Cationic and Anionic Carbon Dioxide Responsive Switchable Surfactants

Application to Temporary Heavy Crude Oil-in-Water Emulsions

and

Application to Reversibly Stable Latex by Emulsion Polymerization

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Abstract

Tail modified amidine type cationic switchable surfactants were synthesized. The modified structures included ethylene oxide units in the tail to increase water solubility. Surfactants with different hydrophile-lipophilic balance were available by virtue of the commercial availability of the alcohol precursors.

Low viscosity emulsions of heavy crude oil were generated by activating indigenous crude oil surfactants with a water-soluble base. The emulsions containing approximately 70 wt% heavy crude oil were visually stable under ambient conditions for two weeks. Immediate phase separation was found to occur with the addition of carbon dioxide gas. Free water was easily separated from high viscosity crude oil. Improvements in the quality of phase separation were possible with water-soluble organic bases. Amidine surfactants with appropriate structure were also capable of stabilizing heavy crude oil emulsions.

Anionic switchable surfactants were developed. The surfactants reacted with carbon dioxide to cause changes to interfacial properties. Carbon dioxide in aqueous solution was able to neutralize the anionic form of the surfactant. Examples include carboxylic acids and phenols. Heating and removal of carbon dioxide was, in most cases, sufficient to cause the surfactant to become anionic again. Interfacial properties such as surface tension and emulsion stability were controlled using the anionic switchable surfactant system. Otherwise stable emulsions were triggered to separate by addition of carbon dioxide.

Polystyrene particles of 30 nm to 40 nm in diameter were made by emulsion polymerization using anionic switchable surfactants. The latex was stabilized by electrostatic charges with measured zeta potential below –30 mV. Treating the latex with carbon dioxide was found to cause aggregation of polymer particles. The aggregates were much larger with diameter of approximately 100 μm and readily separated by flotation and dried into a fine free flowing powder. Re-dispersion of the aggregates was possible after heating and mixing the slurry in water. The re-dispersed latex was found to be stabilized by electrostatic charges with measured zeta potential below –30 mV.

For my mom, my dad, and my brother;
To whom I owe everything;
Without whom I have nothing.

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List of Abbreviations

API	American Petroleum Institute
AZTMA	4-butylazobenzene-4’-(oxyethyl)trimethylammonium
b	broad
Bz	benzyl
CMC	critical micelle concentration
d	doublet
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
EO	ethylene oxide
FTMA	ferrocenylundecyl trimethylammonium
HLB	hydrophile-lipophile balance
m	multiplet
O/W	oil-in-water
PDVSA	Petróleos de Venezuela, S.A.
Phth	phthalimide
PO	propylene oxide
q	quartet
quint	quintuplet
s	singlet
SARA	saturates,aromatics, resins, asphaltenes
t	triplet
TAN	total acid number

TBN	total base number
Ts	tosylate
W/O	water-in-oil

Chapter 1 – Introduction

Fossil fuels will continue to be an important cheap and abundant source of energy and chemical feedstock. As conventional crude oil supplies become scarcer, the need to tap into alternative resources such as heavy crude oil, extra-heavy crude oil, oil sand, and oil shale becomes greater [1-3]. Heavy crude oil presents challenges at various production stages including extraction, transportation, and refining [3, 4].

The difficulty in heavy crude oil transportation lies in its high viscosity. Conventional pipelines cannot handle high viscosity fluids at ambient temperature. Heavy crude oil pipelining is assisted by heating, dilution, or emulsion [5]. Heating lowers viscosity by reducing the internal interactions between crude oil molecules but requires energy as well as heated pipelines. Heavy crude oil can be mixed with lighter petroleum fractions [6]. However, diluents are costly and not always available on site in the required quantity [7]. The viscosity of crude oil can be reduced by dispersing the heavy crude oil in water creating an emulsion [5, 8-12]. Emulsification requires stabilizers to prevent phase separation. The main challenge of emulsification is the removal of water once an emulsion is no longer desired. Separation of stable emulsions requires energy and time.

The hypothesis of this research is that the application of switchable surfactants to crude oil pipeline transport has the potential to greatly reduce the amount of energy and time dedicated to separation. The general scheme is illustrated in Figure 1. One form of the surfactant would lower the bulk viscosity by stabilizing the crude oil emulsion. Once the surfactant switch is triggered, the surfactant no longer provides stabilization. Oil separates from the destabilized emulsion and is readily recovered.

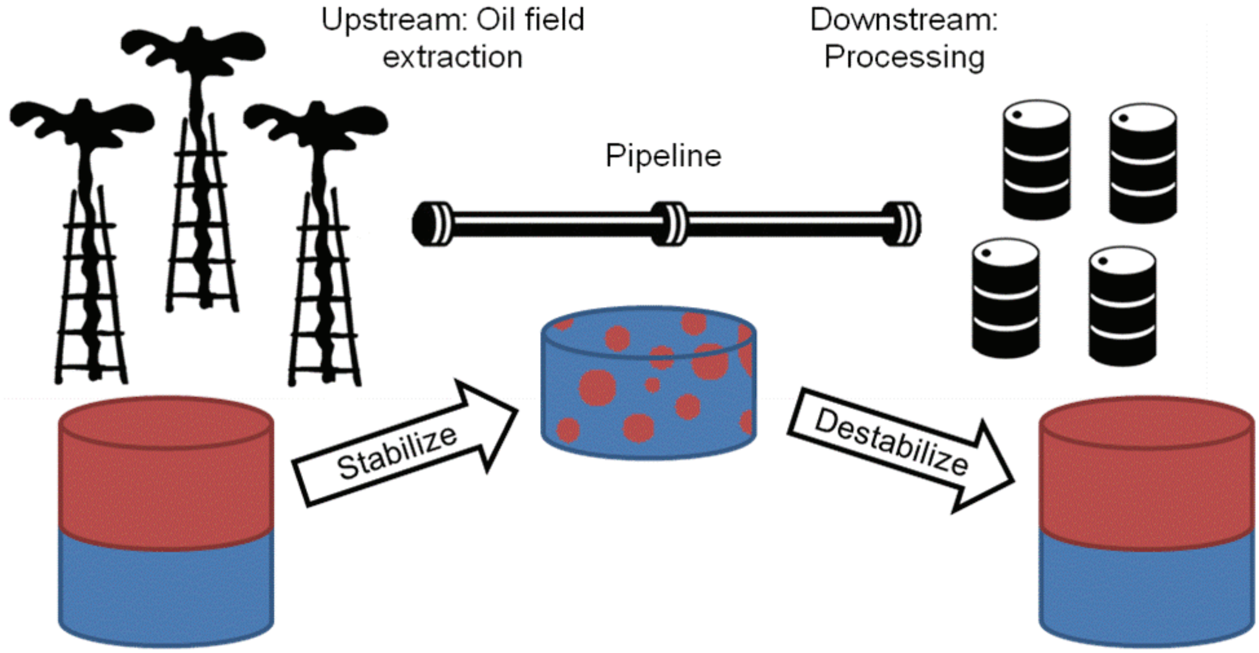

Figure 1 – Switchable surfactant used to form low viscosity crude oil transport emulsions. After extraction, crude oil is treated with stabilizer and emulsified. The emulsion travels through pipelines to its destination. The crude oil emulsion is then destabilized leading to spontaneous and timely separation.

