methyl-2-octyl-2-imidazoline (3a)

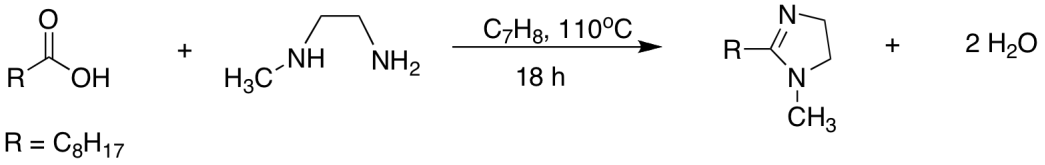
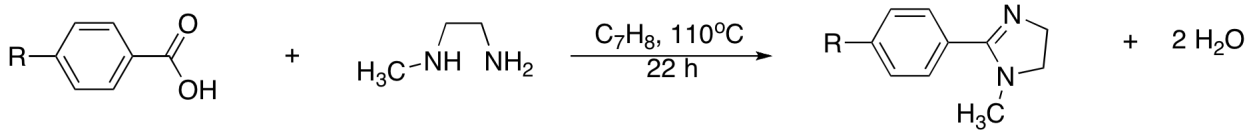


Figure 2.3 Synthesis of 1-methyl-2-octyl-2-imidazoline.

A modification of Shi *et al.* synthetic method was used in the preparation of 3a employing *N*-methylethylenediamine.[64] Nonanoic acid (4.43 mL, 30.9 mmol) was added along with *N*-methylethylenediamine (2.65mL, 0.0421mol) in toluene (40mL) to a round bottom flask. The colourless reaction mixture was refluxed for 18 h employing a Dean-Stark trap apparatus to remove the water by-product. Toluene was removed from the clear, yellowish liquid product mixture by rotary evaporation. The residual orange liquid was purified by vacuum distillation producing a clear, yellowish liquid (2.80 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.60 Hz, 3H, CH_2CH_3), 1.28 (m, 10H, C_5H_{10}), 1.62 (m, 2H, CH_2CH_2C), 2.21 (t, *J* = 7.81 Hz, 2H, CH_2CH_2C), 2.79 (s, 3H, NCH_3), 3.28 (t, *J* = 9.61 Hz, 2H, $=NCH_2CH_2N$-), 3.65 (t, *J* = 9.61 Hz, 2H, $=NCH_2CH_2N$-).^{13}C NMR (100 MHz, DMSO-d^6): δ = 13.1, 21.6, 25.3, 26.6, 28.1, 28.3, 28.6, 30.8, 32.8, 50.4, 52.2, 167.6. IR (neat, cm^{-1}): 1004 (m), 1267 (m), 1456 (s), 1618 (s, υ (C=N)), 2855 (s), 2925 (s), 3208 (w). HRMS (EI$^+$) m/z calc. for $[C_{12}H_{24}N_2]^+$ 196.1939, observed 196.1940.

2.3.4 1-methyl-2-(4-heptylphenyl)-2-imidazoline

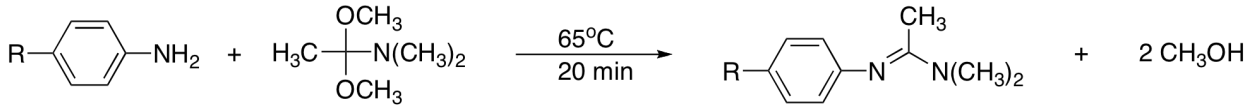


R = C_7H_{15}

Figure 2.4 Synthesis of 1-methyl-2-(4-heptylphenyl)-2-imidazoline.

A similar synthetic method as that outlined for **3a** was used to form *N*-methyl-2-(4-heptylphenyl)-2-imidazoline. 4-Heptylbenzoic acid (4.9871 g, 0.022637 mol) and *N*-methylethylene diamine (2.38 mL, 27.2 mmol) were added together in toluene (40 mL) in a round bottom flask. The colourless reaction mixture was refluxed for 22 h employing a Dean-Stark trap apparatus to remove the water by-product. Vacuum distillation and chromatographic techniques were attempted on the dark orange product mixture; however, a clean separation to isolate pure product was not achieved.

2.3.5 *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidine (4a)



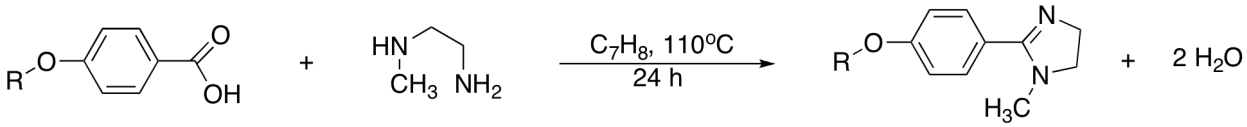
R = C_7H_{15}

Figure 2.5 Synthesis of *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidine.

A modification of Scoggin's procedure for producing acetamidines[63] was used in the preparation of **4a**. 4-Heptylaniline (5.11 g, 26.7 mmol) was added together with *N,N*-dimethylacetamide dimethyl acetal (3.55 g, 26.7 mmol). The yellow reaction mixture was heated at 65°C for 20 min, during which time an orange solution was

formed. The methanol by-product was removed by rotary evaporation and the resulting liquid was purified by vacuum distillation to yield a pale yellow liquid (6.26 g, 24.1 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3H, CH_2CH_3), 1.29 (m, 8H, C_4H_8), 1.58 (m, 2H, CH_2CH_2C), 1.85 (s, 3H, CCH_3), 2.53 (t, *J* = 7.8 Hz, 2H, CH_2C), 3.00 (s, 6H, $N(CH_3)_2$), 6.61 (d, *J* = 8.0 Hz, 2H, C_6H_6), 7.02 (d, *J* = 8.0 Hz, 2H, C_6H_6). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.9, 22.7, 29.2, 29.3, 31.7, 31.9, 35.4, 37.9, 115.2, 122.2, 128.6, 135.6, 149.8, 157.3. IR (neat, cm^{-1}): 1008 (m), 1184 (m), 1259 (m), 1343 (m), 1455 (s), 1629 (s, υ (C=N)), 2853 (m), 2925 (s). HRMS (EI^+) m/z calc. for $[C_{17}H_{29}N_2]^+$ 261.2330, observed 261.2333.

2.3.6 1-methyl-2-(4-(octyloxy)phenyl)-2-imidazoline



R = C_8H_{17}

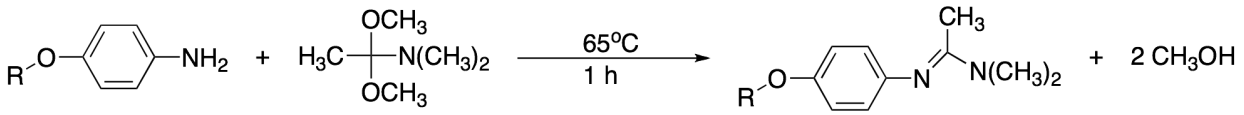
Figure 2.6 Synthesis of 1-methyl-2-(4-(octyloxy)phenyl)-2-imidazoline.

A similar synthetic method was used to form 1-methyl-2-(4-(octyloxy)phenyl)-2-imidazoline as outlined for **3a**. 4-(Octyloxy)benzoic acid (4.11 g, 16.4 mmol) and *N*-methylethylenediamine (1.71 mL, 19.7 mmol) were added in toluene (40 mL). The yellow reaction mixture was refluxed for 24 h employing a Dean-Stark trap apparatus to remove the water by-product. The toluene was removed by rotary evaporation, producing a dark brown liquid which was shown to contain the desired product by ^{1}H

and ^{13}C NMR spectroscopy but in very small amount. Vacuum distillation and chromatographic techniques were attempted on the product mixture, however, a clean separation to isolate pure product could not be achieved.

2.3.7 *N'*-(4-(oxyoctyl)phenyl)-*N,N*-dimethylacetamidine (5a)

Method 1



R = C_8H_{17}

Figure 2.7 Method 1 of the synthesis of *N'*-(4-(octyloxy)phenyl)-*N,N*-dimethylacetamidine.

4-(Octyloxy)-aniline (4.92 g, 22.2 mmol) and *N,N*-dimethylacetamide dimethyl acetal (3.00 g, 22.5 mmol) were combined together. The opaque black liquid was heated at 65°C for 1 h and the methanol by-product was removed by rotary evaporation. The residual black liquid was purified by vacuum distillation, although distillation was not successful in removing all impurities from the product, achieving an estimated 78% purity through integration of NMR signals. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_2CH_3), 1.28 (m, 8H, C_4H_8), 1.44 (m, 2H, $CH_2CH_2CH_2O$), 1.76 (m, 2H, CH_2CH_2O),1.86 (s, 3H, CCH_3), 3.02 (s, 6H, $N(CH_3)_2$), 3.90 (t, *J* = 6.56 Hz, 2H, CH_2CH_2O), 6.62 (d, *J* = 8.72 Hz, 2H, C_6H_4), 6.79 (d, *J* = 8.68 Hz, 2H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.9, 22.7, 26.1, 29.3, 29.4, 29.5, 31.8, 38.0, 68.3, 114.8, 123.1, 145.4, 154.2, 157.9. IR (neat, cm^{-1}): 787 (m), 837 (s), 962 (m), 1019 (s), 1101

(m), 1235 (m), 1390 (m), 1506 (m), 1614 (s, υ (C=N)), 2360 (w), 2855 (m), 2927 (s), 3033 (w), 3271 (m). HRMS (EI^+) m/z calc. for $[C_{18}H_{30}N_2O]^+$ 290.2358, observed 290.2348.

Method 2

Step 1:

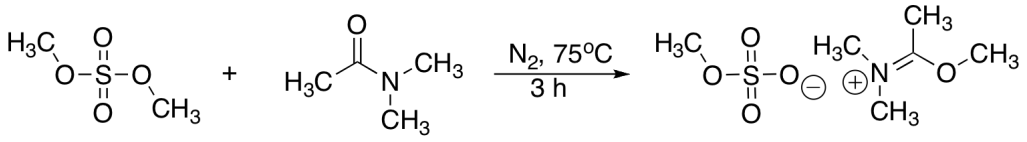


Figure 2.8 Method 2, step 1 of the synthesis of *N'*-(4-(octyloxy)phenyl)-*N,N*-dimethylacetamidine.

Dimethyl sulfate (33.1 g, 262 mmol) and dimethylacetamide (23.4 g, 269 mmol) were added together and flushed with N_2 gas. The reaction mixture was heated at 75°C under N_2 gas for 3 h. The clear yellow liquid was then extracted with ether (3 x 40 mL) to remove any by-products or starting materials. The water was removed from the aqueous layer by rotary evaporation to yield the pure product as a clear, yellowish liquid (51.5 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 3H, N=C(C*H*$_3$)(OCH$_3$)), 2.61 (s, 3H, O$_3$SOC*H*$_3$), 2.79 (s, 3H, (C*H*$_3$)(CH$_3$)N=C), 2.88 (s, 3H, (CH$_3$)(C*H*$_3$)N=C), 3.61 (s, 3H, N=C(CH$_3$)(OC*H*$_3$)). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.44, 38.45, 40.96, 53.30, 60.10, 176.26.

Step 2:

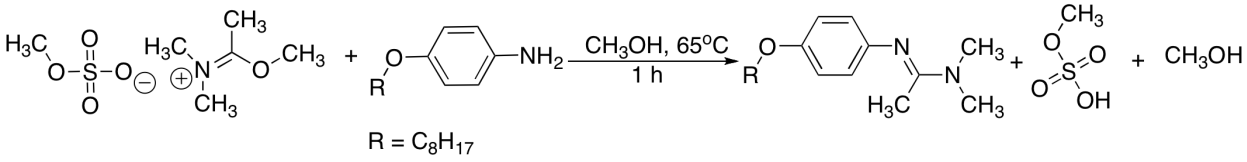


Figure 2.9 Method 2, step 2 of the synthesis of *N'*-(4-(octyloxy)phenyl)-*N,N*-dimethylacetamidine.

The intermediate synthesized in step 1 (4.50 g, 21.2 mmol) and 4-(octyloxy)-aniline (4.68 g, 21.2 mmol) were added together in methanol (50 mL). The opaque black liquid was heated at 65°C for 1 h. The methanol by-product was removed by rotary evaporation and 11 mL of 2.0 M $NaOH_{(aq)}$ solution and 40 mL of ether were added to the reaction mixture. The aqueous layer was removed and two further ether extractions were performed on this layer. The ether layers were combined and dried with adequate $MgSO_4$. Upon filtration, the solvent was removed by rotary evaporation to yield a thick, black liquid. Both ^1H and ^{13}C NMR spectra were obtained for the crude product; however, the desired product was not formed in an appreciable amount.

2.3.8 *N'*-(4-(oxymethyl)phenyl)-*N,N*-dimethylacetamidine (6a)

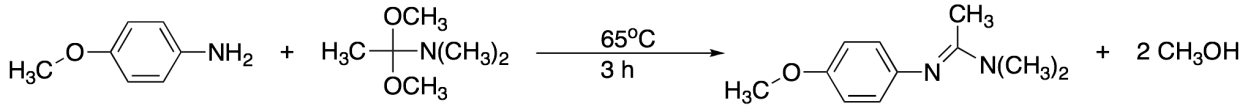


Figure 2.10 Synthesis of *N'*-(4-(methyloxy)phenyl)-*N,N*-dimethylacetamidine.

*p-A*nisidine (5.23 g, 42.4 mmol) and *N,N*-dimethylacetamide dimethyl acetal (6.28 g, 47.2 mmol) were added together. The opaque black solution was heated at 65°C for 3 h. The methanol by-product was removed by rotary evaporation yielding a

pure dark liquid product (8.03 g, 98 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (s, 3H, CC*H*$_3$), 2.89 (s, 6H, N(C*H*$_3$)$_2$), 3.64 (s, 3H, OC*H*$_3$), 6.50 (d, *J* = 8.6, 2H, C_6H_6), 6.67 (d, *J* = 8.7, 2H, C_6H_6). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 38.0, 55.5, 114.1, 123.1, 145.7, 154.6, 157.9. IR (neat, cm^{-1}): 753 (w), 842 (m), 1037 (m), 1277 (m), 1390 (m), 1505 (m), 1614 (s, υ (C=N)), 2832 (m), 2935 (s). HRMS (EI^+) m/z calc. for $[C_{11}H_{16}N_2O]^+$ 192.1263, observed 192.1266.

2.3.9 *N'*-propyl-*N,N*-dimethylbenzamidine

Step 1:

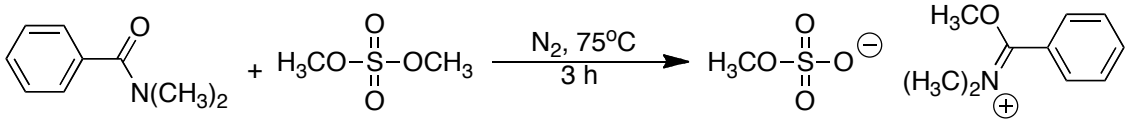


Figure 2.11 Step 1 of the synthesis of *N'*-propyl-*N,N*-dimethylbenzamidine.

Dimethylsulfate (10.2 g, 80.9 mmol) and *N,N*-dimethylbenzamide (12.0 g, 80.2 mmol) were added together and flushed with nitrogen gas. The mixture was heated at 75°C for 3 h, after which water was added and the mixture was extracted with ether (3 x 30mL). The water was removed from the aqueous layer by rotary evaporation to yield a clear liquid product (9.96 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (s, 3H, C*H*$_3$OC), 3.61 (s, 3H, $N^+(CH_3)(CH_3)$), 3.75 (s, 3H, $N^+(CH_3)(CH_3)$), 4.00 (s, 3H, C*H*$_3$$OSO_3^-$), 7.65 (m, 1H, C_6H_6), 7.67 (m, 2H, C_6H_6), 7.80 (d, *J* = 6.2, 2H, C_6H_6). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.85, 42.95, 54.60, 62.69, 124.03, 127.10, 128.04, 130.07, 133.22.

Step 2:

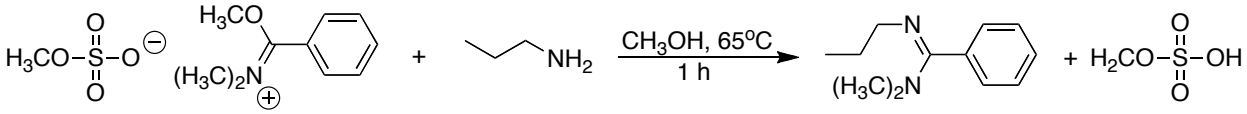


Figure 2.12 Step 2 of the synthesis of *N'*-propyl-*N,N*-dimethylbenzamidine.

The product from step 1 (4.92 g, 17.9 mmol) and propylamine (2.11 g, 35.7 mmol) were both added to methanol (60 mL). The clear colourless liquid was heated at 65°C for 1 h and then the methanol was removed by rotary evaporation. Many separation techniques were attempted including an acid extraction and distillation, but pure product was not obtained.

2.4 Synthesis of a Guanidine

2.4.1 *N*-octyl-*N',N',N'',N''*-tetramethylguanidine (7a)

Step 1:

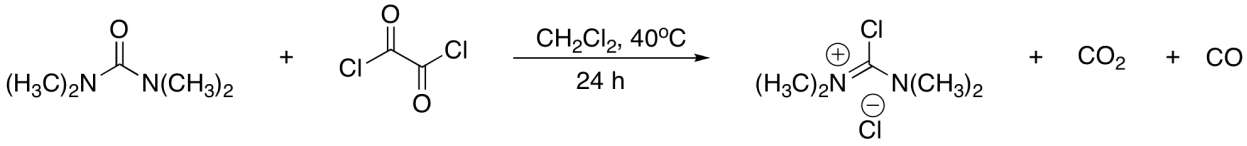
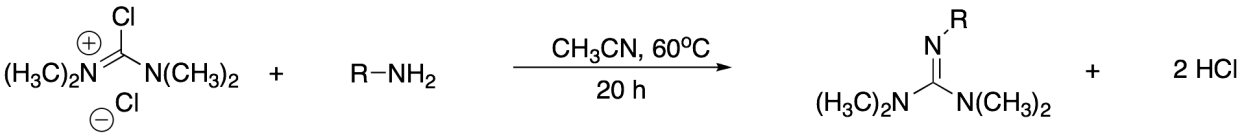


Figure 2.13 Step 1 of the synthesis of *N*-octyl-*N',N',N'',N''*-tetramethylguanidine.

A modified preparation of *N,N,N",N"*-tetramethylchloroformamidinium chloride as reported by Fujisawa and co-workers was employed.[65] All starting materials and solvents were dried prior to use and the reaction was performed under inert conditions. Tetramethyl urea (8.00 mL, 68.0 mmol) was dissolved in methylene chloride (15 mL) and then oxalyl chloride (8.74 mL, 116 mmol) was added slowly to the mixture. After

refluxing the reaction mixture for 24 h, the solvent was removed *in vacuo* yielding a brown/grey powder. The product was used in Step 2 without further purification.

Step 2:



R = C_8H_{17}

Figure 2.14 Step 2 of the synthesis of *N*-octyl-*N′,N′,N″,N″*-tetramethylguanidine.

Preparation of **7** followed a similar procedure to that reported by Wieland.[66] Octyl amine was dried over potassium hydroxide overnight and distilled prior to use. The intermediate synthesized in Step 1 (6.89 g, 40.3 mmol) was dissolved in dry acetonitrile (15 mL). In a separate flask octyl amine (20.0 mL, 121 mmol) was dissolved in dry acetonitrile (15 mL). The octyl amine solution was added dropwise and the reaction mixture was heated at 60°C for 20 h producing a dark brown liquid. The solvent was removed and ether (135 mL) was added. The solution was cooled in an ice bath. An aqueous solution of 3.75 M sodium hydroxide (54 mL) was saturated with potassium carbonate and was slowly added to the cooled solution. The organic layer was removed and the aqueous phase was extracted with ether (2 x 50 mL). The organic layers were combined, dried with potassium carbonate and filtered through a Buchner funnel. Molecular sieves (3Å) were added to the solution and the ether was removed by rotary evaporation. The orange liquid was purified by vacuum distillation to yield a clear

liquid (1.81 g, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8, 3H, CH_2CH_3), 1.29 (m, 10H, C_5H_{10}), 1.51 (m, 2H, $C_5H_{10}CH_2CH_2N$=), 2.65 (s, 6H, $N(CH_3)_2$), 2.74 (s, 6H, $N(CH_3)_2$), 3.10 (t, *J* = 7.0, 2H, CH_2N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 27.4, 29.3, 29.5, 31.8, 32.8, 38.7, 39.5, 49.6, 159.8. IR (neat): 914 (m), 1037 (w), 1065 (m), 1138 (m), 1237(m), 1237 (m), 1363 (s), 1455 (m), 1494 (m), 1625 (s, υ (C=N)), 2854 (m), 2925 (s). HRMS (EI^+) calc. for $[C_{13}H_{30}N_3]^+$ 228.2434, observed 228.2428.

2.5 Reaction of Compounds with CO_2 and H_2O

2.5.1 Attempted Isolation of Amidinium Bicarbonates

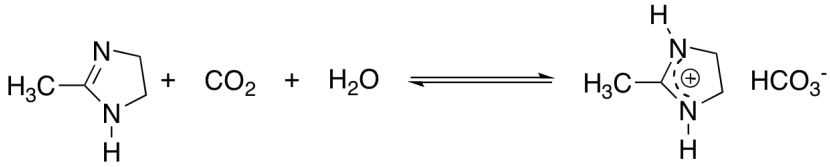


Figure 2.15 Reaction of 2-methyl-2-imidazoline with CO_2 and H_2O to form amidinium bicarbonate salt.

A qualitative experiment was performed in which 2-Methyl-2-imidazoline was dissolved in chloroform and distilled water was added, then CO_2 was then bubbled through the mixture. A white precipitate formed and was isolated by suction filtration. The protonated form was found to be soluble in methanol and water.

2-Methyl-2-imidazoline:

^{1}H NMR (400 MHz, CD_3OD): δ = 1.96 (s, 3H, CC*H*$_3$), 2.99 (s, 4H, NC$_2$*H*$_4$N). ^{13}C NMR (100 MHz, CD_3OD): δ = 15.18, 50.02, 164.34. IR (neat, cm^{-1}): 948 (w), 1036 (m), 1091 (m), 1267 (m), 1297 (m), 1395 (w), 1439 (m), 1621 (s, υ (C=N)), 2343 (m), 2363 (s), 2958 (w), 3351 (s).