1.1 Heavy Crude Oil

Crude oil is a complex mixture of various hydrocarbons [13]. Also present are dissolved salts, heavy metals, organic acids, and mineral solids. Although predominantly made of carbon and hydrogen, crude oil contains varying amounts of nitrogen, oxygen, and sulphur. The composition of crude oil is highly variable due to differences in reservoir history [14].

Crude oil is often categorized based on its viscosity. Light crude oils are more desirable because of easier processing properties and greater amount of high value distillates (gasoline, diesel, fuel oil). Heavy crude oil is distinguished as having API[*] gravity less than 20˚API. Heavy crude oil has a greater proportion of high molecular weight hydrocarbons and a lower proportion of low molecular weight hydrocarbons.

Oil sand is a special type of petroleum deposit predominantly found in Canada. Bitumen is a heavy form off crude oil found within oil sand deposits. Unique conditions during its formation and subsequent microbial degradation lead to a high viscosity material devoid of low molecular weight hydrocarbons [2]. Bitumen does not flow under ambient conditions and may contain large amounts of sulphur and heavy metals.

Crude oil is also analyzed for its composition. Various types of analysis include density, chloride content, hydrocarbon distribution, neutralization number, pour point, salt content, sediments and water, sulphur content, trace metal content, and vapour pressure [15]. Further spectroscopic analysis techniques can be used to determine the specific structure of a specific fraction [16].

The composition of heavy crude oil is often described using SARA (saturates, aromatics, resins, asphaltenes) fractionation analysis [17]. This method categorizes the crude oil components based on solubility and polarity (see Figure 2). Asphaltenes are insoluble in n-alkanes such as pentane, hexanes, or heptane. The fraction of crude oil that is soluble

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[*] American Petroleum Institute gravity is an empirical measure of density relative to water. API gravity decreases for heavy crude oil.

in n-alkanes is known as maltenes. The maltene fraction is further subdivided into resins, which have polar functional groups; aromatics, which have highly unsaturated and aromatic structures; and saturates, which are generally non-polar low molecular weight alkanes [18].

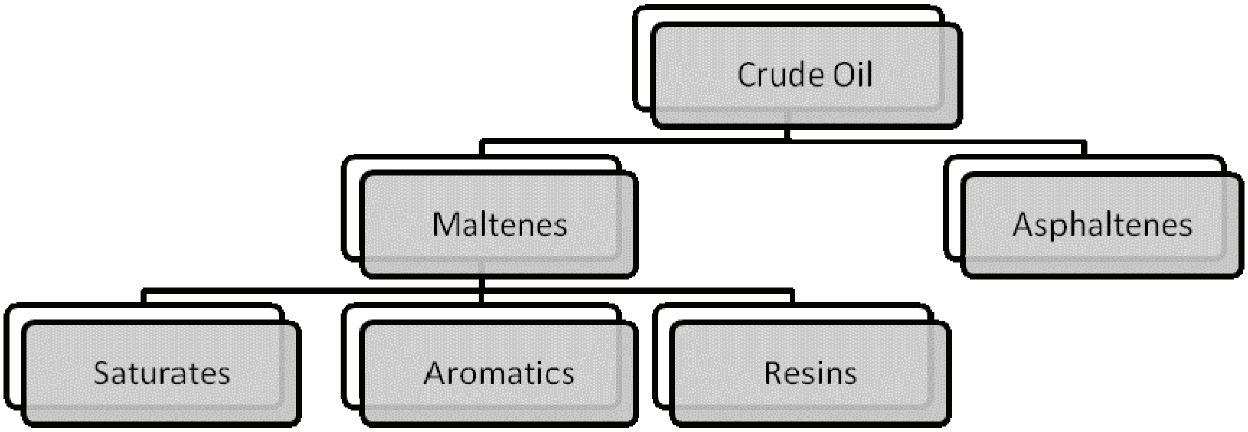


Figure 2 – SARA fractionation of crude oil based on solubility and polarity.

Resins and asphaltenes are much more prevalent in heavy crude oil. Resins contain aromatic rings as well as polar functional groups. Asphaltenes consist of high molecular weight aromatic compounds that can contain relatively high amounts of heteroatoms. Asphaltenes and resins both contain acidic and basic functional groups. Asphaltenes are surface active due to partial incompatibility with alkane and often concentrate at interfaces to stabilize water-in-oil petroleum emulsions [19, 20].

1.2 Surfactants

Surfactants are a general class of molecules with the ability to influence interfacial properties such as surface tension, contact angle, and detergency. They are used in a wide range of industries with annual worldwide production of over eighteen million tonnes [21].

Surfactant molecules contain both hydrophobic and hydrophilic regions. This inherent incompatibility in both aqueous and organic phases leads to a preference for the interface. The head and tail analogy is often used to describe the structure of a surfactant. The hydrophilic moiety is known as the head (often an ionic functional group). The hydrophobic moiety is known as the tail (often a long hydrocarbon chain). The structure of a common surfactant, sodium dodecyl sulfate, is illustrated in Figure 3.

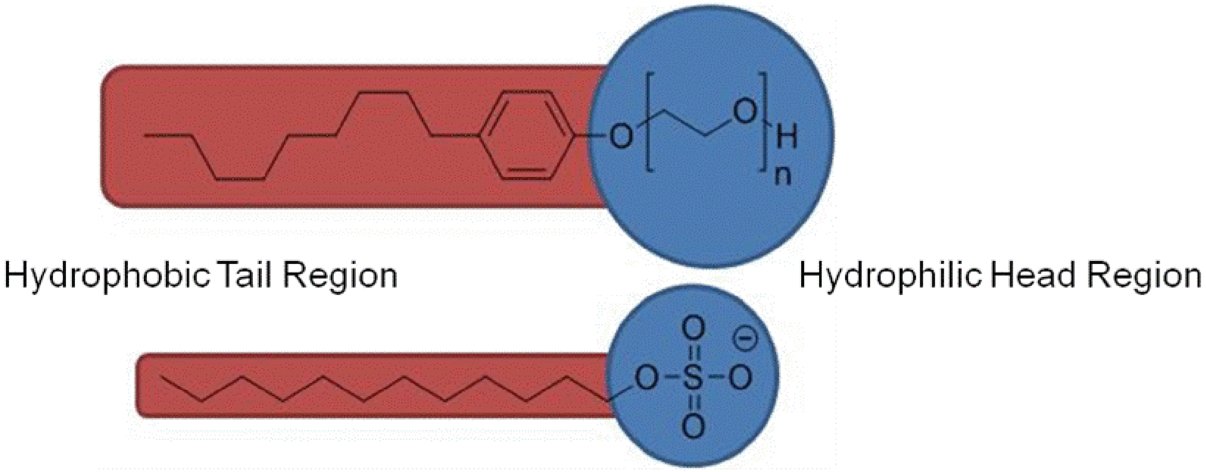
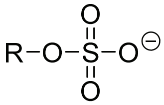
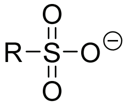
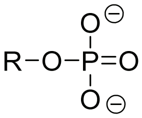
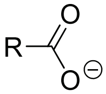
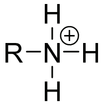
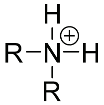
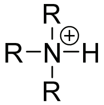
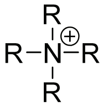
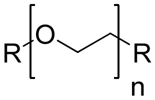
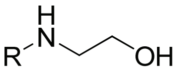
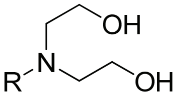
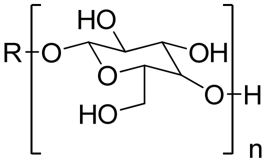


Figure 3 – General structure of a surfactant including hydrophobic tail [RED] and hydrophilic head [BLUE]. Nonylphenol ethoxylates [TOP] are common non-ionic surfactants. Sodium dodecyl sulfate [BOTTOM] is a common anionic surfactant (counter-ion not shown).

Surfactants are generally classified based on their charge [22]. Charged surfactants are anionic, cationic, or zwitterionic. Uncharged surfactants include polymeric materials such as block copolymers, ethoxylates, and glucosides. Typical surfactant hydrophilic head groups are presented in Table 1.

Table 1 – Typical structure of anionic, cationic, non-ionic, and polymeric hydrophilic surfactant head groups.

Type	Class	Structure
Anionic	Sulfate	 $R-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{\ominus}$
Anionic	Sulphonate	 $R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{\ominus}$
Anionic	Phosphate	 $R-O-\overset{\overset{O^{\ominus}}{\mid}}{\underset{\underset{O^{\ominus}}{\mid}}{P}}=O$
Anionic	Carboxylate	
Cationic	Primary ammonium	 $R-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{N}}{}^{\oplus}-H$
Cationic	Secondary ammonium	 $R-\overset{\overset{H}{\mid}}{\underset{\underset{R}{\mid}}{N}}{}^{\oplus}-H$
Cationic	Tertiary ammonium	 $R-\overset{\overset{R}{\mid}}{\underset{\underset{R}{\mid}}{N}}{}^{\oplus}-H$
Cationic	Quaternary ammonium	 $R-\overset{\overset{R}{\mid}}{\underset{\underset{R}{\mid}}{N}}{}^{\oplus}-R$
Non-ionic	Polyoxyethylene	
Non-ionic	Ethanolamine	
Non-ionic	Diethanolamine	
Non-ionic	Polyglucoside	

Surfactant tails are often based on hydrocarbon chains. They can be straight or branched, saturated or unsaturated, and can contain other atoms. Many surfactant properties such as critical micelle concentration (cmc), solubility, and Krafft temperature [†] can be tuned by adjusting the properties to the surfactant tail (e.g. length and chemical nature). The structure of the surfactant tail is often determined by the raw material used to make the surfactant. Common starting materials include linear paraffins and olefins, long-chain alcohols, and fatty acids [23]. Ethylene oxide and propylene oxide based surfactant tails are commonly found in non-ionic surfactants and are made using various polymerization methods. Polyethylene oxide is hydrophilic while propylene oxide is more hydrophobic [23]. Surfactants with perfluoroalkyl chain have very high surface activity and are both water-repellent and oil-repellent [23].

Special types of surfactant structures also exist including gemini surfactants. These surfactants are dimeric structures made up of two regular surfactants (*i.e.* they contain two hydrophobic tail and two hydrophilic heads) chemically linked by a spacer. Gemini surfactants have greater surface activity than regular surfactants and comparatively low critical micelle concentrations [24].

The hydrophile-lipophile balance (HLB) is a measure of the surfactant's internal proportion of hydrophobic and hydrophilic regions. This system was originally designed for non-ionic surfactants but can be empirically applied to others. A low HLB value indicates greater lipophilicity and organic solubility. A high HLB value indicates greater

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[†] The Krafft temperature is the minimum temperature for surfactant micelle formation.

hydrophilicity and water solubility. The HLB concept has been successfully used to describe various surfactant based on their end use [25]. The HLB concept does not take into account many factors including temperature, electrolyte concentration, phase ratio, or the nature and composition of the organic phase.

Table 2 – Classification of surfactants by HLB [25].

HLB	Application	Water Solubility
4 – 6	W/O emulsifier	Poor solubility
7 – 9	Wetting agents	Milky dispersion
8 – 18	O/W emulsifier	Milky dispersion
13 – 15	Detergents	Translucent solution
15 – 18	Solubilising agents	Clear solution

Surfactants at low concentration occupy interfacial sites. Excess surfactants are dissolved species. However, as the concentration increases, surfactant molecules tend to self assemble into micelles. This behaviour is characteristic of surfactants. The critical micelle concentration signals the onset of surfactant self assembly into micelles. The critical micelle concentration can be determined by monitoring physical properties at various surfactant concentrations [26]. Typical behaviour for a surfactant is illustrated in Figure 4.