2-Methyl-2-imidazolinium bicarbonate salt:

^{1}H NMR (400 MHz, CD_3OD): δ = 2.23 (s, 3H, CC*H*$_3$), 3.92 (s, 4H, NC$_2$*H*$_4$N). ^{13}C NMR (100 MHz, CD_3OD): δ = 10.77, 44.80, 159.88 (HCO_3^-)[67], 168.15. IR (neat, cm^{-1}): 703 (m), 832 (m, υ out-of-plane (HCO_3^-))[68,69], 1007 (m), 1038 (w), 1270 (w), 1293 (m), 1402 (s), 1623 (s, υ (C=N)), 2706 (w), 2967 (m), 3200 (m).

The same procedure was attempted for compounds **2a** and **3a**, the longer chain imidazolines, in chloroform, methanol, acetone and toluene; however, precipitation of amidinium bicarbonate salts did not occur.

2.5.2 *In situ* Preparation and Characterization of Protonated Bicarbonate Salts

General procedure for IR spectra characterization:

The compound being studied was dissolved in dichloromethane with a slight excess of distilled H_2O added. CO_2 was bubbled through the solution that was being

stirred until the majority of dichloromethane had evaporated. An infrared spectrum of the residual product was obtained.

General procedure for ^{1}H and ^{13}C NMR spectra characterization:

The compound being studied was dissolved in a deuterated solvent with a 10 equivalents molar excess of distilled H_2O in an NMR tube. CO_2 was bubbled through the solution for 20 minutes and NMR spectra were recorded. Not all coupling constants could be determined due to peak broadening.

Protonated Data:

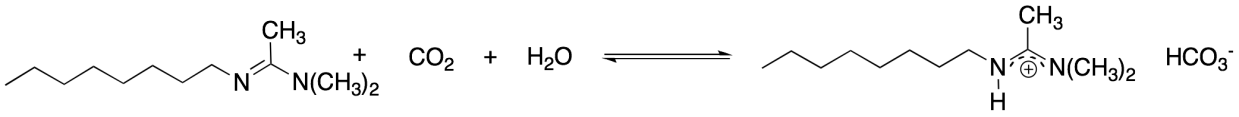


Figure 2.16 Reaction of **1a** with CO_2 and H_2O to form **1b**.

Compound **1b**: *N'*-octyl-*N,N*-dimethylacetamidinium bicarbonate.

^{1}H NMR (400 MHz, DMSO-d^6): δ = 0.833 (t, 3H, CH_2CH_3), 1.29 (m, 10H, C_5H_{10}), 1.52 (2H, CH_2CH_2N), 2.20 (CCH_3), 3.10 (s, 3H, $N(CH_3)_2$), 3.29 (2H, $C_5H_{10}CH_2N$). ^{13}C NMR (100 MHz, DMSO-d^6): δ = 14.37, 14.61, 22.55, 26.52, 29.13, 29.19, 30.17, 31.73, 44.81, 44.88, 159.61 (HCO_3^-), 164.00. IR (neat, cm^{-1}): 689 (m), 834 (m, υ out-of-plane (HCO_3^-)), 1005 (m), 1380 (s), 1650 (s, υ (C=N)), 1924 (w), 2664 (w), 2855 (m), 2925 (m).

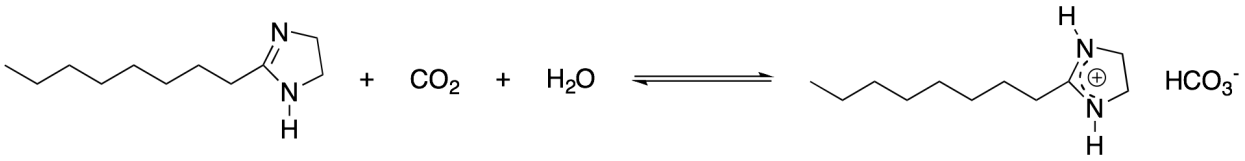


Figure 2.17 Reaction of **2a** with CO_2 and H_2O to form **2b**.

Compound **2b**: 2-octyl-2-imidazolinium bicarbonate.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.833 (t, 3H, CH_2CH_3), 1.22 (m, 10H, C_5H_{10}), 1.47 (m, 2H, $CH_2CH_2CH_2C$), 2.38 (2H, CH_2CH_2C), 3.69 (s, 4H, NC_2H_4NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.08, 22.64, 26.68, 29.15, 29.17, 29.29, 29.40, 31.83, 49.23, 155.41 (HCO_3^-), 168.52. IR (neat): 706 (m), 833 (m, υ out-of-plane (HCO_3^-)), 996 (m), 1377 (s), 1617 (s), 1695 (s, υ (C=N)), 1923 (w), 2546 (w), 2855(w), 2925 (m), 3446 (s).

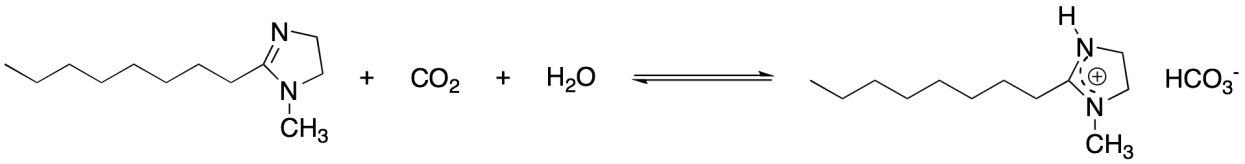


Figure 2.18 Reaction of **3a** with CO_2 and H_2O to form **3b**.

Compound **3b**: 1-methyl-2-octyl-2-imidazolinium bicarbonate.

^{1}H NMR (400 MHz, DMSO-d^6): δ = 0.833 (t, 3H, CH_2CH_3), 1.23 (m, 10H, C_5H_{10}), 1.51 (m, 2H, $CH_2CH_2CH_2C$), 2.41 (t, 2H, CH_2CH_2C), 2.92 (s, 3H, NCH_3), 3.64 (s, 4H, NC_2H_4NH). ^{13}C NMR (100 MHz, DMSO-d^6): δ = 13.21, 22.31, 24.65, 25.05, 28.78,

31.55, 31.91, 42.39, 51.42, 159.91 (HCO_3^-), 170.14. IR (neat, cm^{-1}): 703 (m), 833 (m, υ out-of-plane (HCO_3^-)), 1006 (m), 1372 (s), 1400 (s), 1622 (s), 1659 (s, υ (C=N)), 1922 (w), 2623 (w), 2855 (m), 2925 (m), 3400 (m).

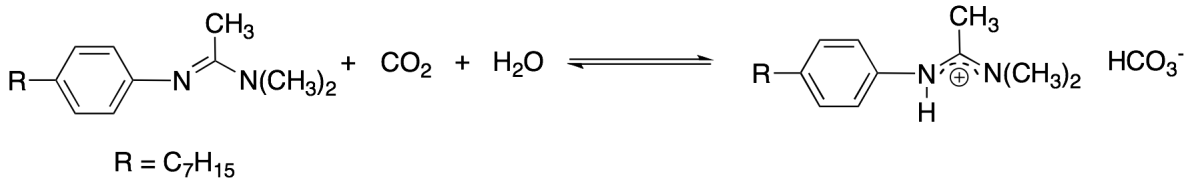


Figure 2.19 Reaction of **4a** with CO_2 and H_2O to form **4b**.

Compound **4b**: *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidinium bicarbonate.

^1H NMR (400 MHz, D_2O): δ = 0.89 (3H, CH_2CH_3), 1.29 (8H, C_4H_8), 1.52 (2H, CH_2CH_2C), 1.84 (3H, CCH_3), 2.47 (2H, CH_2C), 3.11 (6H, $N(CH_3)_2$), 6.90 (2H, C_6H_6), 7.04 (2H, C_6H_6). ^{13}C NMR (100 MHz, D_2O): δ = 13.05, 21.67, 28.05, 28.37, 30.44, 31.24, 34.65, 38.57, 122.17, 127.59, 159.30, 161.67. IR (neat, cm^{-1}): 704 (m), 833 (m, υ out-of-plane (HCO_3^-)), 1009 (m), 1391 (s), 1622 (s, υ (C=N)), 1924 (w), 2579 (w), 2855 (m), 2926 (m), 3431 (w).

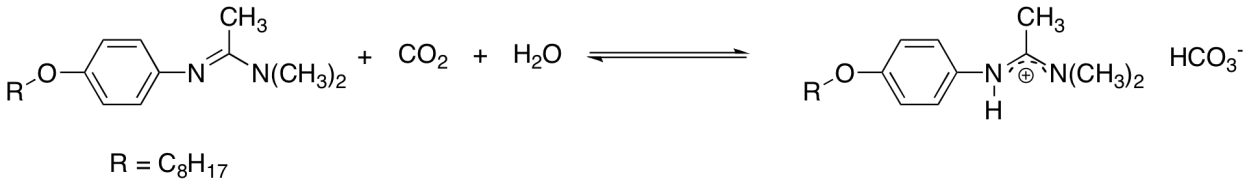


Figure 2.20 Reaction of **5a** with CO_2 and H_2O to form **5b**.

Compound **5b**: *N'*-(4-(octyloxy)phenyl)-*N,N*-dimethylacetamidinium bicarbonate.

^{1}H NMR (400 MHz, D_2O): δ = 0.92 (3H, CH_2CH_3), 1.30 (8H, C_4H_8), 1.37 ($CH_2CH_2CH_2O$), 1.64 (2H, CH_2CH_2O),1.92 (3H, CCH_3), 3.14 (6H, $N(CH_3)_2$), 3.79 (2H, CH_2CH_2O), 6.79 (2H, C_6H_4), 7.03 (2H, C_6H_4). ^{13}C NMR (100 MHz, D_2O): δ = 13.03, 21.75, 25.14, 28.36, 28.64, 31.03, 67.28, 126.94, 156.99, 159.32, 162.89. IR (neat, cm^{-1}): 834 (w, υ out-of-plane (HCO_3^-)), 1020 (w), 1246 (m), 1397 (m), 1512 (m), 1646 (s, υ (C=N)), 2077 (m), 2341 (m), 2360 (m), 2924 (w), 3448 (s).

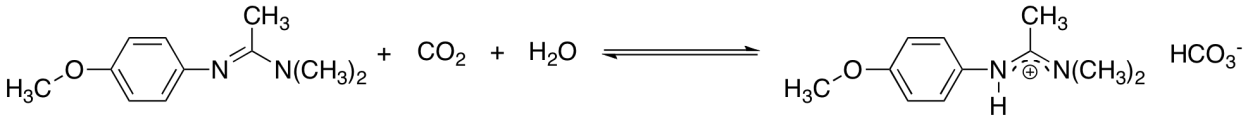


Figure 2.21 Reaction of **6a** with CO_2 and H_2O to form **6b**.

Compound **6b**: *N'*-(4-(methyloxy)phenyl)-*N,N*-dimethylacetamidinium bicarbonate.

^{1}H NMR (400 MHz, D_2O): δ =1.97 (s, 3H, CCH_3), 3.21 (s, 6H, $N(CH_3)_2$), 3.76 (s, 3H, OCH_3), 6.98 (d, J = 7.4, 2H, C_6H_6), 7.12 (d, J = 7.4, 2H, C_6H_6). ^{13}C NMR (100 MHz, D_2O): δ = 14.83, 37.99, 40.20, 54.79, 127.62, 128.14, 158.00, 159.32, 163.95. IR (neat,

cm^{-1}): 832 (m, υ out-of-plane (HCO_3^-)), 1027 (m), 1174 (w), 1248 (m), 1404 (w), 1514 (m), 1646 (s, υ (C=N)), 2068 (m), 3427 (w).

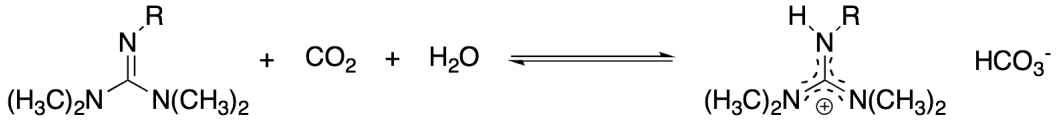


Figure 2.22 Reaction of **7a** with CO_2 and H_2O to form **7b**.

Compound **7b**: *N*-octyl-*N',N',N",N"*-tetramethylguanidinium bicarbonate.

^{1}H NMR (400 MHz, DMSO-d^6): δ = 0.833 (t, 3H, CH_2CH_3), 1.23 (m, 10H, C_5H_{10}), 1.50 (m, 2H, $C_5H_{10}CH_2CH_2$), 2.86 (s, 12H, $(N(CH_3)_2)_2$), 3.07 (t, 2H, CH_2N). ^{13}C NMR (100 MHz, DMSO-d^6): δ = 14.37, 22.51, 26.49, 26.56, 29.04, 29.56, 29.62, 31.64, 31.69, 44.81, 159.19 (HCO_3^-), 161.41. IR (neat, cm^{-1}): 703 (m), 834 (m, υ out-of-plane (HCO_3^-)), 1005 (m), 1378 (s), 1625 (s, υ (C=N)), 1924 (w), 2636 (w), 2855 (m), 2926 (m).

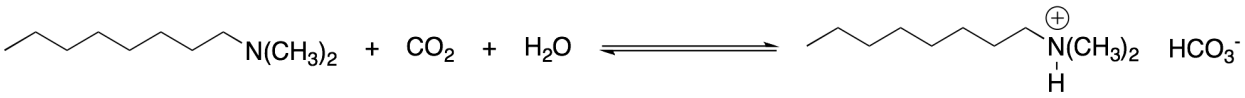


Figure 2.23 Reaction of **8a** with CO_2 and H_2O to form **8b**.

Compound **8a***:* Dimethyloctylamine

^{1}H NMR (400 MHz, DMSO-d^{6}): δ = 0.86 (t, *J* = 6.6 Hz, 3H, CH_2CH_3), 1.25 (m, 10H, $CH_3C_5H_{10}$), 1.37 (m, 2H, $C_5H_{10}CH_2CH_2N$), 2.09 (s, 6H, $N(CH_3)_2$), 2.16 (t, *J* = 7.0 Hz, 2H, CH_2CH_2N). ^{13}C NMR (100 MHz, DMSO-d^{6}): δ = 13.88, 22.01, 26.70, 26.76, 28.59, 28.83, 31.18, 44.85, 58.95. IR (neat, cm^{-1}): 1042 (m), 1170 (m), 1267 (w), 1379 (w), 1466 (s), 2359 (m), 2762 (s), 2813 (m), 2854 (m), 2927 (s).

Compound **8b***:* Dimethyloctylammonium bicarbonate

H NMR (400 MHz, DMSO-d^{6}): δ = 0.86 (t, *J* = 6.6 Hz, 3H, CH_2CH_3), 1.25 (m, 10H, $CH_3C_5H_{10}$), 1.38 (m, 2H, $C_5H_{10}CH_2CH_2N$), 2.13 (s, 6H, $N(CH_3)_2$), 2.21 (t, *J* = 7.0 Hz, 2H, CH_2CH_2N). IR (neat, cm^{-1}): 832 (m, υ out-of-plane (HCO_3^-)), 999 (m), 1377 (m), 1466 (m), 1660 (s), 2076 (w), 2342 (m), 2360 (m), 2762 (m), 2856 (m), 2927 (m), 3446 (s). ^{13}C NMR (100 MHz, DMSO-d^{6}): δ = 159.32 (HCO_3^-). There was no apparent change in the other signals from the neutral form in the ^{13}C NMR spectra.

2.6 Determination of Chemical Properties and Reactivity of Compounds

2.6.1 Solubility of Compounds in D_2O

The surfactant being studied (0.20 mmol) was dissolved in 3 mL of D_2O and stirred for 30 min in a sample vial. The mixture was allowed to stand for 30 min allowing any undissolved surfactant to sediment, which allowed for collection of the aqueous solution. A 200 μL aliquot of the aqueous solution was combined together in an NMR tube with DMF as an internal standard. The NMR tube was topped up with D_2O to 0.6

mL and a ^{1}H NMR spectrum was obtained. The amount of internal standard was 10 μL for octylamine and compounds **1**, **2**, and **3** while 5 μL was used for compounds **4** and **5**. 0.20 mmol of compound **9** was fully miscible with 3 mL of D_2O so an increased amount of the compound was needed as well as an increased amount of the internal standard (25 μL).

2.6.2 Thermogravimetric Analysis

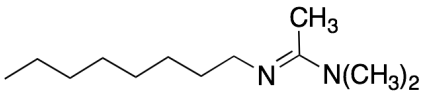
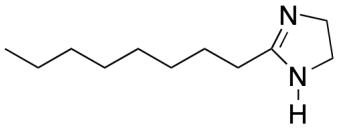
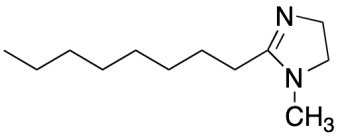
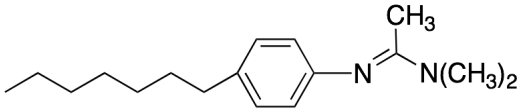
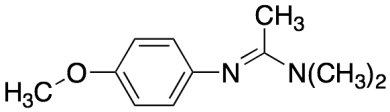
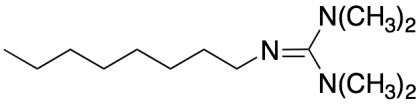
Preparation method 1:

The exact procedure that was used for the IR spectroscopic characterization of the "On" form was used to isolate the bicarbonates but after the thermogravimetric analysis (TGA) was performed it was found that some dichloromethane still remained which did not allow for the proper mass loss.

Preparation method 2:

A slight molar excess of distilled H_2O was added to a vial containing the compound being studied. The mixture was bubbled with CO_2 gas for 20 min and all showed physical changes, as described in the table below (Table 2.1). A small amount of the mixture was heated to 350 °C at the rate of 5 °C per minute. Only compound **1b** showed the proper mass loss ratio.

Table 2.1 Physical changes between the bases (**a**) and their protonated bicarbonate form (**b**).

#	Compound	a	b
1		clear liquid	white gel
2		yellowish white crystalline solid	yellowish clear liquid
3		yellowish clear liquid	viscous yellowish clear liquid
4		yellow clear liquid	white gel
6		black opaque liquid	thicker black liquid
7		clear liquid	viscous clear liquid

2.6.3 Measurement of the Extent of Conversion by ^{1}H NMR Spectroscopy

Determination of the 1H NMR spectrum of the cation

^{1}H NMR spectroscopy was employed as a characterization method to determine the percentage of conversion to the bicarbonate salt that could be produced when CO_2 was introduced to a solution of each amidine, guanidine, or amine. These studies first involved determination of the ^{1}H NMR spectra of the cations formed by protonation of those bases employing the addition of strong acids to a solution of the base. In a typical experiment using compound **1a** as the base, a large molar excess of hydrochloric acid

was added to a mixture of **1a** dissolved in DMSO-d_6 and a ^{1}H NMR spectrum was obtained. To ensure that the counter anion introduced by the acid did not affect the ^{1}H NMR data, this same procedure was also carried out using acetic acid and trifluoroacetic acid (TFA). The ^{1}H NMR spectra of the salts of **1a** with each acid studied were similar. The chemical shift values for the cations were averaged to give the expected chemical shifts for the bicarbonate salt of **1a**. These shifts were used in the development of a formula in which the percentage of the protonated form **1b** could be calculated, as explained in section 3.6.

Transformation of base to bicarbonate salt using CO_2

In a typical experiment, **1a** (40 mg) was put into an NMR tube along with a 10 times molar excess of distilled H_2O and in DMSO-d_6 (0.6 mL). An ^{1}H NMR spectrum was taken of **1a**, and then CO_2 was bubbled through the solution for 1 second and another ^{1}H NMR spectrum was obtained. This process was repeated twice more. It was observed that the chemical shift of certain protons of **1a** shifted slightly downfield with each successive bubbling of CO_2.

Temperature dependence of the transformation

The transformation between the base and bicarbonate salt compounds was evaluated at 40 °C and 60 °C to determine the effect of temperature on the reaction with CO_2. The temperature studies were performed to investigate: (i) the reaction with the base with CO_2 and (ii) the loss of CO_2 from the bicarbonate form.

(i) "From Off"

Compound **1a** (0.11 mmoles) was weighed out into a 5 mm NMR tube, 25.0 μl of distilled H_2O was added along with 0.60 mL of DMSO-d^6. The tube was set in a 40 °C water bath and CO_2 was bubbled through the mixture for 4 minutes. A ^1H NMR spectrum was taken immediately with the internal temperature of the NMR being kept constant at 40 °C. The tube was then placed back into the 40 °C water bath and bubbled again with CO_2 for 2 minutes. A second ^1H NMR spectrum was obtained at 40 °C and this procedure was repeated twice more.

(ii) "From On"

The sample was prepared as outlined above for the "From Off" procedure; however, the mixture was first bubbled with CO_2 for 20 minutes at room temperature, then bubbled with CO_2 for 3 minutes at 40 °C in the water bath. An ^1H NMR spectrum was obtained at 40 °C. The tube was then placed back into the 40 °C water bath and bubbled again with CO_2 for 2 minutes. A second ^1H NMR spectrum was obtained at 40 °C and this procedure was repeated twice more.

Compounds **1a**, **2a**, **3a**, **4a**, **6a**, **7a**, and **8a** were tested at 40 °C and compounds **1a** and **7a** were also tested at 60 °C. Each experiment, "From Off" and "From On", was performed twice to ensure consistent results for each compound. Both **4b** and **6b** were insoluble in DMSO-d_6, acetone-d_6, and acetonitrile-d_3; however, they possessed slight solubility in D_2O. Similar experiments were conducted employing D_2O as solvent for **4a** and **6a**, although reproducible results could not be obtained.

2.6.4 Calorimetry

Calorimetry experiments were conducted to determine the heat of protonation for the formation of amidinium salts employing a strong acid. Prior to investigation of the heat of protonation of the novel compounds reported here, a general procedure was developed for triethylamine (in water) and aniline (in DMSO) to ensure the known literature values could be reproduced with reasonable accuracy using this methodology. The calorimeter apparatus employed is shown in Figure 2.24 and involved measurement of both a sample and reference vial to eliminate any influence of dissolution enthalpies.