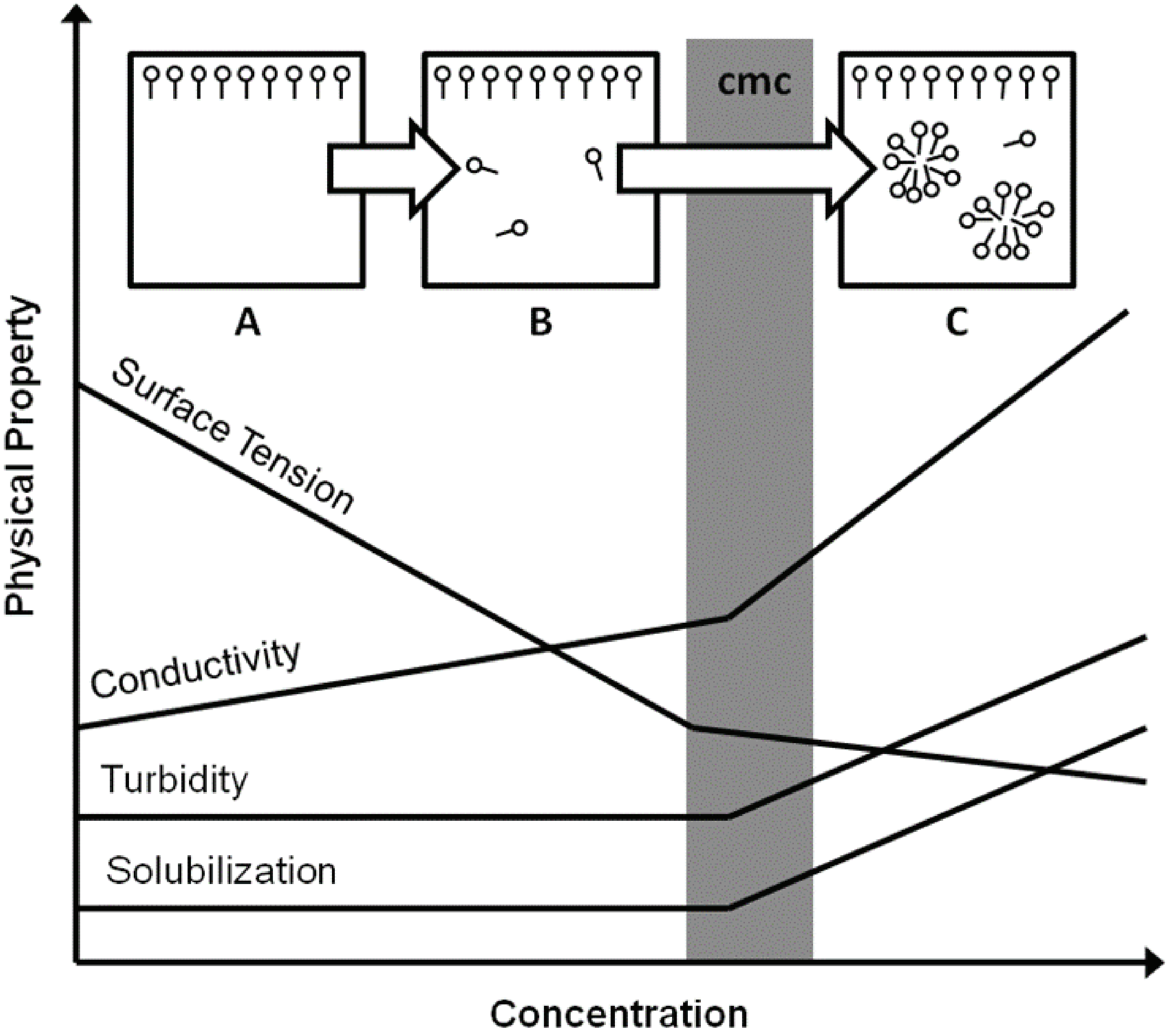


Figure 4 – Surfactant behaviour at various concentrations. Surfactant molecules concentrate at interfaces [A]. Dissolved surfactant molecules [B] are present when all surface sites are occupied. Physical properties of an emulsion change drastically after reaching the critical micelle concentration (cmc). Past this point, addition of more surfactant molecules causes self-assembly into micelles [C].

1.3 Responsive Surfactants

A responsive surfactant is able to change its effect on interfacial properties. They include cleavable surfactants and switchable surfactants. Both have the ability to deactivate once a specific trigger is applied. Switchable surfactants have the added capability to revert to their original level of surface activity.

Cleavable surfactants deactivate when the link between the hydrophobic and hydrophilic regions is severed. This can be achieved by installing a sensitive linker between head and tail. Acid, base, light, or even ozone have been used to trigger the breakdown of the linker [27, 28].

A surfactant is switchable if it is able to reversibly alter its surfactant properties. A switchable surfactant is triggered through a conformational or chemical change. The 11-ferrocenylundecyl trimethylammonium (FTMA) bromide surfactant contains a ferrocenyl functional group which is sensitive to redox chemistry [29]. Its critical micelle concentration was found to be dependent on the oxidation state of iron. Viologenpolysoaps respond to an electrochemical stimulus which can be used to control the solubility of various hydrophobic dyes in aqueous solution [30]. The 4-butylazobenzene-4'-(oxyethyl)trimethylammonium (AZTMA) bromide surfactant undergoes a reversible *cis*-*trans* photo-isomerization under ultraviolet and visible light irradiation, respectively. This change in conformation was shown in conjunction with sodium dodecylbenzenesulfonate to disrupt and reform vesicles[‡] in aqueous solutions [31]. Both systems are illustrated in Figure 5. A recent switchable peptide surfactant used to stabilize foams responds to changes in pH, ionic strength, and concentration of metal ions [32].

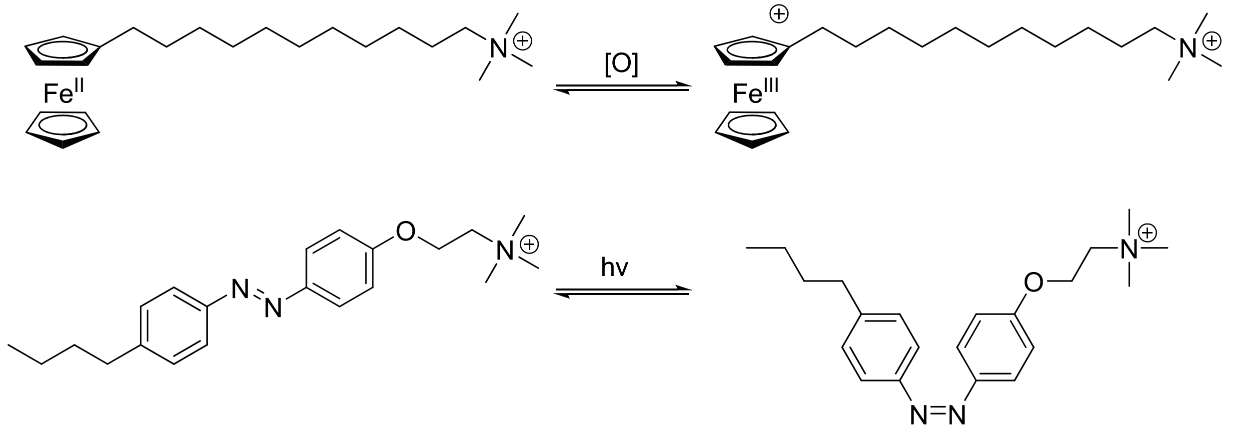


Figure 5 – Two switchable surfactant systems: 11-ferrocenylundecyl trimethylammonium bromide surfactant [TOP] and 4-butylazobenzene-4’-(oxyethyl)trimethyl-ammonium bromide surfactant [BOTTOM].

The amidine surfactant system uses gaseous carbon dioxide in a reversible reaction to form amidinium bicarbonate [33]. The two species have contrasting surface properties. The ionic form stabilizes emulsions while the uncharged neutral form is an active demulsifier. The N’-octyl-N,N-dimethylacetamidine surfactant system is illustrated in Figure 6.

[‡] A vesicle is a pocket of fluid separated from the bulk by a bilayer.

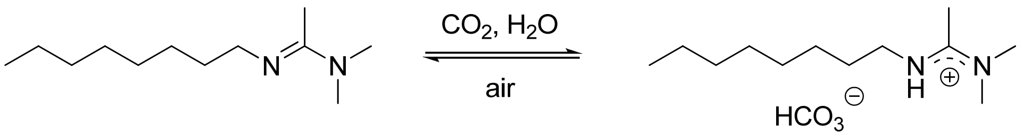


Figure 6 – N’-octyl-N,N-dimethylacetamidine surfactant system. Carbon dioxide turns the amidine into N’-octyl-N,N-dimethylacetamidinium bicarbonate while an inert gas such as nitrogen or air reverts the surfactant back to uncharged form.

The effectiveness of the amidine switchable surfactants was demonstrated with reversible emulsions of light crude oil, as well as easily separated polymer particles made by emulsion polymerization [33].

1.4 Emulsions

Emulsions are mixtures of immiscible phases in which one phase (the dispersed phase) is dispersed in another (the continuous phase). The physical properties of an emulsion depend greatly on the role of each phase. At identical overall compositions, an emulsion of dispersed water in oil (W/O) will have notably different properties than an emulsion of dispersed oil in water (O/W) [34]. Generally, the bulk properties of an emulsion are closer to those of the continuous phase. For example, an O/W emulsion will have significant conductivity while a similar W/O emulsion will have negligible conductivity.

The century-old Bancroft rule [35, 36] predicts that the continuous phase of an emulsion with similar proportions of aqueous and organic phases will be determined by the solubility of the surfactant. A water-soluble surfactant will yield a water continuous emulsion (*i.e.*O/W) while an oil-soluble surfactant will yield an oil continuous emulsion (*i.e.*W/O). The Bancroft rule should only be used as a general guideline because many exceptions exist [37].