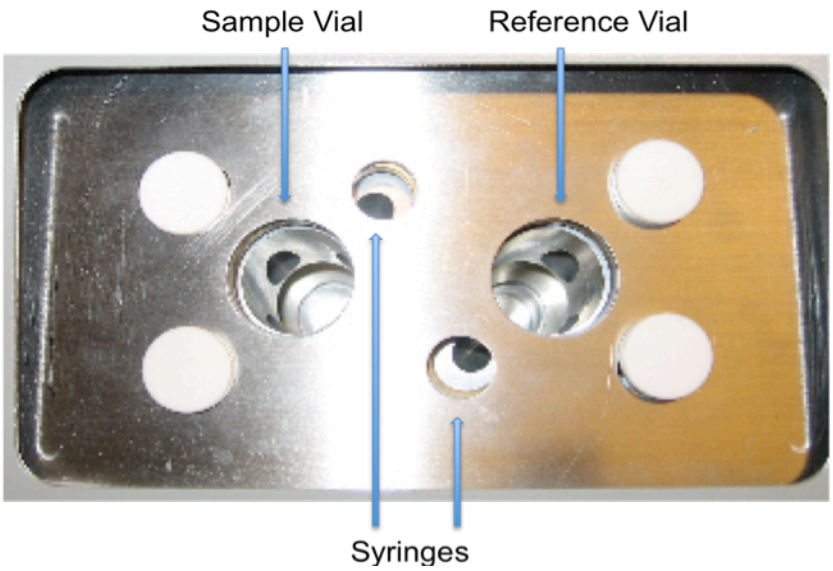


Figure 2.24 Calorimeter apparatus (birds' eye view).

In a typical experiment, the base being studied (0.3 mmol) was weighed out into a sample vial. The sample vial was filled with solvent to a total volume of 2.0 mL and the reference vial was filled with only 2.0 mL of solvent and none of the base. A stir bar

was added to both vials and the samples were stirred at 570 rpm. Identical syringes were employed for the sample and reference and contained 0.15 mL of 12 M HCland 0.85 mL of DMSO (Figure 2.25). The syringe needles were inserted into the vials, with no contact to the solution to ensure that the vials could be lowered in and out of the calorimeter without disturbing the samples. Once the vials were placed into the calorimeter, the system was allowed to equilibrate for 15-20 min to establish the temperature and heat flow. The solution contained in the syringe was then added simultaneously to both the sample and reference vials and the system was left until equilibrium was reached (20-40 min depending on the sample). The software was used to integrate the heat flow peak to obtain the heat of the reaction, which provided the heat of protonation when divided by the molar amount in the sample employed.

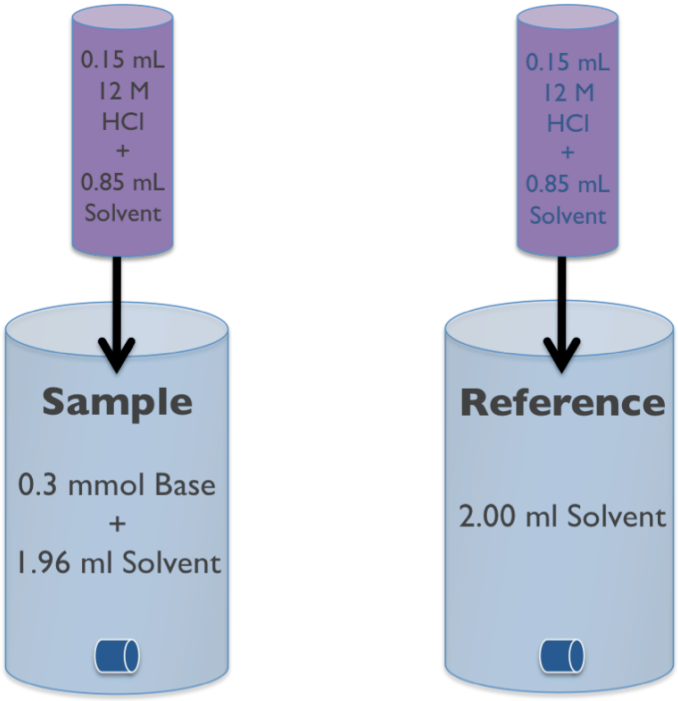


Figure 2.25 Schematic representation of the calorimetry experimental setup.

2.6.5 Demulsifying of crude oil and water emulsions

Crude oil/water without base

Crude oil (Chevron, North Sea, 4 mL) and deionized water (2 mL) were added to a vial. The vial was shaken in a Retsch MM2 mixer mill at the speed setting of 100 for 10 min. The vial was placed on the bench top and was monitored for separation by height measurements at certain time intervals with a cathetometer.

Crude oil/water with base

Crude oil (Chevron, North Sea, 4 mL), deionized water (2 mL) and "Off" surfactant (0.29 mmol) were added to a vial. The vial was shaken in a Retsch MM2 mixer mill at the speed setting of 100 for 10 min. The vial was placed on the bench top and was monitored for separation by height measurements at certain time intervals with a cathetometer. Only compounds **1a**, **2a**, **3a**, **4a**, **5a**, **7a**, and **8a** were tested and each stability test was performed twice.

3 Results and Discussion

3.1 Synthesis and Characterization of Amidines

The goal of this work was to synthesize a series of neutral amidine and guanidine compounds to investigate their capabilities as demulsifiers. Jessop and co-workers reported the employment of acetamidines, of varying alkyl chain lengths, as effective emulsifying and demulsifying agents of O/W emulsions.[2] This thesis work builds upon previous research by examining the influence of the head group structure on the surfactant properties of these compounds. Alterations to the head group impacts the basicity of the molecule and ultimately the ability of the base to demulsify emulsions. The research plan started with the synthesis of a first generation switchable surfactant, similar to that first reported by our group, to use as a standard against which to compare this novel series of amidines and guanidines.

3.1.1 *N'*-octyl-*N,N*-dimethylacetamidine (1a)

The first generation surfactant, *N'*-octyl-*N,N*-dimethylacetamidine, was synthesized by a modified Scoggins' procedure for acetamidines[63] that was previously developed by the Jessop group (Figure 3.1).[2]

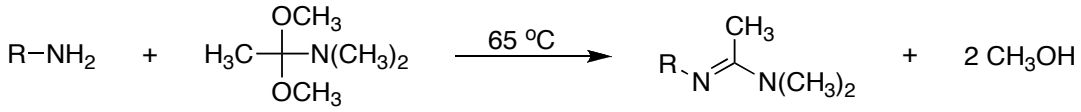


Figure 3.1 Modified Scoggins' procedure for the synthesis of acetamidine compounds.

This procedure was previously employed for the synthesis of dodecyl (R = $C_{12}H_{25}$) and hexadecyl (R = $C_{16}H_{33}$) derivatives; however, the octyl (R = C_8H_{17}) chain acetamidine, **1a,** was desired for this work. All compounds in this work employed the octyl chain to allow for comparison to be directly related to the variance in head group structure. Compound **1a** was synthesized from octylamine and purified via vacuum distillation to achieve pure product. Purification of the dodecyl and hexadecyl acetamidines involved the formation and isolation of the amidinium bicarbonate, but this purification method was unsuccessful for the octyl derivative and was therefore replaced with distillation.

3.1.2 Synthesis of Imidazoline Compounds

The second amidine structure identified as a potential head group candidate was the imidazoline moiety and four target molecules were chosen (Figure 3.2). A literature search revealed a general procedure for the synthesis of imidazolines reported by Shi et *al.*[64] The initial imidazoline targets were selected to provide a variety of structures possessing different basicities as a result of the alkylation of the nitrogen at position 1 or the alteration of the substituent at position 2. The synthesis of imidazolines involved refluxing an ethylene diamine and a carboxylic acid in toluene while removing the water that is formed to force the equilibrium towards the product (Figure 3.3). As such, this procedure allowed for the synthesis of various imidazolines by employing different ethylene diamines and carboxylic acids.

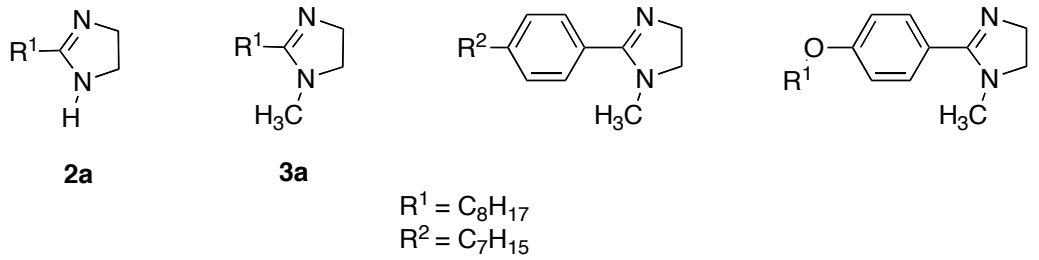


Figure 3.2 Initial four target molecules as the second generation amidine switchable surfactants.

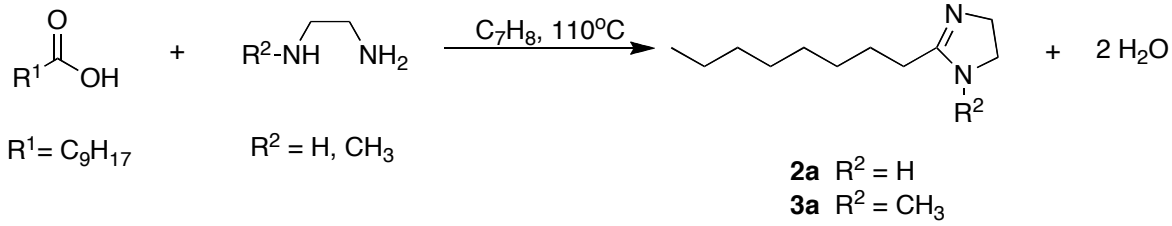


Figure 3.3 General procedure for the synthesis of imidazoline compounds.

3.1.3 2-octyl-2-imidazoline (2a)

The synthesis of **2a** involved the reaction between ethylenediamine and nonanoic acid. The first step of the reaction produces an amide intermediate that through further dehydration ring closure occurs to form the product. Even though the desired product was formed, the separation of the product, starting materials, and the amide intermediate proved to be challenging. After the reaction cooled a white precipitate formed which was filtered and the yellow filtrate was rotoevaporated to yield a yellow powder. In the NMR spectra for the mixture it was found to be difficult to distinguish between the intermediate and product and so 2-methyl-2-imidazoline was purchased for determining the characteristic chemical shifts for both the ^{1}H NMR

spectra and the ^{13}C NMR spectra of an imidazoline. Through these NMR spectra the product was determined to be in the yellow powder along with starting material and intermediate in about a 2:1:1 ratio. Many separation techniques were attempted. Both acid and base extractions were attempted but were found to cause ring opening of the imidazoline moiety. Chromatographic separation on basic alumina was tried to trap the carboxylic starting material, but the intermediate and product were found to have similar retentions, causing separation to be unsuccessful. Finally, vacuum distillation of the crude mixture, as with compound **1a**, was found to be an effective purification method and a white crystalline solid, **2a**, was obtained.

3.1.4 1-methyl-2-octyl-2-imidazoline (3a)

Compound **3a** was synthesized as outlined for **2a** employing *N*-methylethylenediamine (Figure 3.3, R_2=CH_3) and nonanoic acid. The reaction provided a dark brown viscous liquid, which was purified through vacuum distillation to provide pure product **3a**.

3.1.5 Aryl imidazolines

Synthesis of the aryl target compounds was attempted as outlined for **2a** employing *N*-methylethylenediamine (R_2=CH_3) and 4-heptylbenzoic acid or 4-(octyloxy)benzoic acid. Formation of the desired products was achieved however, distillation of the crude products proved to be unsuccessful due to the high boiling points

of the aryl imidazolines. Various separation methods were also not able to achieve the purification of the aryl derivatives.

3.1.6 Aryl acetamidines

Synthesis of the target aryl imidazolines could not be achieved however, the investigation of phenyl based amidines was important to this work. To this end, three aryl acetamidine target molecules were identified (Figure 3.4), in which the synthesis of these molecule was achieved using the modified Scoggins' procedure (Figure 3.1).

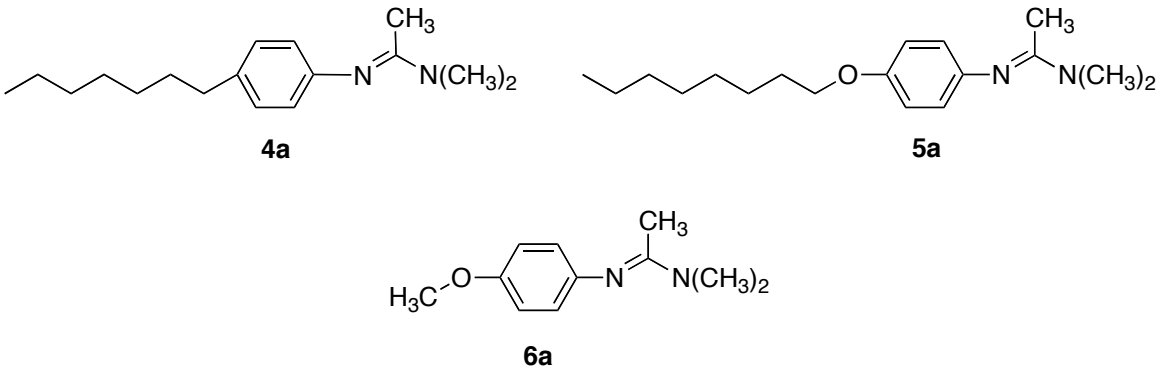


Figure 3.4 Three aryl acetamidine molecules that were synthesized.

3.1.7 *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidine (4a)

Compound **4a** was synthesized as was outlined for **1a,** employing 4-heptylaniline as the amine starting material. Purification of the crude mixture was achieved through vacuum distillation to provide pure product **4a**.

3.1.8 *N'*-(4-(alkyloxy)phenyl)-*N,N*-dimethylacetamidines (5a) and (6a)

Compound **5a** was synthesized as outlined for **4a** employing 4-(octyloxy)aniline (Figure 3.1); although, due to the high boiling point of **5a**, vacuum distillation and all other purification attempts of the crude mixture were unsuccessful. In order to obtain an amidine derivative of 4-(alkyloxy)aniline, the alkyl chain was altered from octyl to methyl. Compound **6a** was synthesized as was outlined for **1a** employing 4-(methyloxy)aniline and vacuum distillation provided pure compound **6a**.

3.1.9 Synthesis of *N'*-propyl-*N,N*-dimethylbenzamidine

The placement of the aryl group was also a structural feature under investigation. To this end, the synthesis of amidines substituted with an aryl group at the 2-position would provide a comparison between these compounds and *N*-arylated compounds (**4a**, **5a**, and **6a**). The synthesis of *N*'-propyl-*N,N*-dimethylbenzamide was proposed however, the isolation of this amidine could not be achieved.

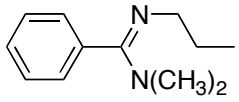
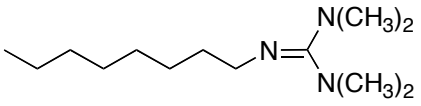


Figure 3.5 *N*'-propyl-*N,N*-dimethylbenzamide.

3.2 Synthesis and Characterization of a Guanidine

Guanidine compounds were postulated to have similar characteristics to amidines, but with an increased basicity. As such, guandines were identified as potential head

groups in the development of switchable surfactant. A synthetic route to guanidines was modified from the literature[65,66] to provide the octyl derivative, compound **7a** (Figure 3.6). This two-step procedure was carried out employing octyl amine and after purification via vacuum distillation, a clear liquid product was obtained. The overall product yield was low, although, the reaction conditions were not optimized. (Figure 2.13 and Figure 2.14).



7a

Figure 3.6 Compound **7a**, *N*-octyl-*N′,N′,N″,N″*-tetramethylguanidine.

3.3 Reaction of Compounds with CO_2 and H_2O

Amidines have been shown to form amidinium bicarbonate salts when reacted with H_2O and CO_2.[38] Additional research in the Jessop group involved extensive isolation and characterization of amidinium bicarbonate salts to prove their formation.[43] The goal of this work was to also synthesize the amidinium bicarbonate salts of the novel amidine and guanidine compounds. Seven amidine and guanidine compounds were synthesized to be tested as CO_2 switchable surfactants (Figure 3.7). Dimethyloctylamine (**8a**) was purchased and also tested in the reaction with CO_2 to compare the reactivity of an amine versus varying amidines and a guanidine head group. All tests were first developed using the first generation compound **1a**, as it was readily available.

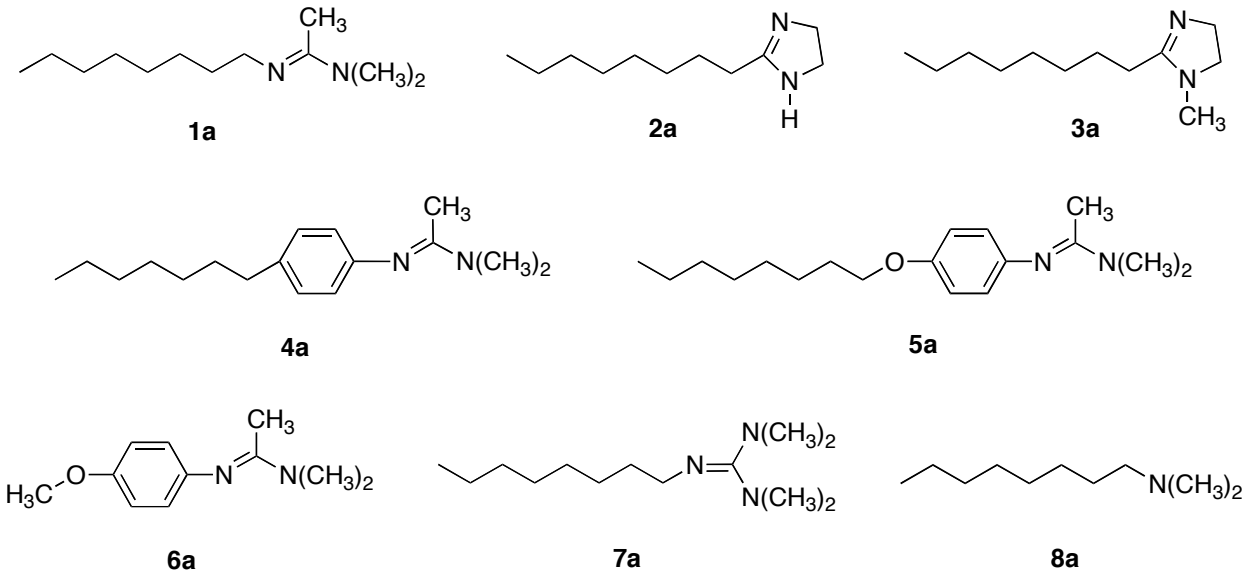


Figure 3.7 Schematic representation of amidine and guanidine compounds tested in the reaction with CO_2 and H_2O.

The reaction with CO_2 involved the dissolution of **1a** in dichloromethane, and an equal molar amount of H_2O was added. CO_2 was bubbled through the solution until little solvent remained. An IR spectra was obtained of **1a** and then of **1b**. The spectrum of **1b** showed the appearance of a new signal near 835 cm^{-1} which was indicative of the formation of a bicarbonate salt.[68,69] There was no appearance of a carbonate anion which is known to have a signal at 880 cm^{-1}.[68,69] Compounds **2a** through **8a** were reacted and analyzed as outlined for **1a**.

Additional characterization of the reactivity of **2a** with CO_2 was required as it has been reported that CO_2 can insert into the N-H bonds of amines.[70,71] Furthermore, amines have H-bonding ability, which may affect the hydrophilicity as a base by decreasing or eliminating the capability of the molecule to demulsify oil and water

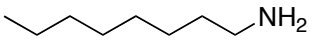
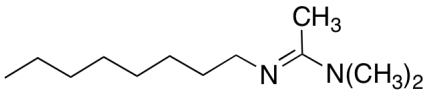
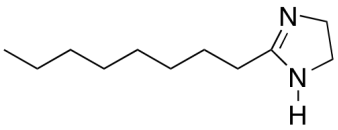
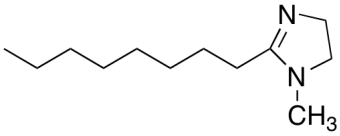
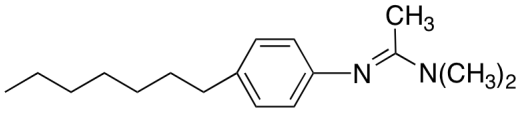
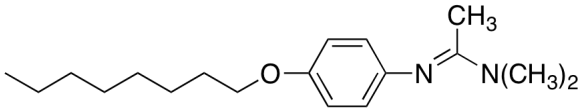
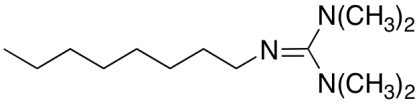
mixtures. To test these influences on the reactivity with CO_2, 2-methyl-2-imidazoline was employed as a model of **2a** since isolation of the amidinium bicarbonate could be achieved, where the corresponding salt of **2a** could not be isolated. The precipitate that formed from the reaction of 2-methyl-2-imidazoline with CO_2 showed a downfield shift of the ^{1}H NMR signals near the amidinium moiety and the appearance of a new ^{13}C signal at 159.88 ppm which is the chemical shift of a bicarbonate anion (in contrast to a carbonate anion that would have a chemical shift around 168 ppm).[67] IR analysis of this precipitate also possessed a signal at 832 cm^{-1}, which indicated the formation of the bicarbonate species. Characterization of the salt produced between 2-methyl-2-imidazoline and CO_2 showed that CO_2 insertion at the N-H bond was not occurring because the bicarbonate salt was the product formed.