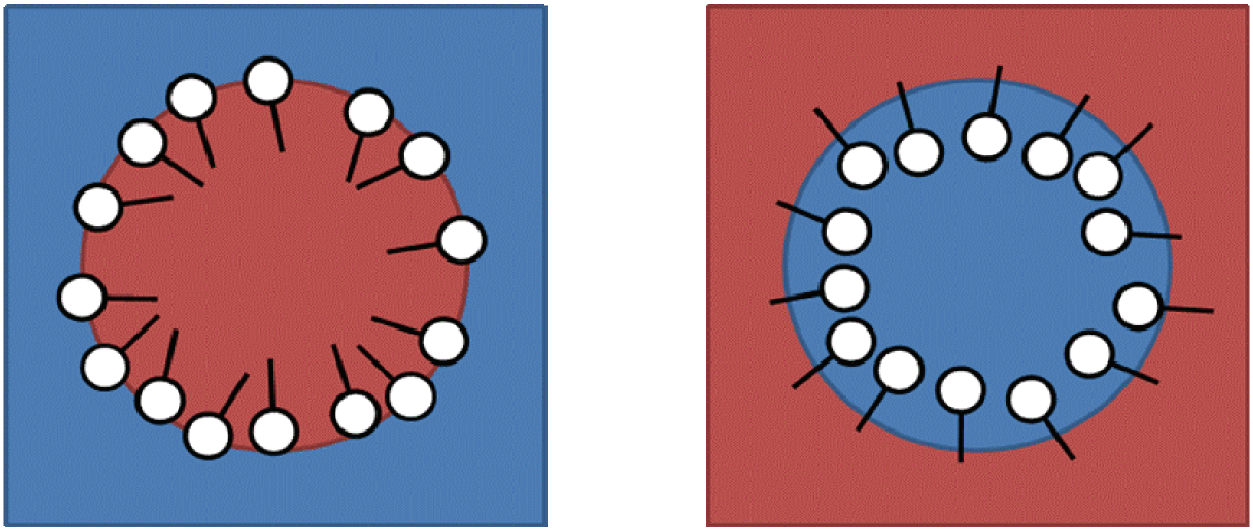


Figure 7 – Illustration of two common emulsion types. Oil-in-water emulsion [LEFT] and water-in-oil emulsion [RIGHT] stabilized using surfactants. There is a direct relationship between the orientation of the surfactant and the continuous phase of the emulsion.

Emulsions have very large interfacial surface area. Mechanical energy in the form of shear is required to generate this high energy surface. The process of mixing is known as emulsification and has a significant effect on the resulting emulsion [38]. The droplet size distribution of emulsions with identical composition can be either monomodal [39] or bimodal [40] depending on the specific method of preparation. Other droplet size distributions are possible. Emulsions are not thermodynamically stable; the tendency for phase separation is driven by the inherent incompatibility of the immiscible phases. However, this process can be incredibly slow for stabilized emulsions. Emulsions that do not separate within a specified process time are considered kinetically stable and referred to as stable. Phase separation occurs by several concurrent mechanisms.

Sedimentation, creaming, coagulation, flocculation, coalescence, and Ostwald ripening are illustrated in Figure 8.

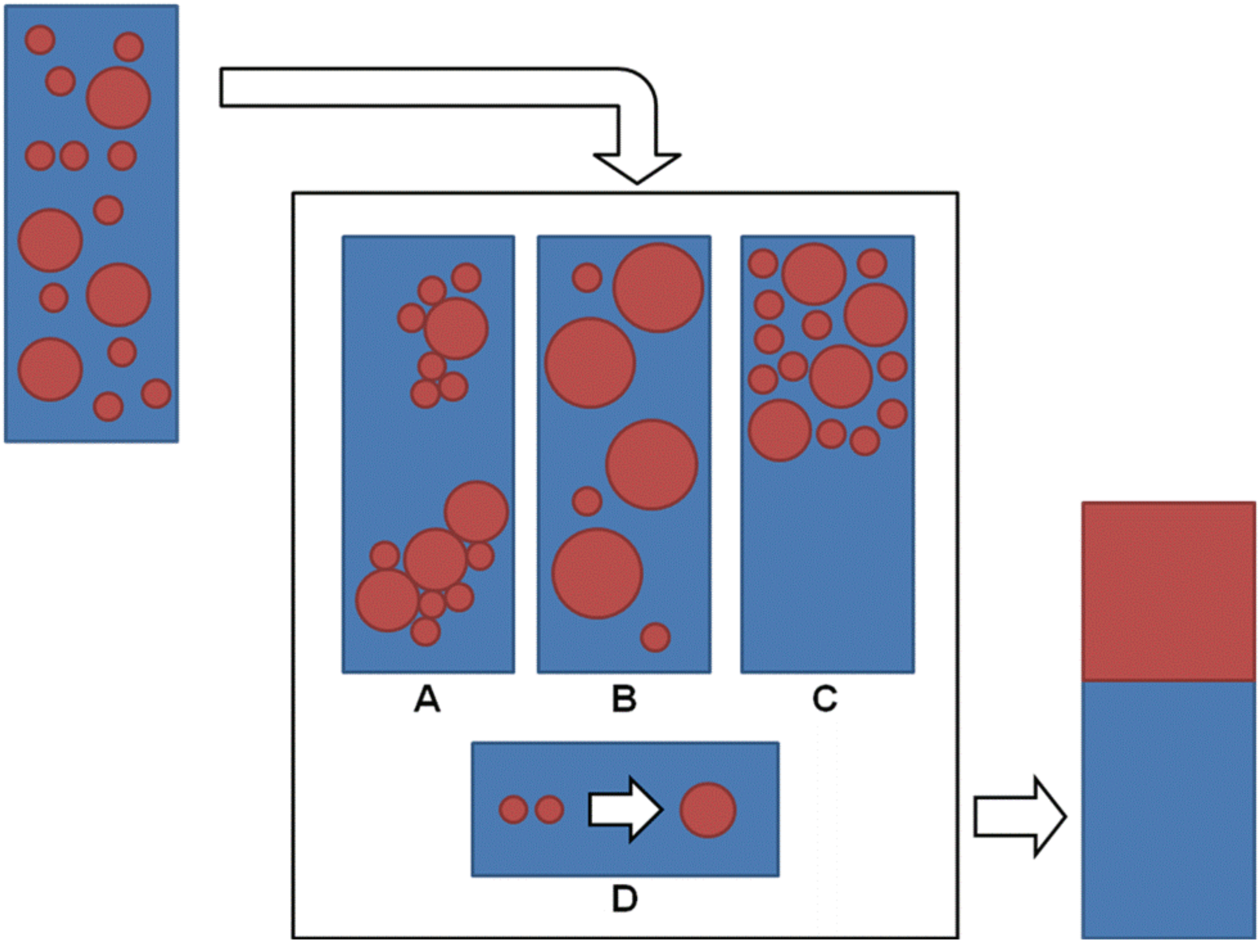


Figure 8 – Emulsion breaking by four mechanisms: flocculation or coagulation [A], Ostwald ripening [B], creaming or sedimentation [C], and coalescence [D].

Sedimentation and creaming occur when there is a difference in density between phases. Dense material will sink, while material that is less dense will rise. The process of flocculation and coagulation involves individual droplets coming together and forming aggregates. Flocs are easily re-dispersed while aggregates formed by coagulation are more difficult to break up. Ostwald ripening is a process by which large droplets grow in size at the expense of smaller droplets. This phenomenon is driven by the fact that smaller droplets have greater surface area per volume [38] and the rate of diffusion is dependent on surface area. The net flux of material is therefore from smaller droplets to larger droplets. The formation of one large droplet from two smaller droplets is known as coalescence. There is an energy barrier that must be overcome before coalescence can occur. Emulsion stability can be enhanced by increasing this energy barrier either through electrostatic or steric repulsion (*e.g.* by addition of a surfactant).

Asphaltenes are known to form rigid films around water droplets preventing coalescence [41]. Fine particles have the same effect forming a rigid protective layer. Disruption of the protective layer is an effective strategy to reduce emulsion stability. Heavy crude oil with high resin to asphaltene ratio is less likely to form stable emulsions because the resins solubilise the ashphaltenes, lowering the concentration at the interface [42].

1.5 Heavy Crude Oil Emulsions

Conventional pipelines cannot be used for heavy crude oil due to its high viscosity at ambient conditions. However, transportation of a stable low viscosity emulsion of heavy crude oil is possible using conventional pipelines. A stable emulsion is imperative to proper pipeline transport as phase separation inside pipelines leads to stratification, blockage, and many other problems. Generally, transportation and storage requires two weeks [43]. The crude oil emulsion must remain stable for the duration of this time.

Heavy crude oil emulsions have been made using various surfactants. The choice of surfactant is important in determining the type of emulsion formed. For emulsions of bituminous asphalt, optimum HLB for W/O type emulsions was 4–6 and optimum HLB for O/W type emulsion was 10–13 [44]. This result is consistent with Bancroft's rule. A practical level of viscosity reduction is possible with an oil content of 70-80% [11, 12]. A higher crude oil concentration is desirable but difficult as stability problems arise.

Orimulsion® is a liquid commercial fuel sold by Petroleos de Venezuela SA (PDVSA). It is an emulsion of heavy crude oil-in-water used as boiler fuel for power plants. Water is not removed before burning which reduces its heating value. Orimulsion® was originally stabilized using a non-ionic surfactant: polyethoxylatednonylphenol with EO[§] numbers ranging from eight to twenty-four [45]. The current surfactant is an alcohol-based derivative. Specifications for the Orimulsion® product are summarized in Table 3.

Table 3 – Specifications for Orimulsion® fuel sold and burned as an emulsion without further separation.

Property	
Water content (wt%)	29.2
Mean droplet size (μm)	14.6
Density at 15°C (g/mL)	1.0091
Viscosity at 30°C (cP)	215

[§] Ethylene Oxide number indicates the approximate number of ethylene oxide units in the tail structure. Higher values indicate greater water solubility.

Other surfactants used to create stable heavy crude oil emulsions include non-ionic surfactant Triton®-X100[**] [9, 46] and Emulgen® 120[††] [11]. The insensitivity of non-ionic surfactants to electrolyte concentration is an advantage. Heavy crude oil emulsions can be stabilized by anionic surfactants such as sodium dodecyl benzene sulfonic acid [47]. Ionic surfactants are more efficient and generally cheaper.

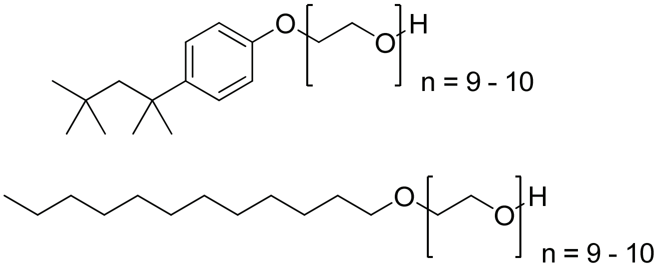


Figure 9 – General structure of Triton-X [TOP] and Emulgen [BOTTOM] non-ionic surfactants.

Heavy crude oil contains natural surfactants [48] composed in part of carboxylic acids and phenols of various structures and molecular weights [41]. These acidic compounds can be made more water-soluble by reaction with bases such as sodium hydroxide [8, 49], sodium carbonate [50], or various amines [51] to produce the corresponding carboxylate or phenolate. The activated natural surfactants, with higher HLB, are able to stabilize O/W emulsions at concentrations between 1000 – 3000 ppm with respects to the oil phase [8, 49-51].

[**] Triton®-X100 is iso-octylphenol polyethyleneoxide with EO number between 9-10; HLB of 13.2

[††] Emulgen 120 is polyethyleneoxide lauryl ether with EO number approximately 13.3; HLB of 15.3

1.6 Breaking Emulsions

Emulsions of heavy crude oil are difficult to break due to the high viscosity of the oil and the similar density of both phases. An emulsion can be broken using various techniques. Mechanical and chemical methods have been employed. Mechanical methods include agitators and separators [52]. Agitators provide energy to promote droplet collision and coalescence. Separators are designed to increase residence time to allow materials of different density to settle out. Settling ponds are commonly employed in water treatment processes. Both heating and dilution can be used to break emulsions of heavy crude oil by decreasing the density and viscosity of the organic phase. Dilution with appropriate solvent can also lead to mobilization of material strongly adsorbed onto an interface [52], therefore reducing the barrier for coalescence.

Chemical treatments include demulsifier agents and other additives. Additives can be used to adjust pH [53], or raise or lower ionic strength. Chemicals may also be added to induce a specific reaction, such as fragmentation of a cleavable surfactant [27, 28] or to trigger a change in a switchable surfactant [33]. Demulsifiers are surfactants that increase the rate of phase separation, especially for stabilized emulsions. Surfactants that break emulsions can be selected based on the antagonistic principle that a substance that will stabilize one type of emulsion (*e.g.* W/O) will destabilize the other type of emulsion (*e.g.* O/W) [54]. Because of the many variations in crude oil composition, demulsifier formulations are usually specific to each situation.

A study of various demulsifiers on Orimulsion® revealed several ineffective commercial compounds described as alkoxylated polyhydric alcohol, alkoxylatedalkylphenol formaldehyde resin, and alkoxylated polyethylenamine [55]. The same study synthesized effective demulsifiers of general structure illustrated in Figure 10 that removed over 85% of water within one hour at 85°C under an applied electrical field of 2100 V/cm. [55].

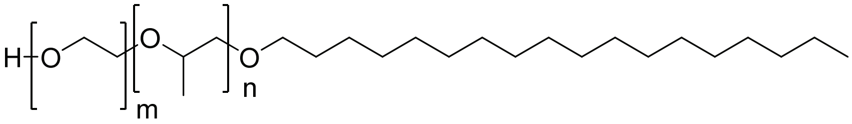


Figure 10 – General structure of a demulsifier with the ability to separate Orimulsion® [55].

The study found that the effectiveness of the demulsifier increased with increasing weight fraction of the ethyleneoxide/polypropyleneoxide moiety. The demulsifier was most effective with an EO:PO ratio of approximately four [55].