NMR spectroscopy was a good method to determine the specific difference between the base and bicarbonate salt compounds, however, solubility issues were encountered as all bicarbonate salts investigated were not soluble in the same solvent as their neutral forms. As such, direct comparison between the NMR data of each compound could not be attained. Some trends in the data were observed including: (1) downfield shift of the ^{1}H NMR signals corresponding to the hydrogen atoms closest to the amidinium functionality and (2) appearance of a new signal in the ^{13}C NMR spectra around 160 ppm. A chemical shift near 160 ppm is consistent with the pure bicarbonate species, while a shift at 168 would be seen for pure carbonate and a shift between 161-166 is a mixture of the two species.[67]

3.4 Solubility in D_2O

The solubility of compounds **1a**, **2a**, **3a**, **4a**, **5a**, **7a** in D_2O was tested. All of the aforementioned compounds were soluble in toluene, but only marginally soluble in water. To quantitatively measure the solubility of each compound in water, an excess of compound was stirred in D_2O in a vial for 30 min open to air and then allowed to settle. 200 μL of the saturated solution was added to an NMR tube along with DMF as an internal standard. The NMR tube was topped off with D_2O to ensure that no temperature changes during the NMR acquisition would cause precipitation and skew the results. The solubilities in D_2O were determined through ^1H NMR signal integration relative to the DMF internal standard. The solubility in D_2O was measured three times and an average was calculated. Verification of this method was performed through the determination of the literature reported solubility of octylamine, 0.2 g/L.[13] The results obtained for the novel compounds are summarized in Table 3.1. From these results, it can be seen that the solubilities of these amidine and guanidine compounds are low, because of the hydrophobicity of the long alkyl chain. The aryl amidines, **4a** and **5a**, had the lowest solubility in D_2O. The guanidine compound **7a** had by far the highest solubility in D_2O.

Table 3.1 Solubilities of selected bases in D_2O at room temperature.

#	Molecule	Solubility in D_2O (g/L)
-		0.2 ± 0.08
1a		4.9 ± 0.08
2a		1.7 ± 0.2
3a		3.0 ± 0.07
4a		0.1 ± 0.06[a]
5a		0.1 ± 0.03[a]
7a		39 ± 4[b]

0.20 mmol of sample, 3 mL of D_2O stirred for 30 min at room temperature. 200 μL aliquot, 10 μL DMF internal standard, 0.6 mL D_2O. [a] Only 5 μL of DMF. [b] 0.40 mmol and 25 μL of DMF.

3.5 Thermogravimetric Analysis

The thermodynamics of the reaction of CO_2 with the various amidine and guanidine compounds was of major interest to this project and was quantified through thermogravimetric (TGA), calorimetric and NMR analysis. Studying the thermodynamics allowed for a comparison between the switchability and the temperature for loss of CO_2 for each compound. This is important data that would allow for speculation of which applications that each compound could be employed.

TGA was used to determine the temperature at which the long alkyl chain bicarbonate salts deprotonated, as the mass loss of CO_2 and H_2O could be observed. Analysis of the first generation compound **1b**, showed a similar mass loss

to that of the predicted mass loss of 23.8% (Figure 3.8). Analysis of the bicarbonate salts of the remaining amidine and guanidine compounds studied were inconclusive as the proper mass loss for CO_2 and H_2O was not present. There were residual amounts of solvent present which caused the mass loss value to be incorrect. Several isolation methods were investigated, although pure samples of the bicarbonate salts could not be attained and TGA's of these salts were unsuccessful.

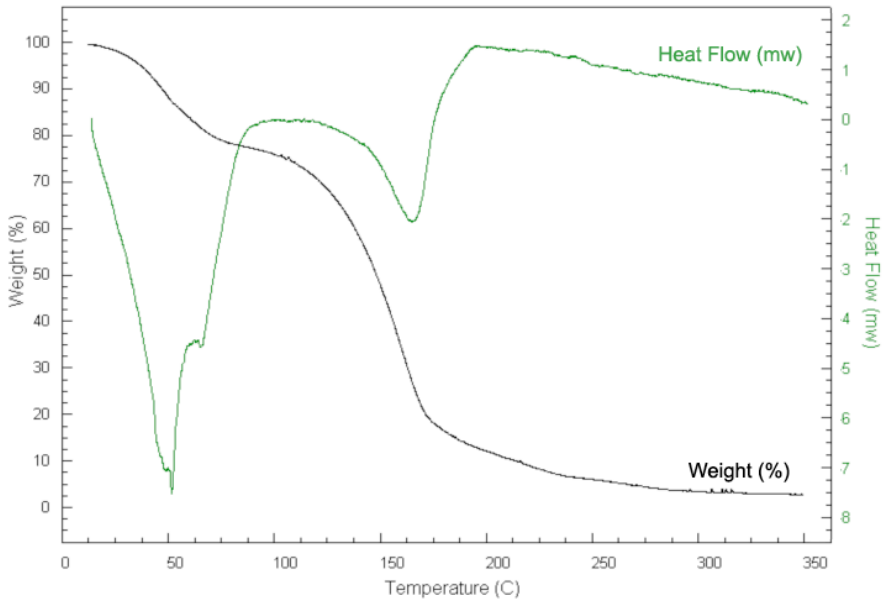
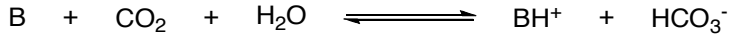


Figure 3.8 Thermogravimetric graph obtained for the bicarbonate salt **1b** that was heated to 350 °C at a rate of 5 °C in a TGA Q500 (Texas Instruments). The green line denotes the heat flow (mW), and the black line denotes the weight relative to the starting weight (%).

3.6 Measurement of the Extent of Conversion by ^{1}H NMR Spectroscopy

Another method to quantify the switching process was through the analysis of solutions of the amidine and guanidines by ^{1}H NMR spectroscopy, as it could be employed to calculate the conversion percentage of the following reaction, where B represents a base.



Equation 3.1

It was found that the conversion of the amidine to the amidinium bicarbonate was affected by the concentration of the surfactant and H_2O. The calculation of the percentage of conversion between the bicarbonate salt and the base was performed and compared for each compound.

A formula of the conversion percentage needed to be obtained to be able to compare the bases to each other at varying temperatures. First the determination of the neutral form was needed and so a ^{1}H NMR spectra of **1a** was conducted by dissolution of the base in DMSO-d_6 and determination of the spectrum as an average of three different samples. Next, an average of the protonated form was needed and three different acids were used to determine this value: $HCl_{(aq)}$, glacial AcOH, and trifluoroacetic acid (TFA). The addition of an excess of one of the acids to a solution of **1a** in DMSO-d_6 was performed and then a ^{1}H NMR spectra was obtained of each of the resulting salts. The anion (i.e. Cl^-, AcO^-, TFA^-) was found to not significantly affect the ^{1}H NMR spectrum of the protonated compound, and thus an average of the chemical shifts of the cations was calculated. The NMR chemical shift differences between the neutral compound **1a** and the protonated form of **1a** allow for the establishment of

formulae to calculate the conversion of the base to its bicarbonate salt. These formulae can be used under any reaction conditions and allows for the comparison between various temperatures and compounds.

3.6.1 Determination of the Conversion Formula

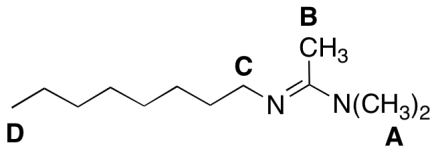


Figure 3.9 The structure of compound **1a** showing positions A-C where the ^{1}H NMR chemical shifts changed significantly upon protonation, and position D (0.8330 ppm), the peak of which was employed to reference the ^{1}H NMR spectra.

Table 3.2 Selected ^{1}H NMR data of compound **1a** employed in the development of the formula for calculating conversion.

Compound	δ A	δ B	δ C
Base	2.7351	1.7677	3.0177
$BH^{+}Cl^{-}$	3.1139	2.2370	3.2983
$BH^{+}AcO^{-}$	3.0854	2.2247	3.2876
$BH^{+}TFA^{-}$	3.0856	2.2340	3.2921
Average BH^{+}	3.0950	2.2319	3.2927
Change	0.3598	0.4642	0.2750
Conversion Formula	$\left(\frac{\delta - 2.7351}{0.3598}\right) x100\%$	$\left(\frac{\delta - 1.7677}{0.4642}\right) x100\%$	$\left(\frac{\delta - 3.0177}{0.2750}\right) x100\%$

0.11 mmol of **1a**, 1.10 mmol acid, 0.6 mL DMSO-d_6 at room temperature.

With the conversion formula in hand, the effect of water concentration and temperature of the switchability of **1a** was determined. The concentration of **1a** in DMSO-d_6 was kept constant, while the concentration of H_2O was altered. The results

obtained from varying the amount of water showed an increase in the conversion of **1a** to the protonated form **1b** at 40 °C with the addition of CO_2, when the concentration of water was increased (Table 3.3). A large excess of H_2O (200 μL) caused an almost quantitative conversion of **1a** to **1b**. As such, all subsequent NMR experiments employed 25 μl of H_2O to allow for a comparison between the switchability of each compound.

These experiments were approached from both sides of the equilibrium and it was found that they converged. The first method was called “From Off”(i) in which the sample was bubbled with CO_2 at 40 °C and so it was brought from the “Off” or neutral form to the protonated form. The second method was called “From On”(ii) in which the sample was bubbled with CO_2 at room temperature for 20 min to convert the compound to its protonated form and then it was bubbled with CO_2 at 40 °C and so it was brought from the “On”, or protonated form, towards the neutral form. Figure 3.10 visually depicts the difference between the two methods.

Table 3.4 presents the raw data for the conversion of **1a** to **1b**; the raw data for the other compounds is in the Appendix. Solubility difficulties were encountered for compounds **4b** and **6b** as they were insoluble in DMSO-d_6. The same experiments were performed in D_2O however, consistent data was not obtained, so that comparable data were not obtained for the aryl acetamidines. The results that were obtained for the series of compounds investigated are summarized in Table 3.5.

Table 3.3 Conversion of **1a** to **1b** at 40 °C with varying amounts of H_2O.

Amount of H_2O Added	Conversion to 1b at 40 °C
25 μL	68 ± 3
50 μL	91± 0.3
200 μL	99 ± 0.7

0.11 mmol of **1a**, varying amounts of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at 40 °C.

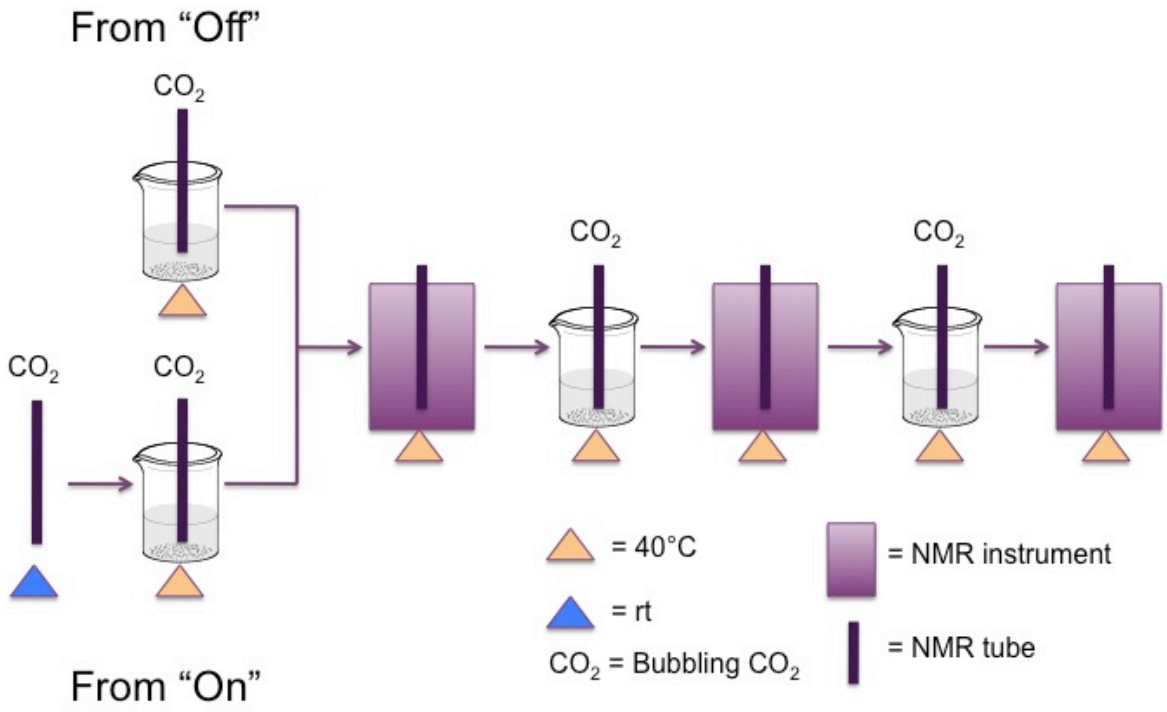


Figure 3.10 Schematic representation of the two procedures employed in determining the conversion percentage of protonated compound.

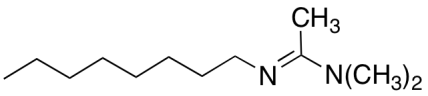
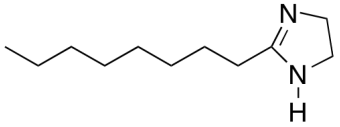
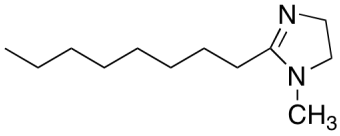
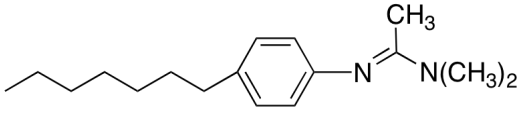
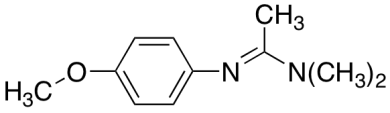
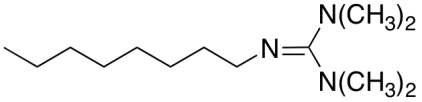
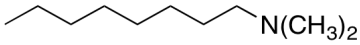
Table 3.4 Example of conversion data from ^{1}H NMR spectra studies of **1a** to **1b** at 40 °C.

40 °C	δ (ppm)			Conversion (%)			Spectra Average	Sample Average
	A	B	C	A	B	C		
				"From Off"				
Sample(1) Spectrum 1	2.9827	2.0665	3.2047	68.8	64.4	68.0	67.1	67.4
Spectrum 2	2.9850	2.0691	3.2068	69.4	64.9	68.8	67.7	
Spectrum 3	2.9840	2.0677	3.2058	69.2	64.6	68.4	67.4	
Sample(2) Spectrum 1	2.9952	2.0826	3.2139	72.3	67.8	71.4	70.5	70.7
Spectrum 2	2.9971	2.0843	3.2156	72.8	68.2	72.0	71.0	
Spectrum 3	2.9963	2.0828	3.2146	72.6	67.9	71.6	70.7	
				"From On"				
Sample(1) Spectrum 1	2.9927	2.0786	3.2123	71.6	67.0	70.8	69.8	69.3
Spectrum 2	2.9896	2.0750	3.2101	70.7	66.2	70.0	69.0	
Spectrum 3	2.9885	2.0740	3.2085	70.4	66.0	69.4	68.6	
Sample(2) Spectrum 1	2.9723	2.0543	3.1972	65.9	61.7	65.3	64.3	63.9
Spectrum 2	2.9691	2.0505	3.1947	65.0	60.9	64.4	63.4	
Spectrum 3	2.971	2.0523	3.1962	65.6	61.3	64.9	63.9	
							Overall Average	68 ± 3

0.11 mmol of **1a**, 25 μL of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at 40 °C.

Compounds **1a** and **7a** had the largest percentage of conversion to the protonated forms and as such their reactivity was also investigated at 60 °C to see if they would still remain mostly in their protonated form (Table 3.5). Compound **7a** was the most basic of all compounds tested and even at 60 °C was almost quantitatively in the guanidinium bicarbonate form. Higher temperatures would be required to convert the guanidinium bicarbonate species back to compound **7a** due to its high basicity, which would limit the application of **7a** as a useful switchable surfactant. Compound **1a** also had a high basicity, but showed a much larger decrease in conversion percentage at 60 °C. This result was not surprising as the longer chain derivatives were previously shown to possess the ability to turn "Off".[2] The tertiary amine **8a** showed a very small conversion to **8b** at 40 °C, resulting from the reduced basicity of the nitrogen donor. The imidazolines, **2a** and **3a**, were still marginally protonated at 40 °C putting their basicity below **1a** and **7a** but above that of **8a**. In comparison with each other, the methylated imidazoline **3a** was more basic than **2a** in DMSO, but as has been shown with pK_{aH} values, the solvent plays a large role in determining the basicity of nitrogen donating species. As outlined in section 1.8.1, polar protic solvents result in further stabilization of secondary amine bases due to the hydrogen bonding and thus the stability of **2b** may be higher than **3b** in a polar protic solvent. The results obtained from these ^{1}H NMR experiments provided evidence for a correlation between basicity and switchability of these amidine and guanidine compounds (Figure 3.11).

Table 3.5 Comparison of conversions to their protonated forms at 40 °C.

#	Molecule	Conversion (%) at 40 °C	Conversion (%) at 60 °C
1a		68 ± 3	28 ± 2
2a		18 ± 1	--
3a		20.8 ± 0.5	--
4a		insoluble	--
6a		insoluble	--
7a		96 ± 0.2	97 ± 0.2
8a		2 ± 0.2	--

0.11 mmol of base, 25 μL of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at the noted temperatures.

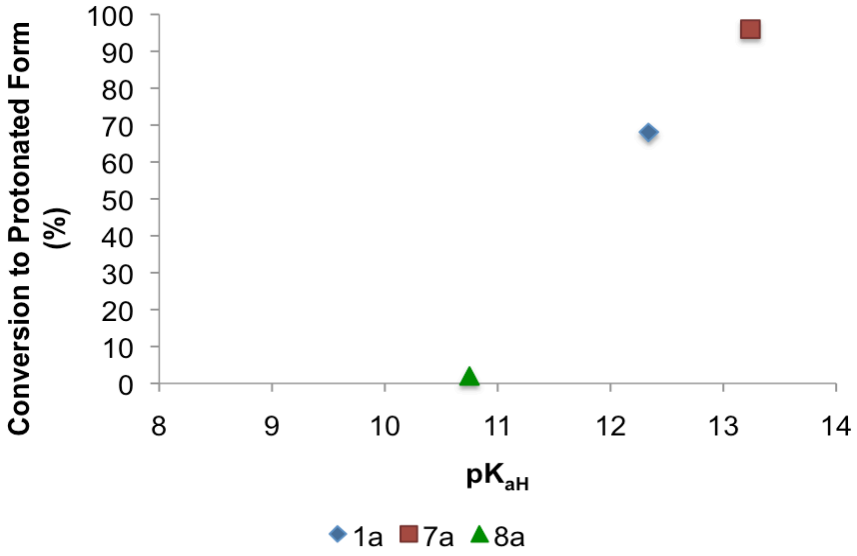


Figure 3.11 Correlation of the conversion to protonated form at 40 °C to the pK_{aH} values.

3.7 Calorimeter Measurements

The overall reaction that occurs when B, which represents any of the amine, amidine, or guanidine bases, is reacted with CO_2 and H_2O is shown below.

$$B + CO_2 + H_2O \rightleftharpoons BH^+ + HCO_3^- \quad \textbf{Equation 3.1}$$

This reaction can be broken down further and is made up of the following three equilibrium expressions:

$$CO_2 + H_2O \xrightleftharpoons{\Delta H^o = -614\ kJ/mol} H_2CO_3 \quad \textbf{Equation 3.2}\ ^{72}$$

$$H_2CO_3 \xrightleftharpoons{\Delta H^o = 1410\ kJ/mol} HCO_3^- + H^+ \quad \textbf{Equation 3.2}\ ^{73}$$

$$B + H^+ \xrightleftharpoons{\Delta H = ?} BH^+ \quad \textbf{Equation 3.3}$$

The first two equilibria have known enthalpy of reaction values and so there was no need to study those reactions further. The last equilibrium (Equation 3.4), the protonation of B using a strong acid, was explored and measured using a calorimeter to determine and compare the enthalpy of reaction (ΔH_{rxn}) of the different head groups. To ensure that the protonation of B was occurring quantitatively and to be able to simplify the expression to exclude equilibrium 2 (Equation 3.2) and 3 (Equation 3.3), $HCl_{(aq)}$ was employed as the acid source.

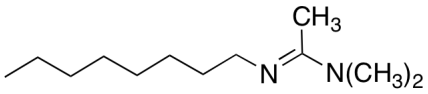
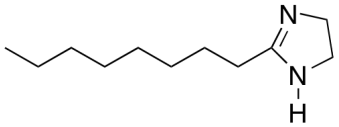
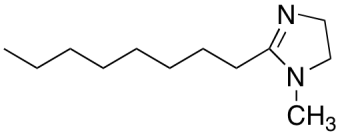
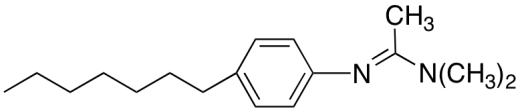
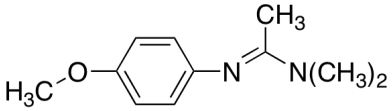
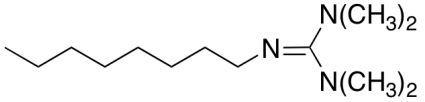
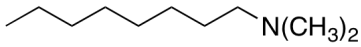
A general procedure was developed by which two syringes containing identical acid solutions were introduced simultaneously into two different vials: a sample vial containing base in a solvent and a reference vial containing the same solvent. The initial volume of both vials was the same and once the solution in the syringes was added, the final volume of the two vials were the same as each other. The method was validated by determining the ΔH_{rxn} for two common nitrogen bases, triethylamine and aniline and comparing them with known literature values (Table 3.6). The values obtained from the developed procedure were in agreement to the literature values, and so the same procedure was used to determine the ΔH_{rxn} for each of the synthesized head groups (Table 3.7). It should be noted that a larger ΔH_{rxn} signifies a higher basicity of the molecule in the solvent used.

Table 3.6 Observed and literature enthalpy of protonation values for triethylamine and aniline determined to verify the calorimetry procedure.