1.7 Emulsion Polymerization

Emulsion polymerization is an important technology originally used to make synthetic rubber. Advantages compared to bulk polymerization include increased reaction rate, high conversion, enhanced temperature control, and low viscosity.

In a heterogeneous system, the bulk properties are closer to that of the continuous phase (*i.e.* water). The viscosity is therefore independent of conversion because the particles remain suspended. Water requires a large amount of energy to heat and evaporate due to its high heat capacity and heat of vaporization. Improved thermal control limits the risk of runaway reactions. In the absence of viscosity effects, very high molecular weight polymers can be made without sacrificing high polymerization rate.

The initiation of the polymerization reaction occurs in the aqueous phase using a water-soluble initiator. Chain propagation continues in the aqueous phase until the length of the growing oligomer chains reaches a solubility threshold after which the polymer chains migrate into the surfactant micelles. Polymerization continues as monomer diffuses into micelles. The process is illustrated in Figure 11.

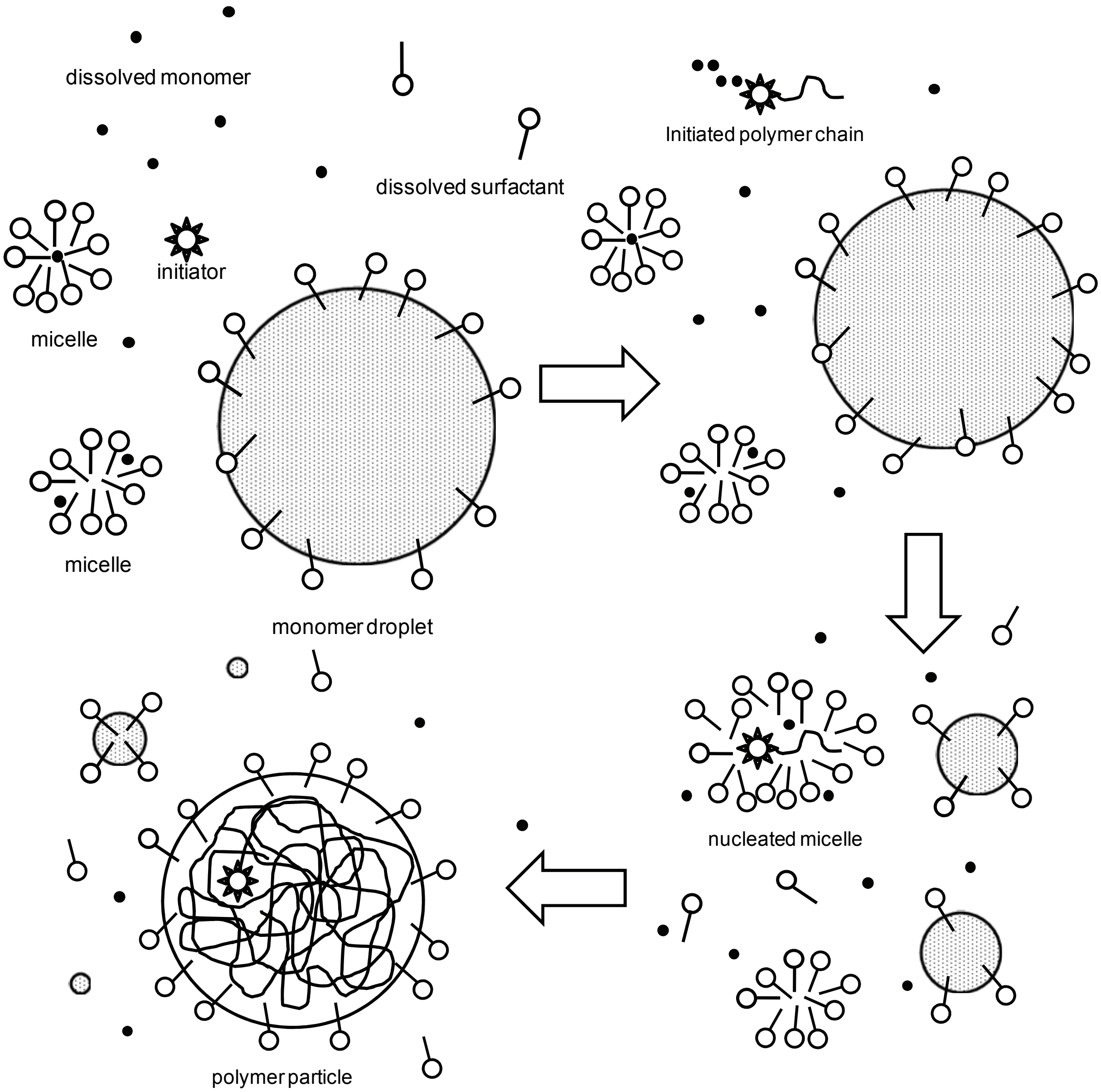


Figure 11 – The emulsion polymerization process illustrating three important steps: initiation, micelle nucleation, and chain propagation inside micelles maintained by monomer diffusion.

1.8 Latex Stability

A latex is a colloidal system consisting of small polymer particles (0.1 µm to 100 µm) dispersed in a liquid. The suspended particles must be stabilized to prevent aggregation. A latex can be stabilized by two general mechanisms: steric stabilization by non-ionic surfactants and electrostatic stabilization by unbalanced repulsive charges on the particle surface. Both mechanisms are illustrated in Figure 12.

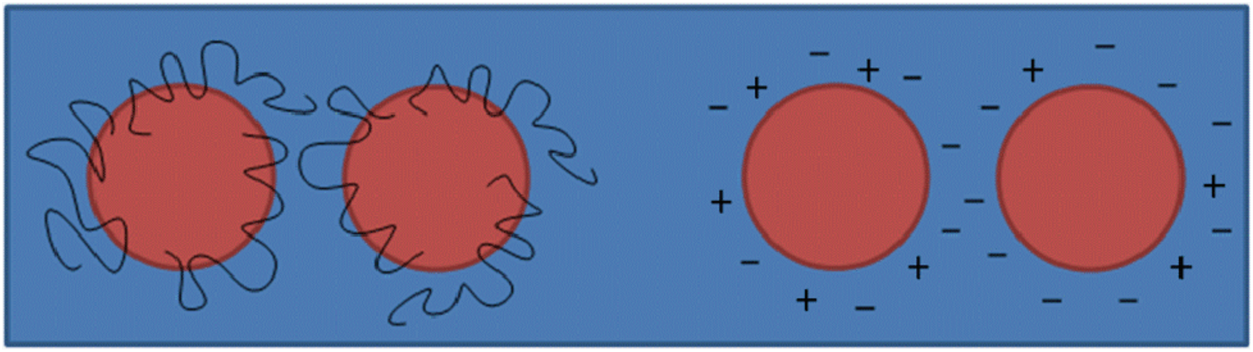


Figure 12 – Illustration of particle stabilization mechanisms. Particles stabilized by polymeric surfactants [LEFT] and surface charges [RIGHT].

In order for two particles to aggregate, they must first overcome electrostatic or steric barriers. Steric stabilizers are often high molecular weight polymers which entangle as the two particles approach each other. The entanglement decrease mobility and forms a physical barrier between the two particles. Unbalanced charges on the surface of particles give rise to an electric double layer. Electrostatic repulsion arises when two particles have the same surface charge.