Base	Literature Value (kJ/mol)	Observed Value (kJ/mol)
Triethylamine in H_2O	43.2 ± 0.2 [74]	43.6 ± 0.5
Aniline in DMSO	31 [75]	30.8 ± 0.5

Because the calorimetry experiments were also performed in DMSO, the basicity here can be related to the NMR conversion experiments (Table 3.7). From the results in Table 3.7, the guanidine compound **7a** was the most basic compound tested, while compound **1a** also had a high basicity. The imidazoline compounds **2a** and **3a** possess basicities that are lower than **1a** and **7a**, with the methylated compound **3a** showing a higher basicity in a polar nonprotic solvent than **2a** due to the lack of hydrogen bonding stabilization. The aryl compounds **4a** and **6a** are close in basicity to **2a** and **3a** but are again substantially less basic than **1a**; a result which arises from the incorporation of the electron-withdrawing phenyl group onto the acetamidine head group. Furthermore, a small increase in basicity of **6a** with comparison to **4a** was shown and was due to the donation of the oxygen lone pair through conjugation to the nitrogen base. The relationships between basicity and molecular structure determined by these calorimetry experiments are similar to those reported in the literature for the enthalpies of protonation and the pK_{aH} values (Figure 3.12, Section 1.8.2 and 1.8.3).

Table 3.7 Enthalpy of protonation values determined for the series of amidine and guanidine compounds.

#	Molecule	Average ΔH_{rxn} (kJ/mol)
1a		71 ± 1
2a		47 ± 0.8
3a		54 ± 0.7
4a		48 ± 0.3
6a		51 ± 2
7a		83 ± 0.2
8a		53 ± 0.5

Sample vial: 0.3 mmol base, topped up to a total volume of 2.00 mL with DMSO; Reference vial: 2.00 mL of DMSO; Syringes: 0.15 mL of 12 M $HCl_{(aq)}$, 0.85 mL of DMSO.

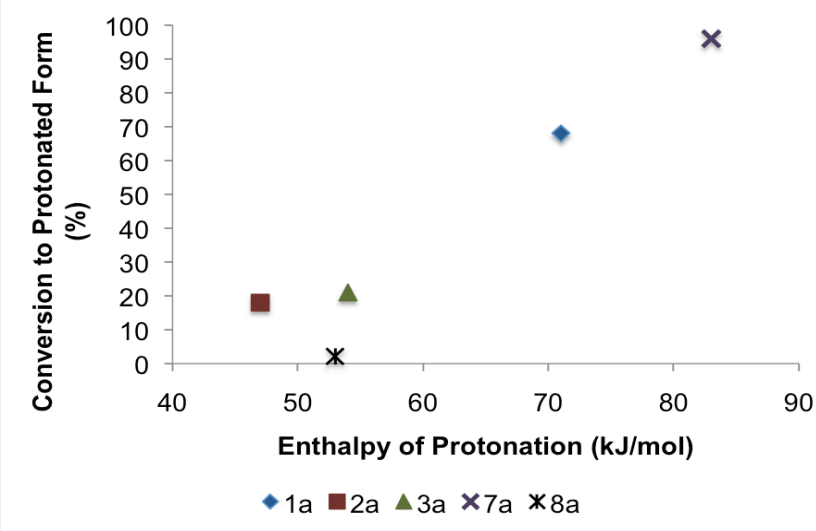
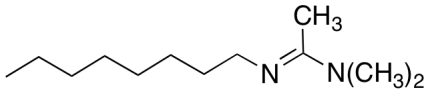
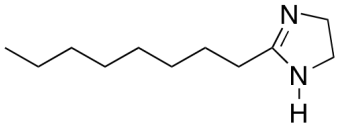
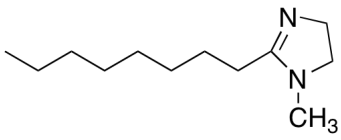
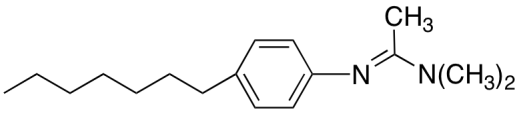
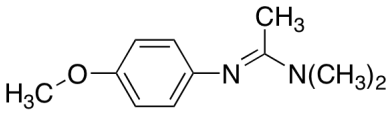
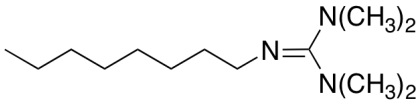
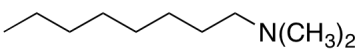


Figure 3.12 Correlation of the enthalpy of protonation to the pK_{aH} values.

Table 3.8 A comparison of the measured ΔH_{rxn} to the conversion percentage at 40 °C.

#	Molecule	Average ΔH_{rxn} (kJ/mol)	Conversion (%) at 40 °C
1a		71 ± 1	68 ± 3
2a		47 ± 0.8	18 ± 1
3a		54 ± 0.7	20.8 ± 0.5
4a		48 ± 0.3	insoluble
6a		51 ± 2	insoluble
7a		83 ± 0.2	96 ± 0.2
8a		53 ± 0.5	2 ± 0.2

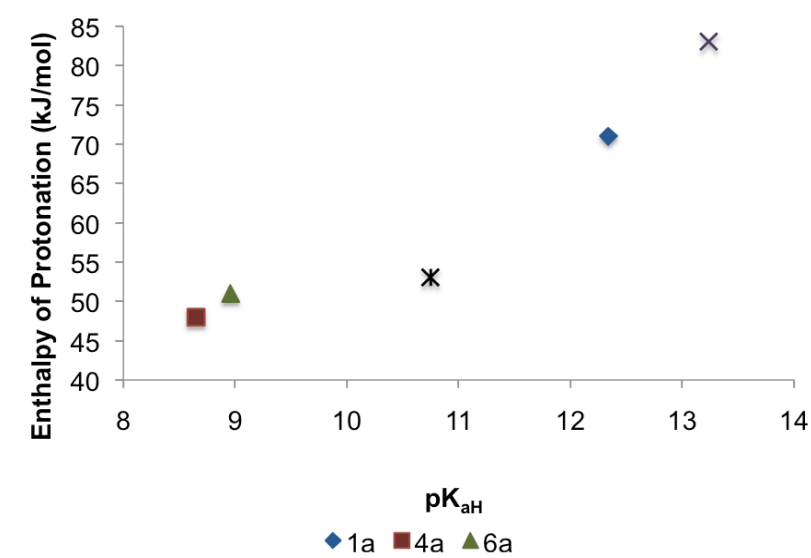


Figure 3.13 Correlation of the enthalpy of protonation and the conversion to the protonated form.

3.8 Demulsifying Ability with Crude Oil

Upon completion of the previous experiments with the amidine and guanidine compounds, tests were conducted to determine whether they could be employed, in their neutral or "Off" forms, as effective demulsifying surfactants of crude oil and water emulsions. The experimental procedure used was similar to that previously reported by the Jessop group (Figure 1.15, Section 1.7.2),[2] except for the usage of a heavier crude oil and deionized water instead of distilled water. A mixture containing the surfactant, oil and water was agitated and then allowed to settle on the bench top. The separation was monitored as a function of time by height measurements of the oil, water and emulsion phases using a cathetometer. Compounds that showed separation of oil formed an organic layer on the top of the emulsion (creaming) and water separation was found at the bottom of the emulsion (sedimentation). The total height of the mixture

was measured over time, along with changes in heights of the developing oil and/or water phases. The total height was found to vary slightly as it was difficult to measure the top of the emulsion because it took a long time to completely come down off the glass. The separations of oil and/or water that occurred within 24 hours were graphed as the height (mm) of the phase with respect to time (h). This included the emulsions that were prepared containing compounds **1a**, **2a**, **3a**, **4a**, and **5a**. Compounds **1a**, **2a**, **4a**, and **5a** showed sedimentation, while compounds **2a**, **3a**, **4a**, and **5a** showed creaming, and compounds **7a**, **8a** showed no changes within the first 24 hours of settling. All prepared emulsions that contained a base were compared to a control, or blank sample, that consisted of just oil and water. The blank showed no changes in its emulsion within the first 24 hours of settling. Sedimentation of the blank occurred after 3 days and was completed in 4 days in which the water layer was completely clear and no emulsion remained. As such, the bases able to demulsify the emulsion in <3 days improved the system and required a closer examination of the separation data.

Compound 1a:

The first generation switchable compound **1a** showed the quickest initial water separation within the first 2 h of settling, however the aqueous layer remained partially cloudy until after 4 days when the original volume of water was fully separated and was clear. A graph was generated from the height measurements that were obtained over the first 24 h (Figure 3.14). The blue line depicts the top of the emulsion and the red line represents the sedimentation of the water over time as it increases in height. The

clarity of the aqueous layer did improve over time and can be seen below in the photographs of the vials containing the emulsion after 2 and 15 h with arrows depicting the top of the sedimentation (Figure 3.15).

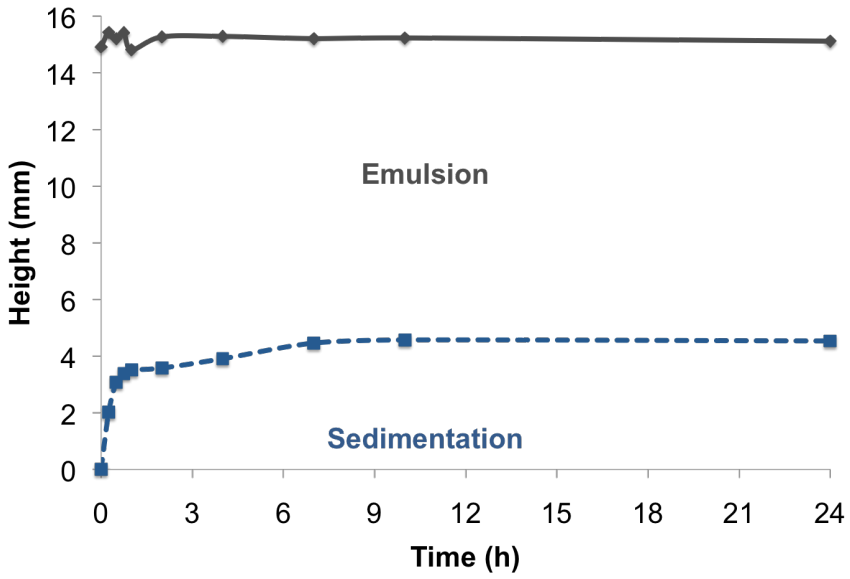


Figure 3.14 Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **1a** (0.29 mmol) over 24 h at room temperature.

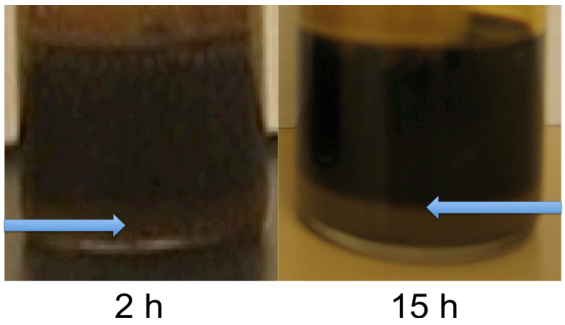


Figure 3.15 Sedimentation from the emulsion of crude oil, water, and compound **1a** after 2 h (left) and 15 h (right) of settling. The blue arrow indicates where the sedimentation layer meets the emulsion.

Compound 2a:

Imidazoline **2a** began to separate water from the emulsion after 2 h but also took 4 days to fully separate the oil and aqueous layers until the water was clear. In the height versus time graph below the red line depicts the creaming that occurred initially until the oil layer was no longer able to be distinguished from the emulsion where the height measurements end (Figure 3.16).

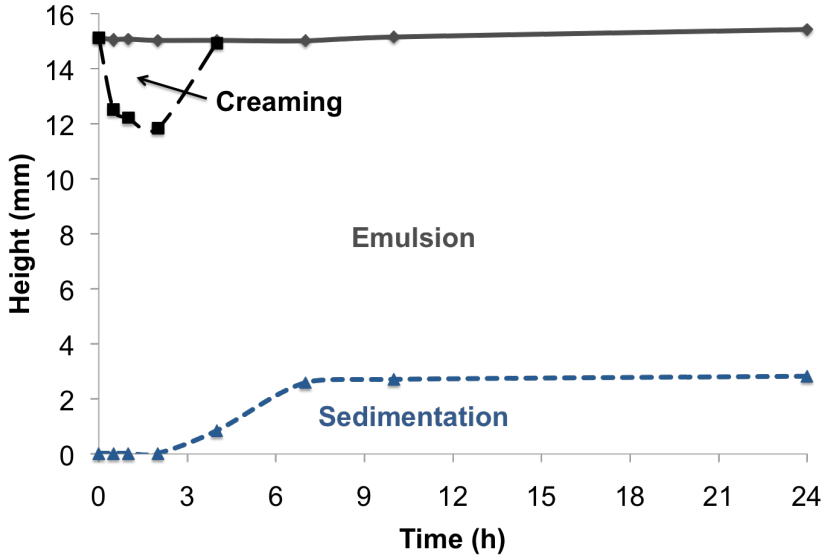


Figure 3.16 Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **2a** (0.29 mmol) over 24 h at room temperature.

Compound 3a:

The other imidazoline, 1-methyl-2-octyl-2-imidazoline, showed no sedimentation even after 7 days of monitoring the emulsion. It did however show some activity in the first day with creaming out of the oil. This is depicted graphically below (Figure 3.17).

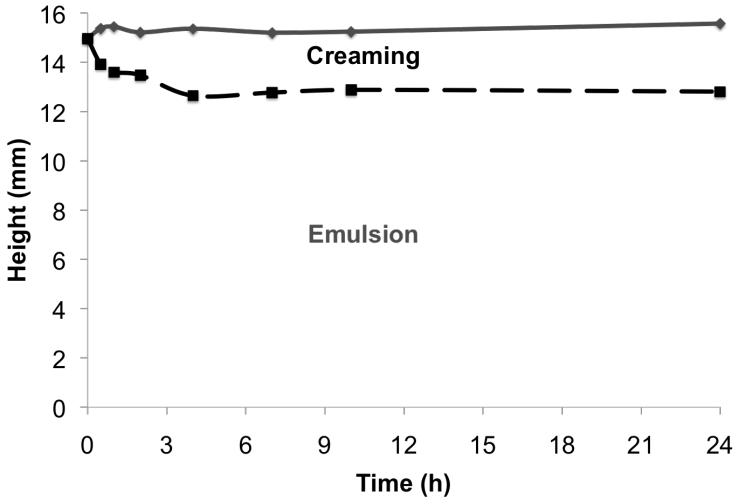


Figure 3.17 Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **3a** (0.29 mmol) over 24 h at room temperature.

Compound 4a:

The aryl acetamidine **4a** was the first compound to complete the demulsification and after only 7 h. A photograph of the vial at 15 h is shown in Figure 3.19.

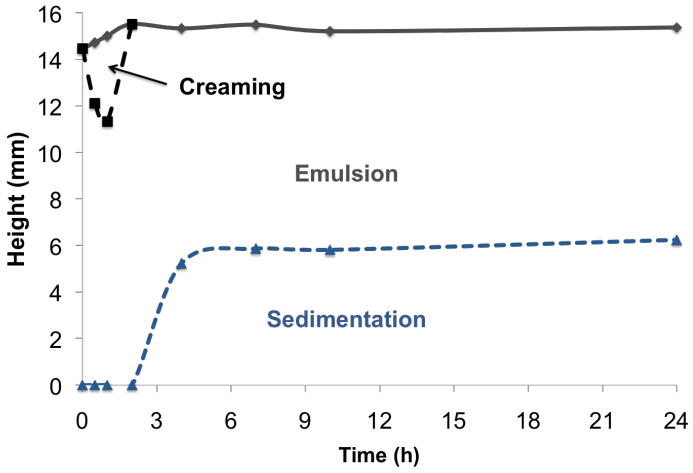


Figure 3.18 Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **4a** (0.29 mmol) over 24 h at room temperature.

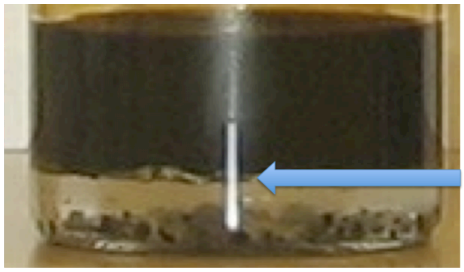


Figure 3.19 Water separation from the emulsion of crude oil, water and base **4a** after 15 h of settling. The blue arrow displays where the water and oil layers meet.

Compound 5a:

The oxygen containing aryl acetamidine **5a** achieved initial water separation quickly, although separation of the emulsion was not completed even after 7 days. The cloudiness of the water that did separate can be seen in the photograph below, which also has an arrow to depict the top of the sedimentation (Figure 3.21).

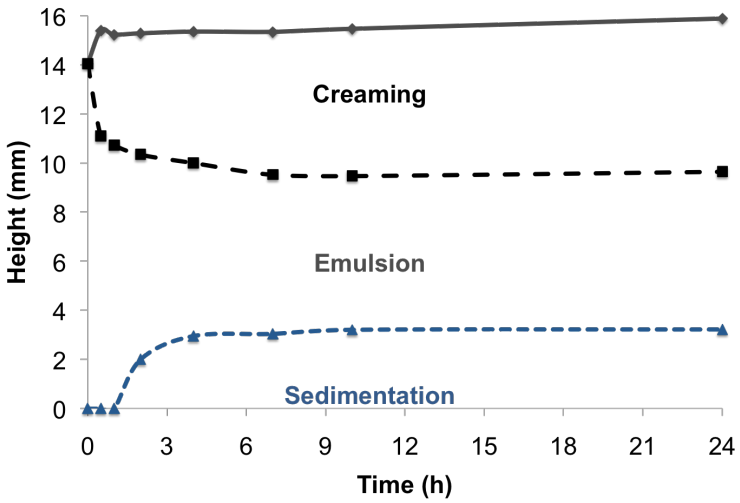


Figure 3.20 Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **5a** (0.29 mmol) over 24 h at room temperature.

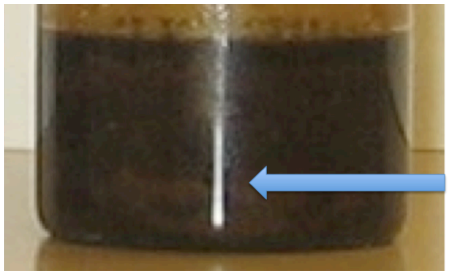


Figure 3.21 Water separation from the emulsion of crude oil, water and base **5a** after 15 h of settling.

The most important comparison within the demulsifying data was the sedimentation that occurred in the first day. Compounds **1a**, **2a**, **4a**, and **5a** were observed to form an aqueous layer and this data was summarized as a chart of the percentage of the height of the water separation relative to the total height of the emulsion (Figure 3.22).

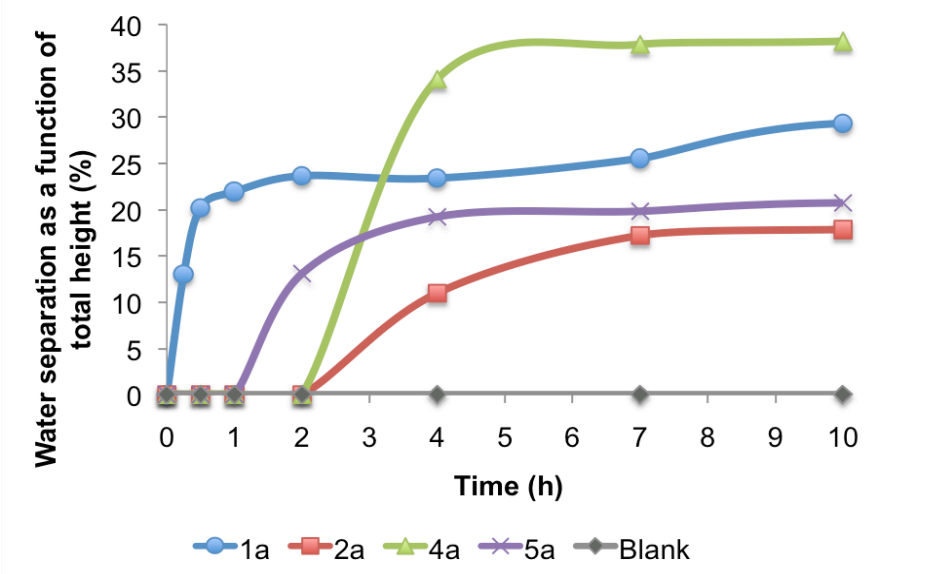
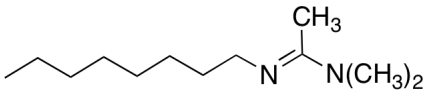
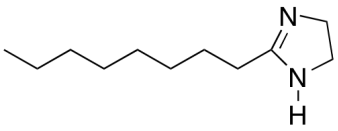
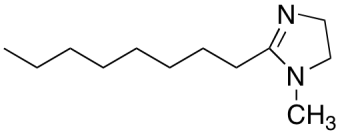
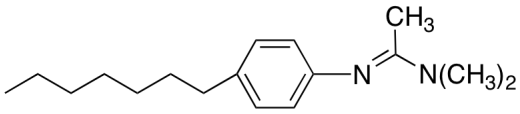
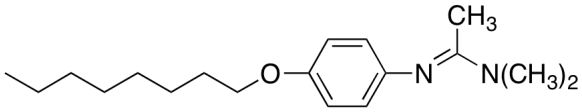
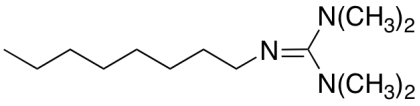
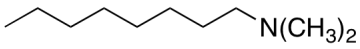


Figure 3.22 Sedimentation over time of crude oil (4 mL) and water (2 mL) emulsions containing **1a**, **2a**, **4a**, or **5a** (0.29 mmol) in comparison to a blank sample over 10 h at room temperature.

Bases **1a**, **2a**, **4a**, **5a** and **8a** began to show water separation before the blank sample (i.e. < 3 days). However, only **4a** and **8a** were able to achieve full demulsification quicker than the blank (i.e. < 4 days). Bases **3a**, **5a**, and **7a** were still incomplete in their demulsification of the crude oil and water even after 7 days. Compound **4a** was the fastest demulsifier when compared to all compounds tested and was the only base to complete separation of the oil and water within 2 days. The water separation for each compound tested was summarized in Table 3.9.

Table 3.9 Water separation from crude oil and water emulsions employing a series of bases.

#	Sample	Sedimentation		Description
		T_i	T_f	
-	Blank	3 d	4 d	Clear water
1a		15 m	4 d	Clear water
2a		4 h	4 d	Clear water
3a		> 7 d	> 7 d	Oil separation on top
4a		4 h	7 h	Clear water
5a		2 h	> 7 d	Cloudy water
7a		> 7 d	> 7 d	Oil separation on top
8a		2 d	3 d	Clear water

Demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing a base (0.29 mmol) at room temperature. T_i was the time that initial sedimentation was observed. T_f was the time that sedimentation was complete with no remaining emulsion and the water was clear.

The demulsifcation of crude oil and water performed with the different compounds studied here showed a significant change in the demulsifying properties with respect to the structure of the head group. Not all of the compounds tested were able to accelerate the separation of an oil and water emulsion. Compound **4a** was the only molecule able to accelerate the separation of the emulsion more than the first generation amidine **1a**. No direct correlation was observed between the demulsifying capability and the basicity of the compounds that were tested.

4 Conclusions and Future Work

4.1 Conclusions

A range of amidine and guanidine compounds were synthesized to examine the effect of varying the head group structure on the solubility, basicity, ability of the compound to turn “On”, and demulsifying capability of these compounds. Previous work with switchable surfactants provided support for the use of acetamidines as effective demulsifying agents. This project employed an octyl derivative of these first generation switchable surfactants as a standard to compare the newly synthesized compounds to. An octyl chain was employed in all new compounds to ensure any alterations to the properties of these compounds resulted from the variances in the head groups only. Three additional acetamidine structures were synthesized to evaluate the incorporation of an aryl moiety onto the acetamidine backbone. Imidazoline and guanidine compounds were synthesized and tested as these compounds would provide different basicity through their head groups. Dimethyloctylamine, a tertiary amine, was purchased and also tested alongside the amidines and guanidine.

The bases were found to be miscible with toluene but showed low solubility in water due to their long alkyl chains. The solubility in D_2O was quantified using NMR spectroscopy and the most soluble compound was the guanidine species having a solubility of 39 ± 4 g/L.

All eight compounds were reacted with CO_2 in the presence of H_2O to test their ability to convert from the "Off" to the bicarbonate salt, or the "On" form. *In situ* characterization of the amidinium and guanidinium bicarbonate salts was achieved by IR and NMR spectroscopy however, isolation of the bicarbonate species could not be accomplished.

The ability of the compounds to convert between the neutral and the protonated species was also investigated using NMR spectroscopy to determine the percent of conversion to the protonated form and the influence that temperature had on the conversion to the protonated form. The percent of conversion was tested in two directions, "From Off" and "From On", and both methods converged to the same result. It was found that both an increase in molar amount of base and water increased conversion. The guanidine **7a** was entirely converted to guanidinium bicarbonate at 40 °C and 60 °C, while the first generation amidine **1a** had the next highest conversion to the amidinium bicarbonate at 40 °C. These experiments showed a direct relation of switchability and basicity, with the strongest bases possessing high concentrations of bicarbonate species at elevated temperatures.

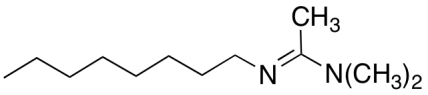
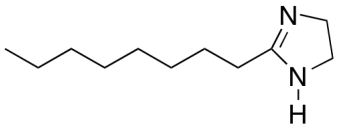
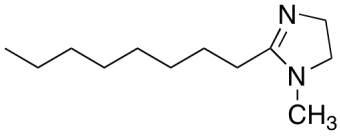
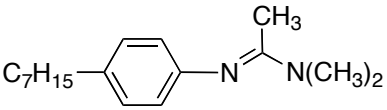
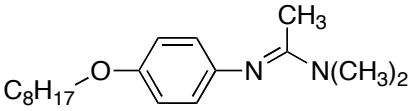
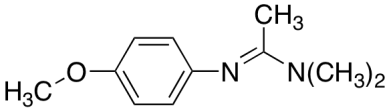
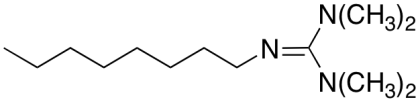
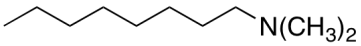
Calorimetry experiments were employed to determine the basicity of the head groups through enthalpy of protonation measurements using a strong acid, $HCl_{(aq)}$. An increase in enthalpy correlates to an increase in basicity and the largest enthalpy was obtained for the protonation of guanidine **7a**. The second highest value was again the first generation amidine **1a**, and a major decrease in ΔH_{rxn} occurred with the more

electron deficient aryl amidines. The calorimetry experiments shared similar trends to that of the NMR conversion experiments.

Crude oil and water emulsions were formed in the presence of all the long alkyl chain compounds and the rate of demulsification was measured using a cathetometer. All compounds were compared against the first generation amidine and a blank sample containing no additional surfactant. *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidine **4a** was the only base that showed significant improvement over **1a** and complete separation of the emulsion occurred within 7 h. Demulsifying ability was determined to differ greatly with the head structure of the varying compounds however, no direct correlation was found between the basicity and the demulsifying capability of these compounds.

A table that summarizes all the major tests that were performed on the bases is shown below (Table 4.1). The bases **1a** and **7a** have the highest ΔH_{rxn} values and the largest conversion at 40 °C. They could have possible application in processes that require the switchable surfactant to be in its surfactant form at higher temperatures. In contrast, the other bases that have lower ΔH_{rxn} values (**2a**, **3a**, **4a**, **5a**, **8a**) could be used in applications that do not require the surfactant to be "On" at higher temperatures or require the emulsion to be broken easily without the use of high temperatures.

Table 4.1 Summary table of ΔH_{rxn}, conversion to protonated form at 40 °C, and demulsifying ability for all tested compounds.

#	Molecule	Average ΔH_{rxn} (kJ/mol)	Conversion (%) at 40 °C	Sedimentation	
				T_i	T_f
1a		71	68	15 m	4 d
2a		47	18	4 h	4 d
3a		54	20.8	> 7 d	> 7 d
4a		48	insoluble	4 h	7 h
5a		--	--	2 h	> 7 d
6a		51	insoluble	--	--
7a		83	96	> 7 d	> 7 d
8a		53	2	2 d	3 d

4.2 Future work

Future work for this research project would involve additional characterization of these amidine and guanidine compounds. Demulsification studies should be performed investigating other reaction parameters including: concentration of base, oil to water ratio, acid-content of the oil, oil viscosity, asphaltenes content, and temperature. Such

reaction conditions may play an important role in the demulsification of oil and water emulsions. Furthermore, determination of the CMC values for these compounds would also be an important parameter to ensure that the surfactants are being employed in appropriate concentrations.

The emulsifying ability under CO_2 needs to be examined for this series of compounds to discover if their protonated forms can stabilize alkane/water and crude oil/water emulsions. These switchability experiments should be attempted to determine if these compounds are able to reversibly convert between the base and bicarbonate salt compound. If switchability can be maintained for these compounds, they could be employed in other applications such as emulsion polymerization.

The long-range goal of the project is to discover recyclable, switchable surfactants to be used in industry for a variety of applications. To this end, the synthesis of additional head group structures can be targeted. Such examples would be benzamidine, which has the phenyl group in a different position, with respect to the amidine functionality or variations to the structure of the best demulsifier **4a**.

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Appendix

Synthesis and Characterization:

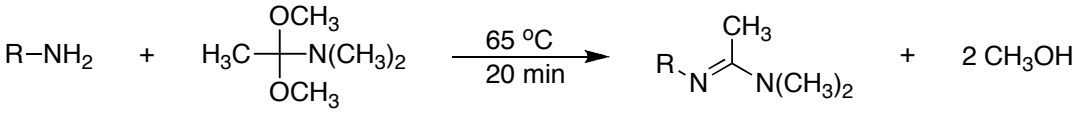
Compound Name: *N'*-octyl-*N,N*-dimethylacetamidine (**1a**)

Molecular Formula: $C_{12}H_{26}N_2$

Molecular Weight: 198.35 g/mol

Appearance: Clear liquid

Synthesis and Structure:



R = C_8H_{17}

Characterization data:

Yield: 76%

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.28 (m, 10H, C_5H_{10}), 1.47 (m, 2H, CH_2CH_2N), 1.84 (s, 3H, CCH_3), 2.84 (s, 6H, $N(CH_3)_2$), 3.14 (t, *J* = 7.2 Hz, 2H, $C_5H_{10}CH_2N$).

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 12.3, 14.1, 22.7, 27.6, 29.3, 29.6, 31.9, 32.4. 37.9, 50.2, 158.6.

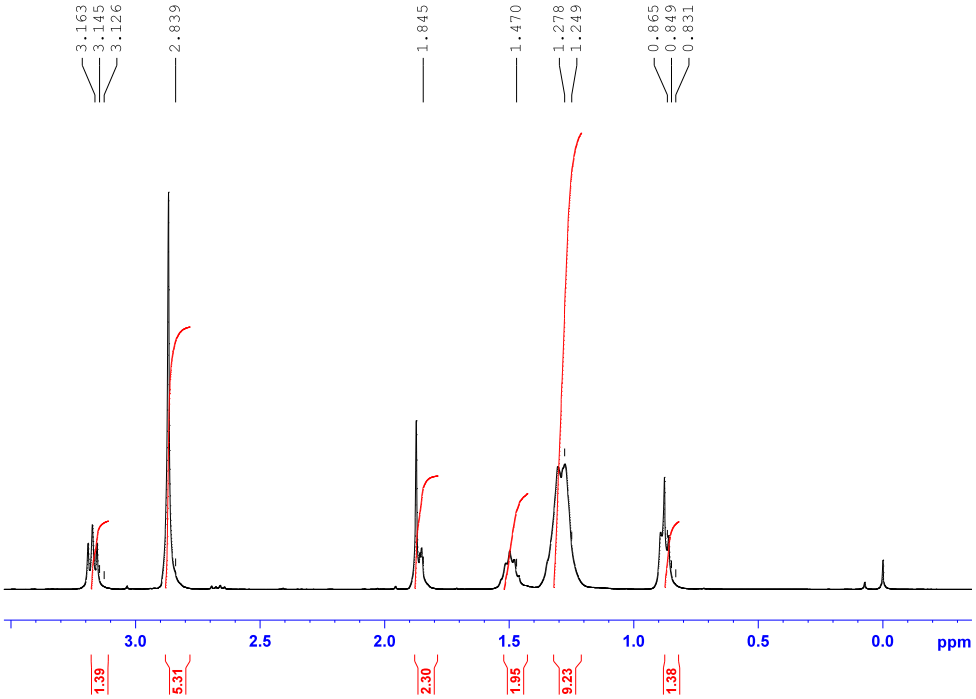
IR: 1629 cm^{-1} (s, υ (C=N))

HRMS (EI$^+$): $[C_{12}H_{27}N_2]^+$

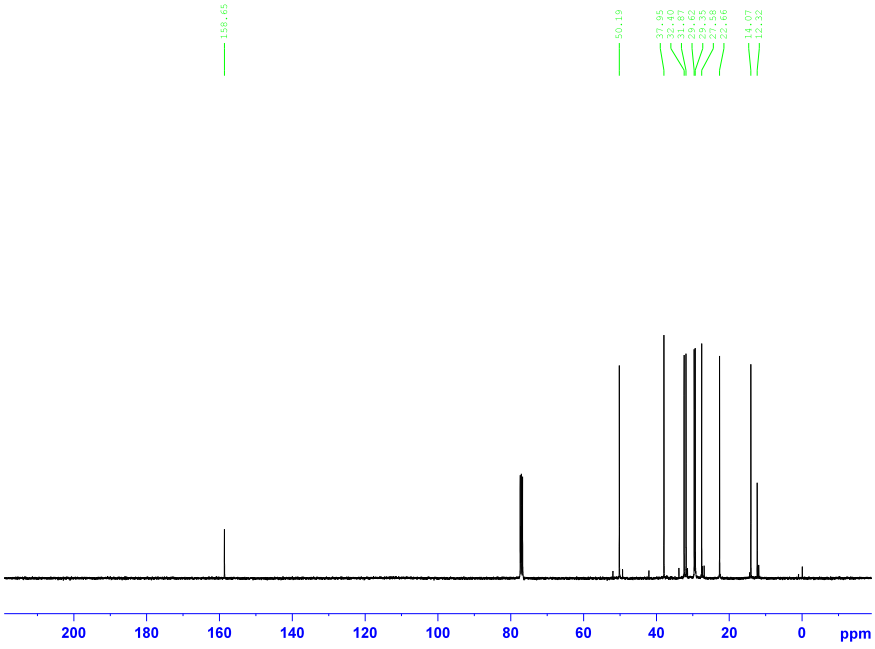
m/z calculated: 199.2168

observed:199.216

^{1}H NMR spectrum of *N'*-octyl-*N,N*-dimethylacetamidine **1a** in $CDCl_3$ obtained using a 400 MHz spectrometer.



^{13}C NMR spectrum of *N'*-octyl-*N,N*-dimethylacetamidine **1a** in $CDCl_3$ obtained using a 100 MHz spectrometer.



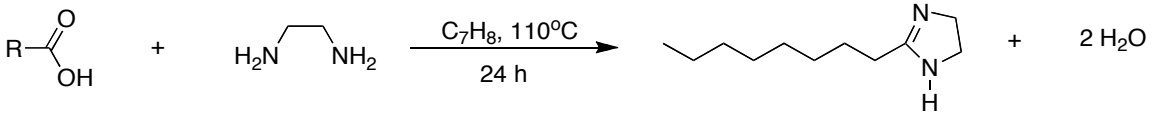
Compound Name: 2-octyl-2-imidazoline (**2a**)

Molecular Formula: $C_{11}H_{22}N_2$

Molecular Weight: 182.31 g/mol

Appearance: White crystalline powder

Synthesis and Structure:



R = C_8H_{17}

Characterization data:

Yield: 18%

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_2CH_3), 1.27 (m, 10H, C_5H_{10}), 1.61 (m, 2H, $CH_2CH_2CH_2C$), 2.24 (t, *J* = 7.8 Hz, 2H, CH_2CH_2C), 3.39 (s, 4H, NCH_2CH_2NH), 5.51 (s, 1H, NH).

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 26.7, 29.1, 29.3, 29.4, 31.8, 49.4, 168.3.

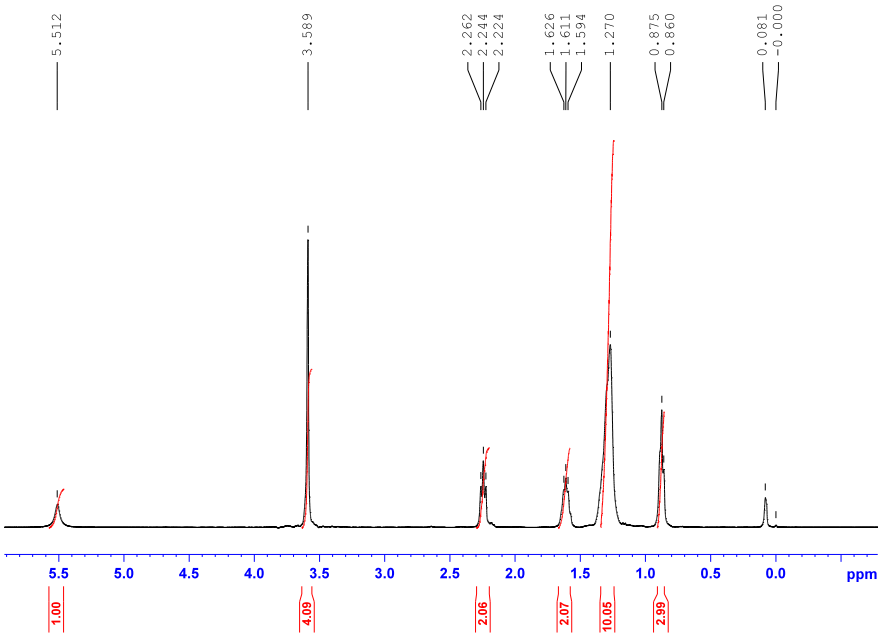
IR: 1647 cm^{-1} (s, υ (C=N))

HRMS (EI^+): $[C_{11}H_{23}N_2]^+$

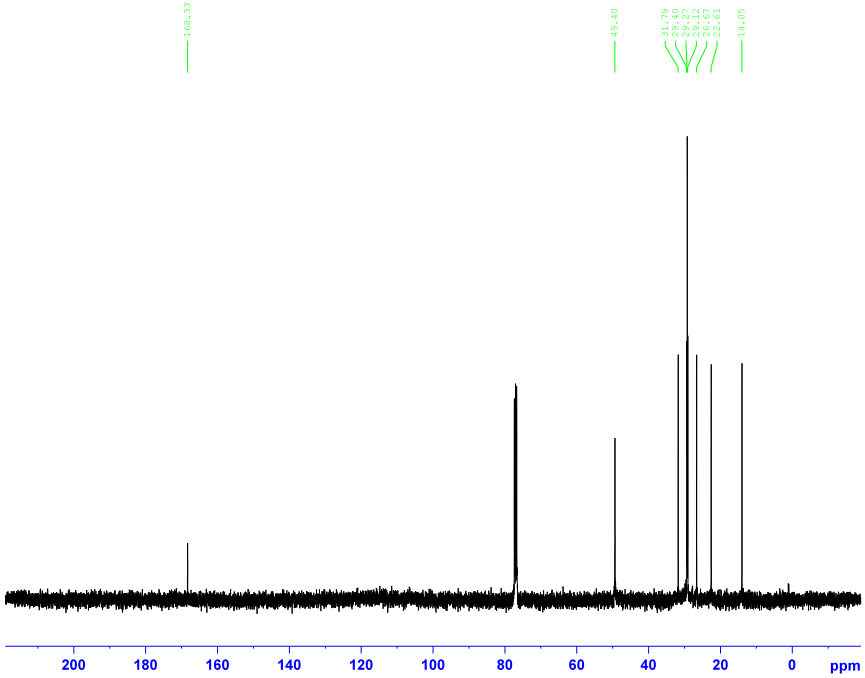
m/z calculated: 183.1861

observed:183.190

^{1}H NMR spectrum of 2-octyl-2-imidazoline **2a** in $CDCl_3$ obtained using a 400 MHz spectrometer.



^{13}C NMR spectrum of 2-octyl-2-imidazoline **2a** in $CDCl_3$ obtained using a 100 MHz spectrometer.



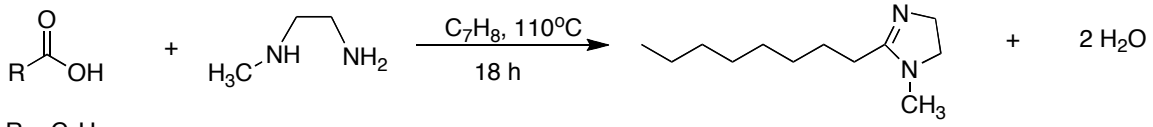
Compound Name: 1-methyl-2-octyl-2-imidazoline (**3a**)

Molecular Formula: $C_{12}H_{24}N_2$

Molecular Weight: 196.33 g/mol

Appearance: Clear yellowish liquid

Synthesis and Structure:



R = C_8H_{17}

Characterization data:

Yield: 56%

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.60 Hz, 3H, CH_2CH_3), 1.28 (m, 10H, C_5H_{10}), 1.62 (m, 2H, CH_2CH_2C), 2.21 (t, *J* = 7.81 Hz, 2H, CH_2CH_2C), 2.79 (s, 3H, NCH_3), 3.28 (t, *J* = 9.61 Hz, 2H, $=NCH_2CH_2N$-), 3.65 (t, *J* = 9.61 Hz, 2H, $=NCH_2CH_2N$-).

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 13.1, 21.6, 25.3, 26.6, 28.1, 28.3, 28.6, 30.8, 32.8, 50.4, 52.2, 167.6.

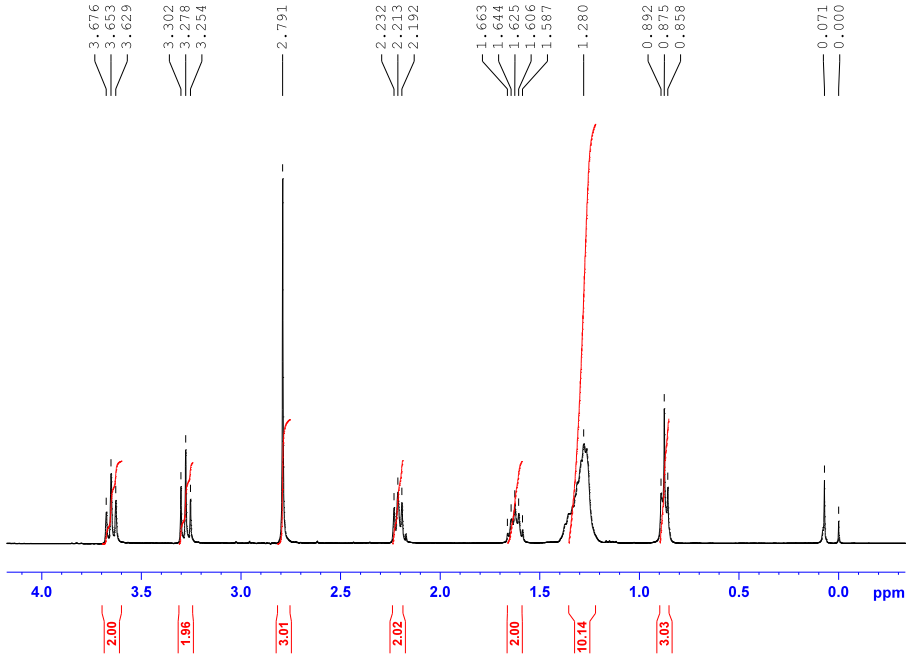
IR: 1618 cm^{-1} (s, υ (C=N))

HRMS (EI^+): $[C_{12}H_{24}N_2]^+$

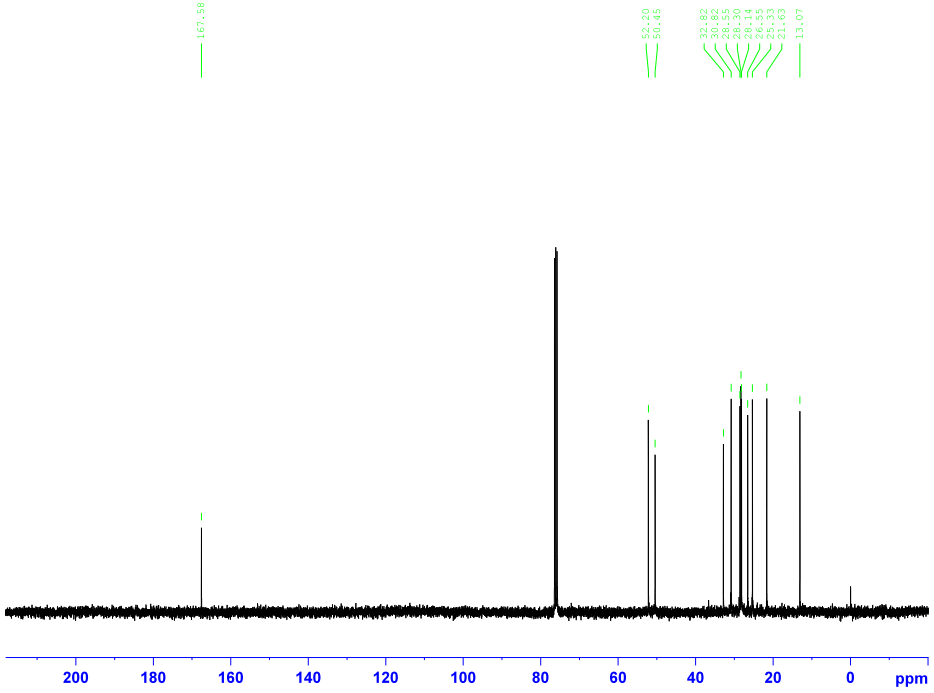
m/z calculated: 196.1939

observed:196.1940

^{1}H NMR spectrum of 1-methyl-2-octyl-2-imidazoline **3a** in $CDCl_3$ obtained using a 400 MHz spectrometer.



^{13}C NMR spectrum of 1-methyl-2-octyl-2-imidazoline **3a** in $CDCl_3$ obtained using a 100 MHz spectrometer.



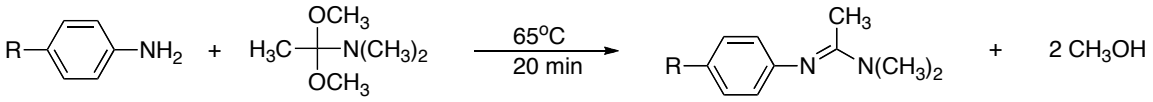
Compound Name: *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidine (**4a**)

Molecular Formula: $C_{17}H_{28}N_2$

Molecular Weight: 260.42 g/mol

Appearance: Clear yellowish liquid

Synthesis and Structure:



R = C_7H_{15}

Characterization data:

Yield: 90%

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3H, CH_2CH_3), 1.29 (m, 8H, C_4H_8), 1.58 (m, 2H, CH_2CH_2C), 1.85 (s, 3H, CCH_3), 2.53 (t, *J* = 7.8 Hz, 2H, CH_2C), 3.00 (s, 6H, $N(CH_3)_2$), 6.61 (d, *J* = 8.0 Hz, 2H, C_6H_6), 7.02 (d, *J* = 8.0 Hz, 2H, C_6H_6).

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 14.1, 14.9, 22.7, 29.2, 29.3, 31.7, 31.9, 35.4, 37.9, 115.2, 122.2, 128.6, 135.6, 149.8, 157.3.

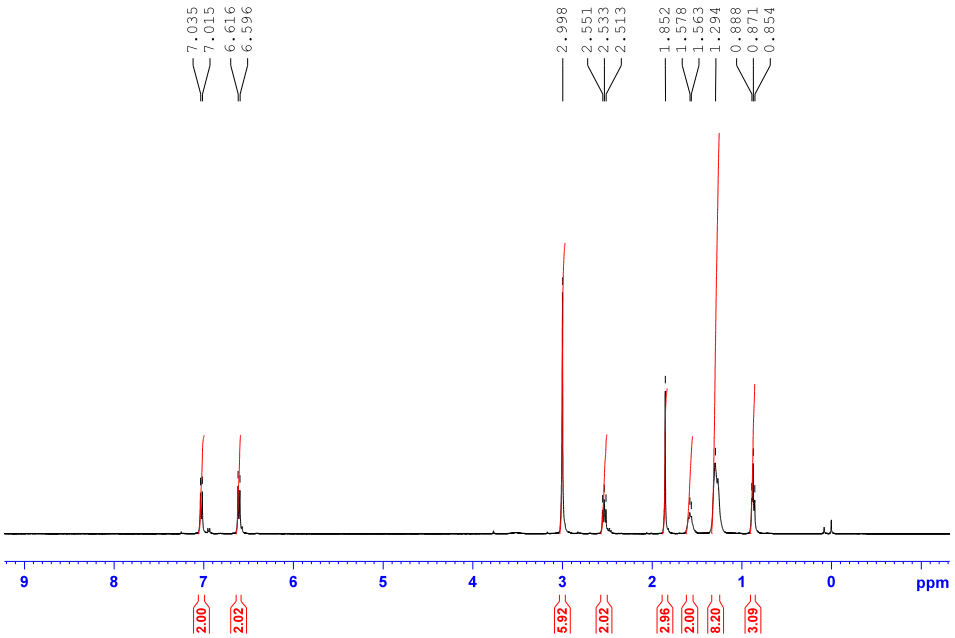
IR: 1629 cm^{-1} (s, υ (C=N))

HRMS (EI$^+$): $[C_{17}H_{29}N_2]^+$

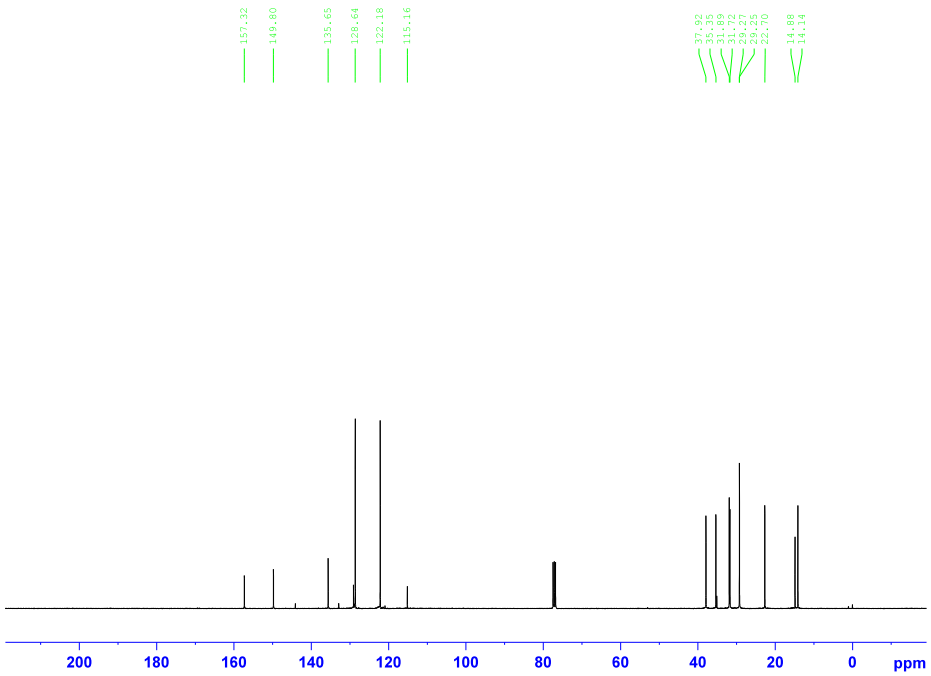
m/z calculated: 261.2330

observed: 261.2333

^{1}H NMR spectrum of *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidine **4a** in $CDCl_3$ obtained using a 400 MHz spectrometer.



^{13}C NMR spectrum of *N'*-(4-heptylphenyl)-*N,N*-dimethylacetamidine **4a** in $CDCl_3$ obtained using a 100 MHz spectrometer.



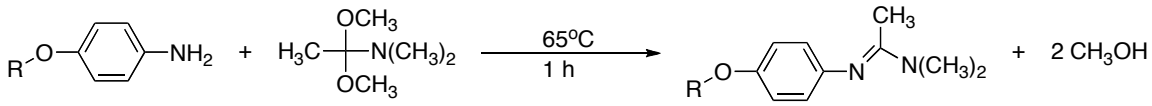
Compound Name: *N'*-(4-(octyloxy)phenyl)-*N,N*-dimethylacetamidine (**5a**)

Molecular Formula: $C_{18}H_{30}N_2O$

Molecular Weight: 290.44 g/mol

Appearance: Black liquid

Synthesis and Structure:



R = C_8H_{17}

Characterization data:

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_2CH_3), 1.28 (m, 8H, C_4H_8), 1.44 (m, 2H, $CH_2CH_2CH_2O$), 1.76 (m, 2H, CH_2CH_2O),1.86 (s, 3H, CCH_3), 3.02 (s, 6H, $N(CH_3)_2$), 3.90 (t, *J* = 6.56 Hz, 2H, CH_2CH_2O), 6.62 (d, *J* = 8.72 Hz, 2H, C_6H_4), 6.79 (d, *J* = 8.68 Hz, 2H, C_6H_4).

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 14.1, 14.9, 22.7, 26.1, 29.3, 29.4, 29.5, 31.8, 38.0, 68.3, 114.8, 123.1, 145.4, 154.2, 157.9.

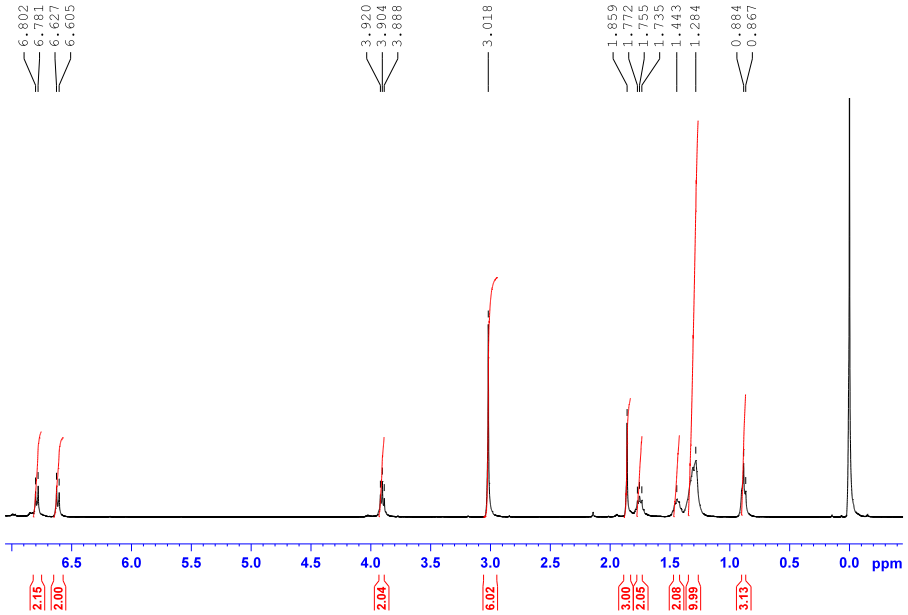
IR: 1614 cm^{-1} (s, υ (C=N))

HRMS (EI$^+$): $[C_{18}H_{30}N_2O]^+$

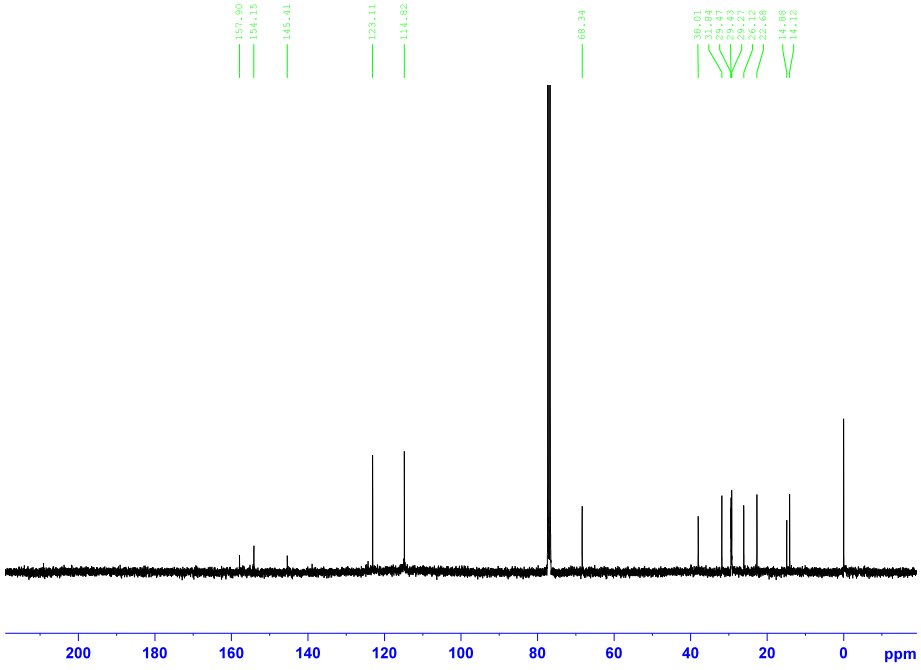
m/z calculated: 290.2358

observed: 290.2348

^{1}H NMR spectrum of *N'*-(4-(octyloxy)phenyl)-*N,N*-dimethylacetamidine **5a** in $CDCl_3$ obtained using a 400 MHz spectrometer.



^{13}C NMR spectrum of *N'*-(4-(octyloxy)phenyl)-*N,N*-dimethylacetamidine **5a** in $CDCl_3$ obtained using a 100 MHz spectrometer.



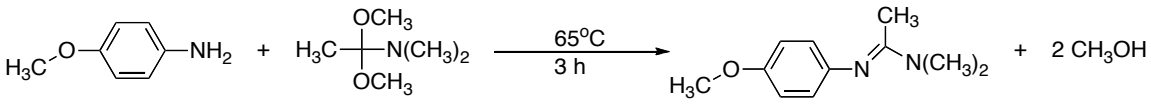
Compound Name: *N'*-(4-(methyloxy)phenyl)-*N,N*-dimethylacetamidine (**6a**)

Molecular Formula: $C_{11}H_{16}N_2O$

Molecular Weight: 192.26 g/mol

Appearance: Black liquid

Synthesis and Structure:



Characterization data:

Yield: 98%

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.73 (s, 3H, CC*H*$_3$), 2.89 (s, 6H, N(C*H*$_3$)$_2$), 3.64 (s, 3H, OC*H*$_3$), 6.50 (d, *J* = 8.6, 2H, C_6H_6), 6.67 (d, *J* = 8.7, 2H, C_6H_6).

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 14.8, 38.0, 55.5, 114.1, 123.1, 145.7, 154.6, 157.9.

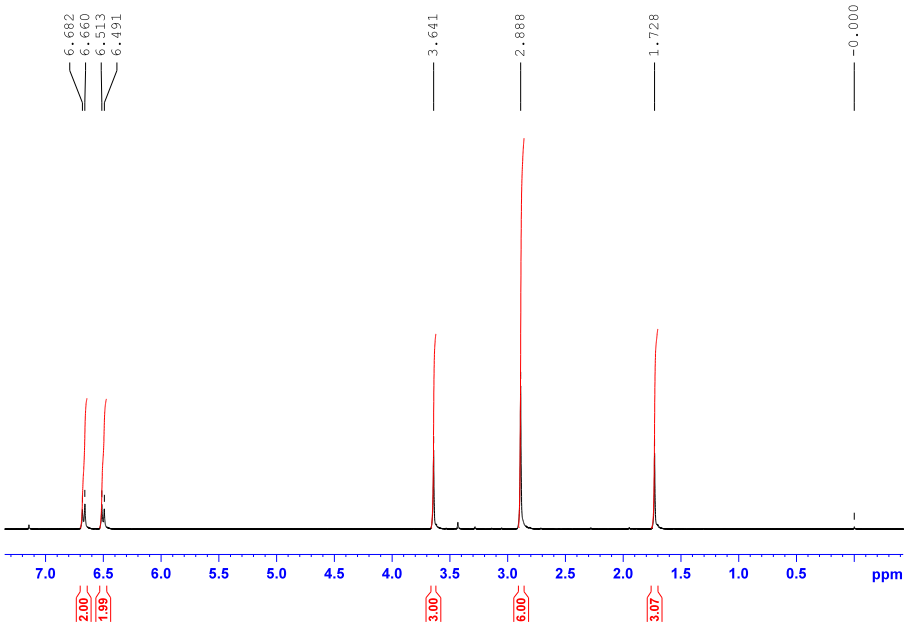
IR: 1614 cm^{-1} (s, υ (C=N))

HRMS (EI$^+$): $[C_{11}H_{16}N_2O]^+$

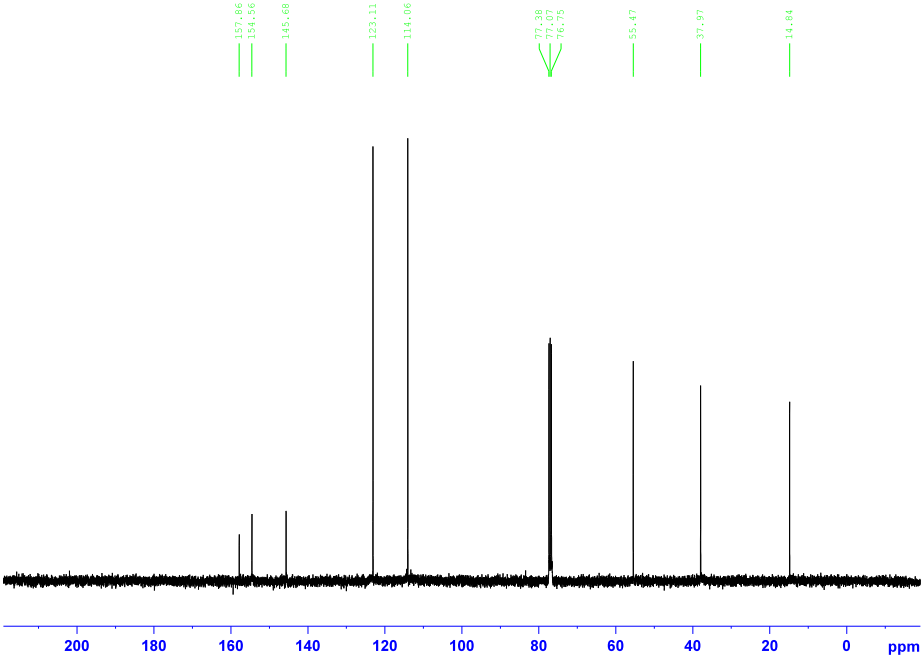
m/z calculated: 192.1623

observed:192.1266

^{1}H NMR spectrum of *N'*-(4-(methyloxy)phenyl)-*N,N*-dimethylacetamidine **6a** in $CDCl_3$ obtained using a 400 MHz spectrometer.



^{13}C NMR spectrum of *N'*-(4-(methyloxy)phenyl)-*N,N*-dimethylacetamidine **6a** in $CDCl_3$ obtained using a 100 MHz spectrometer.



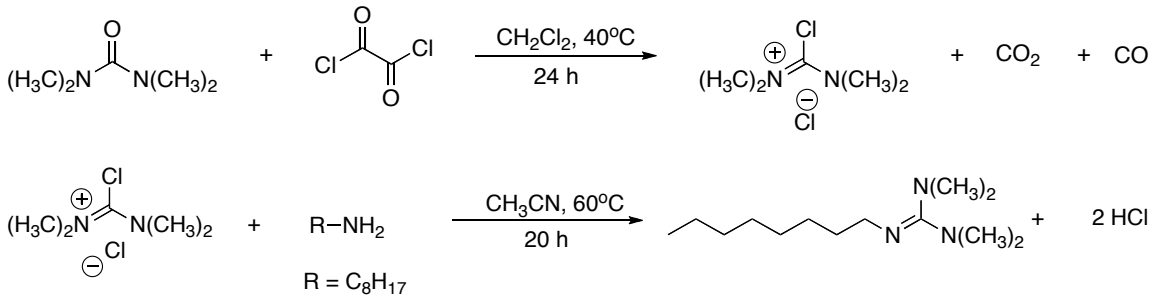
Compound Name: *N*-octyl-*N',N',N'',N''*-tetramethylguanidine (**7a**)

Molecular Formula: $C_{13}H_{29}N_3$

Molecular Weight: 227.39 g/mol

Appearance: Clear liquid

Synthesis and Structure:



Characterization data:

Yield: 20%

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8, 3H, CH_2CH_3), 1.29 (m, 10H, C_5H_{10}), 1.51 (m, 2H, $C_5H_{10}CH_2CH_2N$=), 2.65 (s, 6H, $N(CH_3)_2$), 2.74 (s, 6H, $N(CH_3)_2$), 3.10 (t, *J* = 7.0, 2H, CH_2N).

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 27.4, 29.3, 29.5, 31.8, 32.8, 38.7, 39.5, 49.6, 159.8.

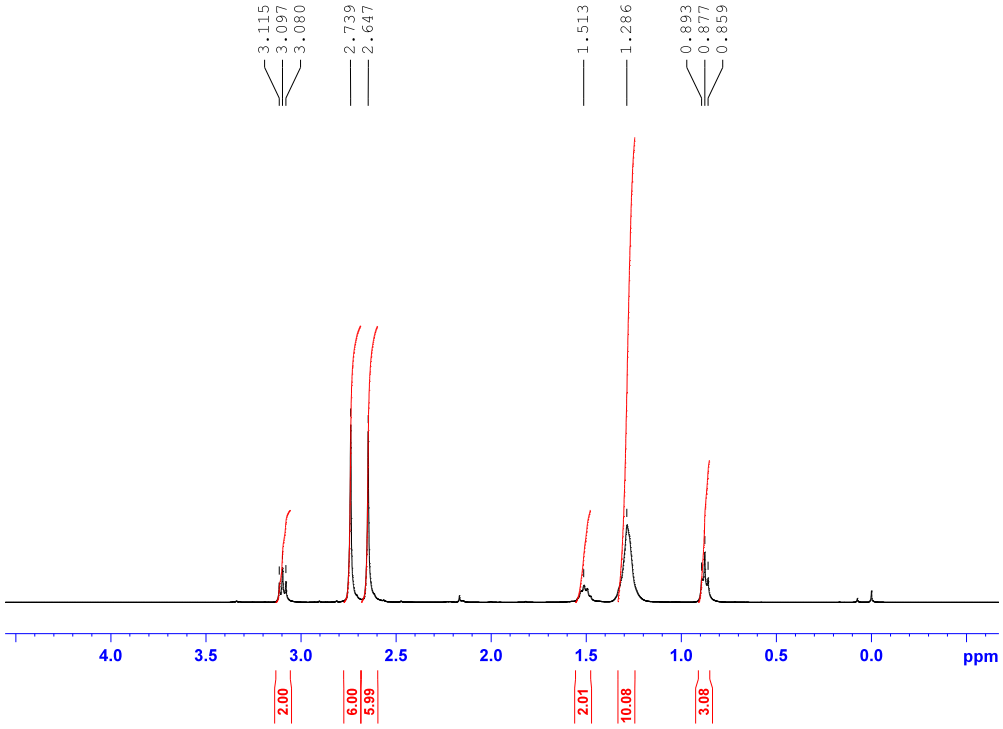
IR: 1625 cm^{-1} (s, υ (C=N))

HRMS (EI$^+$): $[C_{13}H_{30}N_3]^+$

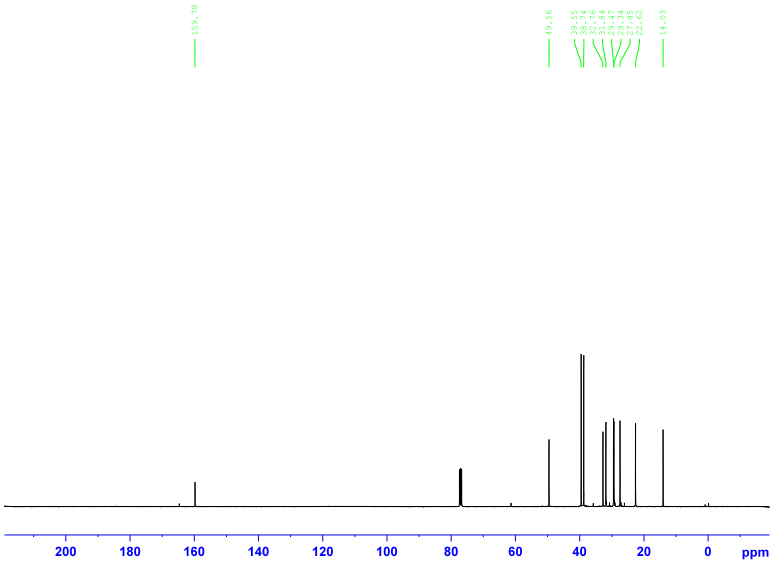
m/z calculated: 228.2434

observed:228.2428

^{1}H NMR spectrum of *N*-octyl-*N',N',N'',N''*-tetramethylguanidine **7a** in $CDCl_3$ obtained using a 400 MHz spectrometer.



^{13}C NMR spectrum of *N*-octyl-*N',N',N'',N''*-tetramethylguanidine **7a** in $CDCl_3$ obtained using a 100 MHz spectrometer.



Solubility Measurements in D_2O:

Molecule	Solubility in D_2O	Average
	0.32	
octyl amine	0.17	0.24 ± 0.08
	0.23	
	4.95	
1a	4.88	4.88 ± 0.08
	4.80	
	1.45	
2a	1.81	1.73 ± 0.2
	1.92	
	2.96	
3a	3.09	3.00 ± 0.07
	2.96	
	0.17	
4a [a]		0.13 ± 0.06
	0.08	
	0.11	
5a [a]	0.08	0.11 ± 0.03
	0.13	
	34.50	
7a [b]	42.98	39.07 ± 4
	39.74	

0.20 mmol of sample, 3 mL of D_2O stirred for 30 min at room temperature. 200 μL aliquot, 10 μL DMF internal standard, 0.6 mL D_2O. [a] Only 5 μL of DMF. [b] 0.40 mmol and 25 μL of DMF.

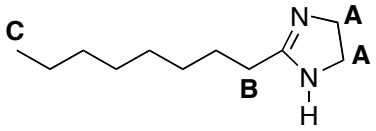
Measurements of the Extent of Conversion by ^{1}H NMR Spectroscopy:

Compound **1a**:

60 °C	δ (ppm)			Conversion (%)			Spectra Average	Sample Average
	A	B	C	A	B	C		
				"From Off"				
Sample(1) Spectrum 1	2.8479	1.9013	3.1088	31.3	28.8	33.1	31.1	
Spectrum 2	2.8358	1.8867	3.1000	28.0	25.6	29.9	27.8	30.0
Spectrum 3	2.8476	1.9010	3.1082	31.3	28.7	32.9	31.0	
Sample(2) Spectrum 1	2.8347	1.8852	3.0990	27.7	25.3	29.6	27.5	
Spectrum 2	2.8385	1.8899	3.1019	28.7	26.3	30.6	28.6	28.6
Spectrum 3	2.8427	1.8951	3.1051	29.9	27.4	31.8	29.7	
				"From On"				
Sample(1) Spectrum 1	2.8284	1.8779	3.0947	25.9	23.7	28.0	25.9	
Spectrum 2	2.8283	1.8780	3.0947	25.9	23.8	28.0	25.9	25.3
Spectrum 3	2.8215	1.8697	3.0896	24.0	22.0	26.1	24.0	
							Overall Average	27.9 ± 2

0.11 mmol of **1a**, 25 μL of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at 60 °C.

Compound **2a**:



Schematic displaying the significant δ of compound **2a** where δ C (0.8330 ppm) was employed to reference the ^{1}H NMR spectra.

Compound	δ A	δ B
Base	3.4226	2.1250
$BH^{+}Cl^{-}$	3.7954	2.4778
$BH^{+}AcO^{-}$	3.772	2.4191
$BH^{+}TFA^{-}$	3.7797	2.4196
Average BH^{+}	3.7824	2.4388
Change	0.3597	0.3139
Conversion Formula	$\left(\frac{\delta - 3.4226}{0.3597}\right) x100\%$	$\left(\frac{\delta - 2.1250}{0.3139}\right) x100\%$

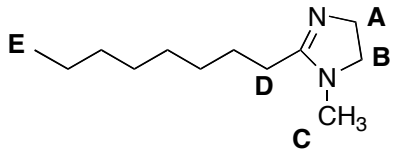
0.11 mmol of **2a**, 1.10 mmol acid, 0.6 mL DMSO-d_6 at room temperature.

40 °C	δ (ppm)		Conversion (%)		Spectra Average	Sample Average
	A	B	A	B		
			"From Off"			
Sample(1) Spectrum 1	3.479	2.1882	15.7	20.2	17.9	16.9
Spectrum 2	3.476	2.1855	14.8	19.3	17.1	
Spectrum 3	3.4714	2.1812	13.6	17.9	15.7	

Sample(2) Spectrum 1	3.481	2.1885	16.2	20.2	18.2	17.3
Spectrum 2	3.4791	2.186	15.7	19.4	17.6	
Spectrum 3	3.4699	2.1843	13.1	18.9	16.0	
			"From On"			
Sample(1) Spectrum 1	3.4844	2.1935	17.2	21.8	19.5	19.2
Spectrum 2	3.4838	2.1934	17.0	21.8	19.4	
Spectrum 3	3.4813	2.1908	16.3	21.0	18.6	
Sample(2) Spectrum 1	3.4835	2.1916	16.9	21.2	19.1	18.3
Spectrum 2	3.4796	2.1879	15.8	20.1	17.9	
Spectrum 3	3.4791	2.1876	15.7	20.0	17.8	
					Overall Average	17.9 ± 1

0.11 mmol of **2a**, 25 μL of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at 40 °C.

Compound **3a**:



Schematic displaying the significant δ of compound **3a** where **δ** E (0.8330 ppm) was employed to reference the ^{1}H NMR spectra.

Compound	Average δ of A&B	δ C	δ D
Base	3.2950	2.6960	2.1144
BH^+Cl^-	3.7757	3.0209	2.5465
BH^+AcO^-	3.7532	3.0029	2.4752
BH^+TFA^-	3.7573	3.0059	2.4778
Average BH^+	3.7552	3.0044	2.4765
Change	0.4602	0.3084	0.3621
Conversion Formula	$\left(\frac{\delta - 3.2950}{0.4602}\right) x100\%$	$\left(\frac{\delta - 2.6960}{0.3084}\right) x100\%$	$\left(\frac{\delta - 2.1144}{0.3621}\right) x100\%$

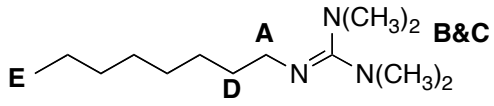
0.11 mmol of **3a**, 1.10 mmol acid, 0.6 mL DMSO-d_6 at room temperature.

40 °C	δ (ppm)			Conversion (%)			Spectra Average	Sample Average
	A&B	C	D	A&B	C	D		
				"From Off"				
Sample(1) Spectrum 1	3.3869	2.759	2.1954	20.0	20.4	22.4	20.9	21.4
Spectrum 2	3.39035	2.7612	2.1985	20.7	21.2	23.2	21.7	

Spectrum 3	3.3893	2.7606	2.1975	20.5	21.0	23.0	21.5	
Sample(2) Spectrum 1	3.3805	2.7551	2.1899	18.6	19.2	20.9	19.5	20.3
Spectrum 2	3.38545	2.7587	2.195	19.7	20.3	22.3	20.8	
Spectrum 3	3.3855	2.7586	2.1941	19.7	20.3	22.0	20.7	
				“From On”				
Sample(1) Spectrum 1	3.3866	2.7589	2.1947	19.9	20.4	22.2	20.8	20.7
Spectrum 2	3.3838	2.757	2.1924	19.3	19.8	21.5	20.2	
Spectrum 3	3.38825	2.7599	2.1963	20.3	20.7	22.6	21.2	
Sample(2) Spectrum 1	3.38035	2.7547	2.1892	18.5	19.0	20.7	19.4	20.2
Spectrum 2	3.38585	2.7583	2.194	19.7	20.2	22.0	20.6	
Spectrum 3	3.3853	2.758	2.1935	19.6	20.1	21.9	20.5	
							Overall Average	20.8 ± 0.5

0.11 mmol of **3a**, 25 μL of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at 40 °C.

Compound **7a**:



Schematic displaying the significant δ of compound **7a** where **δ** E (0.8330 ppm) was employed to reference the ^{1}H NMR spectra.

Compound	δ A	Average δ of B&C	δ D
Base	2.9824	2.5812	1.3736
BH^+Cl^-	3.0829	2.8897	1.5208
BH^+AcO^-	3.0734	2.8669	1.5009
BH^+TFA^-	3.0729	2.8666	1.5007
Average BH^+	3.0764	2.8744	1.5075
Change	0.0912	0.2802	0.1296
Conversion Formula	$\left(\frac{\delta - 2.9824}{0.0912}\right) x100\%$	$\left(\frac{\delta - 2.5812}{0.2802}\right) x100\%$	$\left(\frac{\delta - 1.3736}{0.1296}\right) x100\%$

0.11 mmol of **7a**, 1.10 mmol acid, 0.6 mL DMSO-d_6 at room temperature.

40 °C	δ (ppm)			Conversion (%)			Spectra Average	Sample Average
	A&B	C	D	A&B	C	D		
				"From Off"				
Sample(1) Spectrum 1	3.0687	2.8645	1.5055	91.8	96.6	98.5	95.7	96.0
Spectrum 2	3.0688	2.8652	1.5072	91.9	96.7	99.8	96.2	
Spectrum 3	3.0689	2.8653	1.5074	92.0	96.9	100.0	96.3	

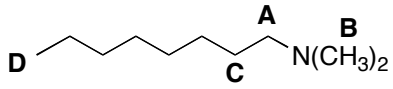
Sample(2) Spectrum 1	3.0687	2.8646	1.5059	91.8	96.7	98.8	95.8	96.0
Spectrum 2	3.0688	2.8651	1.5069	91.9	96.8	99.6	96.1	
Spectrum 3	3.0690	2.8652	1.5071	92.1	96.9	99.7	96.2	
				"From On"				
Sample(1) Spectrum 1	3.0691	2.8654	1.5075	92.2	96.9	100.0	96.4	96.4
Spectrum 2	3.0691	2.8655	1.5075	92.2	97.0	100.0	96.4	
Spectrum 3	3.0690	2.8653	1.5075	92.1	96.9	100.0	96.4	
Sample(2) Spectrum 1	3.0690	2.8654	1.5075	92.1	96.9	100.0	96.4	96.4
Spectrum 2	3.0690	2.8654	1.5076	92.1	96.9	100.1	96.4	
Spectrum 3	3.0691	2.8656	1.5076	92.2	97.0	100.1	96.4	
							Overall Average	96.2 ± 0.2

0.11 mmol of **7a**, 25 μL of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at 40 °C.

60 °C	δ (ppm)			Conversion (%)			Spectra Average	Sample Average
	A&B	C	D	A&B	C	D		
				"From Off"				
Sample(1) Spectrum 1	3.0726	2.8618	1.5060	96.0	95.7	98.9	96.9	
Spectrum 2	3.0727	2.8621	1.5072	96.1	95.8	99.8	97.2	97.2
Spectrum 3	3.0729	2.8628	1.5077	96.3	96.0	100.2	97.5	
Sample(2) Spectrum 1	3.0724	2.8615	1.5067	95.8	95.6	99.4	96.9	
Spectrum 2	3.0725	2.8618	1.5070	95.9	95.7	99.7	97.1	97.1
Spectrum 3	3.0727	2.8623	1.5071	96.1	95.9	99.7	97.2	
				"From On"				
Sample(1) Spectrum 1	3.0711	2.8609	1.5057	94.4	95.4	98.7	96.2	
Spectrum 2	3.0726	2.8614	1.5075	96.0	95.6	100.0	97.2	96.7
Spectrum 3	3.0727	2.8617	1.5075	96.1	95.7	100.0	97.3	
Sample(2) Spectrum 1	3.0717	2.8582	1.5051	95.0	94.5	98.2	95.9	
Spectrum 2	3.0728	2.862	1.5074	96.2	95.8	100.0	97.3	96.8
Spectrum 3	3.0728	2.8624	1.5072	96.2	95.9	99.8	97.3	
							Overall Average	97.0 ± 0.2

0.11 mmol of **7a**, 25 μL of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at 60 °C.

Compound **8a**:



Schematic displaying the significant δ of compound **8a** where **δ** D (0.8330 ppm) was employed to reference the ^{1}H NMR spectra.

Compound	**δ A**	**δ B**	**δ C**
Base	2.1320	2.0643	1.3426
$BH^{+}Cl^{-}$	3.0365	2.7553	1.6464
$BH^{+}AcO^{-}$	2.9039	2.6605	1.5608
$BH^{+}TFA^{-}$	2.9336	2.7418	1.5757
Average BH^{+}	2.9580	2.7192	1.5943
Change	0.8260	0.6549	0.2518
Conversion Formula	$\left(\frac{\delta - 2.1320}{0.8260}\right) x100\%$	$\left(\frac{\delta - 2.0643}{0.6549}\right) x100\%$	$\left(\frac{\delta - 1.3426}{0.2518}\right) x100\%$

0.11 mmol of **8a**, 1.10 mmol acid, 0.6 mL DMSO-d_6 at room temperature.

40 °C	**δ (ppm)**			**Conversion (%)**			**Spectra Average**	**Sample Average**
	A	**B**	**C**	**A**	**B**	**C**		
				"From Off"				
Sample(1) Spectrum 1	2.1481	2.0769	1.3468	1.9	1.9	1.7	1.9	1.8
Spectrum 2	2.1474	2.0764	1.3465	1.9	1.8	1.7	1.8	
Spectrum 3	2.1478	2.0766	1.3470	1.9	1.9	1.8	1.9	

Sample(2) Spectrum 1	2.1447	2.0745	1.3459	1.5	1.6	1.3	1.5	1.4
Spectrum 2	2.1443	2.0742	1.3458	1.5	1.5	1.3	1.4	
Spectrum 3	2.1444	2.0743	1.3458	1.5	1.5	1.3	1.4	
				“From On”				
Sample(1) Spectrum 1	2.1449	2.0744	1.3462	1.6	1.5	1.4	1.5	1.6
Spectrum 2	2.1488	2.0744	1.3462	2.0	1.5	1.4	1.7	
Spectrum 3	2.1454	2.0749	1.3464	1.6	1.6	1.5	1.6	
Sample(2) Spectrum 1	2.1481	2.0769	1.3469	1.9	1.9	1.7	1.9	1.8
Spectrum 2	2.1478	2.0766	1.3470	1.9	1.9	1.8	1.9	
Spectrum 3	2.1475	2.0764	1.3468	1.9	1.8	1.7	1.8	
							Overall Average	1.7 ± 0.2

0.11 mmol of **8a**, 25 μL of H_2O, 0.6 mL of DMSO-d_6 were combined at room temperature while the experiments were performed at 40 °C.

Calorimetry Measurements:

Base	All ΔH_{rxn} in DMSO (kJ/mol)	Average ΔH_{rxn} (kJ/mol)
Triethylamine in H_2O	43.49	43.62 ± 0.5
	44.19	
	43.17	
Aniline	31.37	30.82 ± 0.5
	30.45	
	30.62	
1a	70.57	70.97 ± 1
	69.96	
	72.39	
2a	46.98	46.77 ± 0.8
	47.44	
	45.90	
3a	52.67	53.46 ± 0.7
	54.10	
	53.60	
4a	47.47	47.79 ± 0.3
	48.01	
	47.88	
6a	48.99	50.75 ± 2

	52.07	
	51.18	
	82.76	
7a	82.40	82.67 ± 0.2
	82.80	
	52.59	
8a	53.31	52.79 ± 0.5
	52.48	

Sample vial: 0.3 mmol base, topped up to a total volume of 2.00 mL with solvent; Reference vial: 2.00 mL of solvent; Syringes: 0.15 mL of 12 M $HCl_{(aq)}$, 0.85 mL of solvent.

Demulsifying Ability of Crude Oil and Water emulsions:

Compound **1a**:

Time (min)	Average Total Height (mm)	Average Water Separation (mm)
0	14.91 ± 0.8	0.00
15	15.43 ± 0.07	2.01 ± 1
30	15.21 ± 0.7	3.07 ± 0.7
45	15.42 ± 0.1	3.38 ± 0.1
60	14.81 ± 0.03	3.50 ± 0.3
120	15.27 ± 0.07	3.57 ± 0.5
240	15.29 ± 0.1	3.90 ± 0.1
420	15.21 ± 0.5	4.46 ± 0.4
600	15.23 ± 0.04	4.57 ± 0.5
1440	15.12 ± 0.3	4.53 ± 0.5

Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **1a** (0.29 mmol) over 24 h at room temperature.

Compound **2a**:

Time (min)	Average Total Height (mm)	Average Water Separation (mm)	Average Oil Separation (mm)
0	15.12 ± 0.5	0	0
30	15.07 ± 0.4	0	2.57 ± 1
60	15.08 ± 0.2	0	2.87 ± 0.4
120	15.03 ± 0.3	0	3.20 ± 0.03
240	15.03 ± 0.2	0.83 ± 1	-
420	15.02 ± 0.2	2.58 ± 0.2	-
600	15.15 ± 0.02	2.70 ± 0.01	-
1440	15.42 ± 0.1	2.82 ± 0.07	-

Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **2a** (0.29 mmol) over 24 h at room temperature.

Compound **3a**:

Time (min)	Average Total Height (mm)	Average Oil Separation (mm)
0	14.97 ± 0.06	0.00
30	15.38 ± 0.1	1.44 ± 0.3
60	15.45 ± 0.2	1.84 ± 0.7
120	15.22 ± 0.08	1.74 ± 0.1
240	15.37 ± 0.3	2.71 ± 0.3
420	15.21 ± 0.4	2.42 ± 0.2
600	15.25 ± 0.4	2.35 ± 0.06
1440	15.58 ± 0.3	2.75 ± 0.5

Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **3a** (0.29 mmol) over 24 h at room temperature.

Compound **4a**:

Time (min)	Average Total Height (mm)	Average Water Separation (mm)	Average Oil Separation (mm)
0	14.46 ± 0.4	0	0
30	14.72 ± 0.3	0	2.62 ± 0.1
60	15.01 ± 0.2	0	3.68 ± 0.2
120	15.51 ± 0.2	0	-
240	15.33 ± 0.02	5.23 ± 0.06	-
420	15.49 ± 0.06	5.86 ± 0.08	-
600	15.21 ± 0.3	5.81 ± 0.00	-
1440	15.37 ± 0.01	6.24 ± 0.2	-

Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **4a** (0.29 mmol) over 24 h at room temperature.

Compound **5a**:

Time (min)	Average Total Height (mm)	Average Water Separation (mm)	Average Oil Separation (mm)
0	14.05 ± 0.2	0	0
30	15.40 ± 0.2	0	4.30 ± 0.5
60	15.23 ± 0.2	0	4.50 ± 0.5
120	15.28 ± 0.08	2.00 ± 0.6	4.94 ± 0.06
240	15.35 ± 0.2	2.95 ± 0.03	5.35 ± 0.2
420	15.34 ± 0.5	3.04 ± 0.03	5.82 ± 1
600	15.47 ± 0.6	3.20 ± 0.08	5.99 ± 1
1440	15.89 ± 0.4	3.22 ± 0.1	6.23 ± 1

Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compound **5a** (0.29 mmol) over 24 h at room temperature.

Water separation as a percentage of total height over time:

Time (min)	Water Separation as a Function of Total Height (%)			
	1a	**2a**	**4a**	**5a**
0	13.02 ± 6	0	0	0
30	21.95 ± 0.7	0	0	0
60	23.65 ± 2	0	0	0
120	23.41 ± 4	0	0	13.09 ± 4
240	25.54 ± 0.9	11.04 ± 0.1	34.09 ± 0.2	19.22 ± 0.2
420	29.32 ± 3	16.38 ± 1	37.85 ± 0.2	19.82 ± 0.2
600	29.99 ± 4	17.88 ± 0.07	38.19 ± 0.00	20.72 ± 0.5
1440	29.99 ± 3	18.61 ± 0.5	40.59 ± 0.7	20.27 ± 0.6

Height measurements of the demulsifying of a crude oil (4 mL), and water (2 mL) emulsion employing compounds **1a**, **2a**, **4a**, and **5a** (0.29 mmol) over 24 h at room temperature.