Chapter 2 – Amidine Surfactant Design

Switchable surfactant research was conducted in the Jessop group by independently investigating the effect various of head and tail structures. In a study by another member of the group, the surfactant head group was modified to explore its effect on switching behaviour and demulsifying ability. In my work, the surfactant tail structure was modified in order to tune surfactant performance by changing the hydrophilic-lipophilic balance. The focus of the work described in this thesis was the modification of the tail structure. The inclusion of oxygen atoms was intended to increase overall water solubility of both the ionic and neutral forms of the surfactant.

2.1 Surfactant Naming Convention

The switchable surfactants in this thesis are named after the structure of their neutral forms. An abbreviated naming system was employed to simplify surfactant identification. The system is illustrated in Figure 13. Various surfactant head and tail structures are illustrated in Table 4.

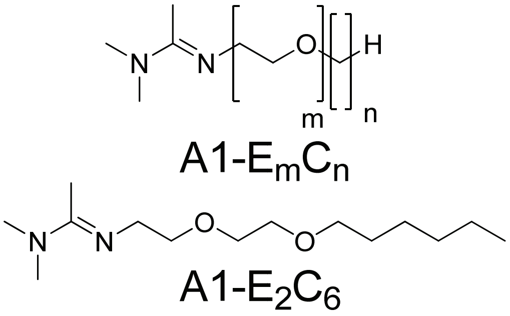
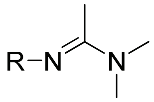
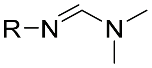
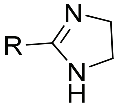
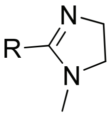
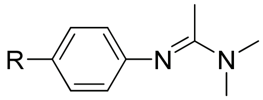
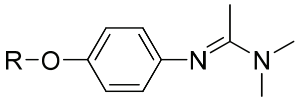
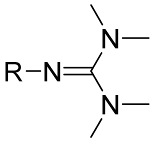
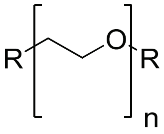
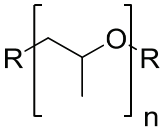
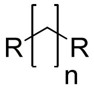


Figure 13 – Switchable amidine surfactant naming convention with example. The head group is first identified: [A1]; followed by the components of the tail group: [E_2C_6].

Table 4 – Various switchable surfactant head and tail group structures and abbreviations.

Structure	Name	Abbreviation
	N,N-dimethylacetamidine	A1
	N,N-dimethylformamidine	A2
	Imidazoline	A3
	Methylimidazoline	A4
	N'-phenyl-N,N-dimethylacetamidine	A5
	N'-(4-oxy)phenyl-N,N-dimethylacetamidine	A6
	Tetramethylguanidine	G1
	Polyethylene glycol	E_n
	Polypropylene glycol	s_n
	Alkyl	C_n

2.2 Experimental

2.2.1 Materials

Chemicals, reagents, solvent, and other material were used as received without further purification or treatment unless specified otherwise. Deionized water was supplied from a Millipore MilliQ® Ultrapure Water purification system. In-house compressors provided air. Sources of chemical reagents, solvents, and other chemical agents are summarized inTable 5.

Table 5 – Chemical reagents used in the synthesis of various surfactants and intermediates.

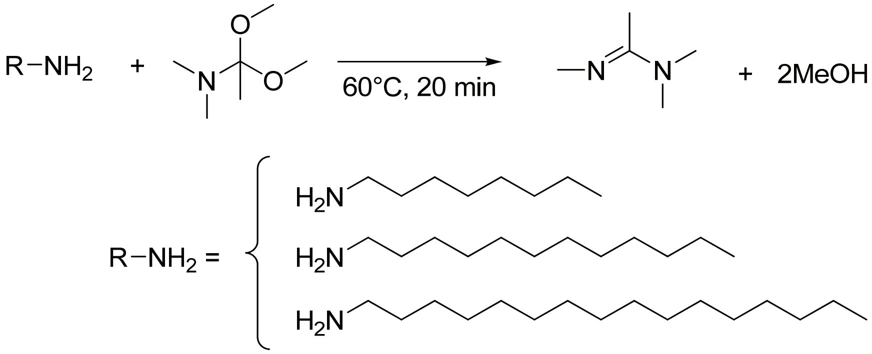
Compound	Supplier	Lot no.
Octylamine, 99%	Aldrich	03112TE
Dodecylamine, 97%	Sigma Aldrich	GS0DT
Hexadecylamine, 90%	Acros Organics	A0235793
Ethylene glycol hexyl ether, 98%	TCI America	Q84U6
Diethylene glycol hexyl ether, 95%	TCI America	FGJ01
Diethylene glycol butyl ether, 98%	TCI America	627EA
Triethylene glycol butyl ether, 97%	TCI America	SP51A
Triethylamine, 99%	Sigma Aldrich	058K0174
Tosyl chloride, 99%	Sigma Aldrich	MKBB0647
Potassium phthalamide, 99%	Fluka	352802

Compound	Supplier	Lot no.
Hydrazine monohydrate, 98%	Sigma Aldrich	05119DD
N,N-dimethylacetamide dimethylacetal, 90%	TCI America	OCGPG
Hydrochloric acid	Fisher	208227
Sodium hydroxide, 99%	BDH	119073
Sodium chloride, 99%	Fisher	081502A
Sodium carbonate hydrate, 99%	Fisher	026001
Sodium bicarbonate, 99%	Fisher	055392
Magnesium sulfate, 99.5%	Alfa Aesar	D20R001
Acetonitrile, 99.9%	Fisher	080692
Ethanol, 99%	Commercial Alcohols	9420
Ethyl acetate, 99.5%	Caladon	71850
Diethyl ether, 99%	Fisher	086214
Dimethylformamide, 99.8%	Fisher	01956KE
Tetrahydrofuran (HPLC)	Fisher	H115672
Toluene (HPLC)	Fisher	091486
Argon (5.0)	Praxair	n/a
Carbon dioxide (SFC)	Praxair	n/a
Carbon dioxide (4.0)	Praxair	n/s

2.3 Surfactant Synthesis

2.3.1 First Generation Surfactants

N'-n-alkyl-N,N-dimethylacetamidine surfactants were synthesized by a modification of Scoggins' procedure for acetamidines [33]. The synthetic pathway is illustrated in Scheme 1.



Scheme 1 – Synthesis of N'-n-alkyl-N,N-dimethylacetamidines by reaction of a primary amine and N,N-dimethylacetamide dimethylacetal.

A known amount of a primary amine was charged into a round bottom flask. N,N-dimethylacetamidedimethylacetal (1.2 equivalents) was added to the reaction mixture. A reflux condenser was attached to the round bottom flask and the reaction mixture was heated to reflux for 20 min. The reaction mixture was a clear orange to colourless liquid. The reaction mixture was concentrated in a rotary evaporator under reduced pressure to remove methanol and unreacted N,N-dimethylacetamidedimethylacetal.

N'-dodecyl-N,N-dimethylacetamidine (A1-C_{12}) and N'-hexadecyl-N,N-dimethylacetamidine (A1-C_{16}) were purified by selective precipitation from acetonitrile, achieved by dissolving the crude product and water (1.0 equivalent) in a liberal amount of acetonitrile.

Carbon dioxide gas was bubbled into the solution. The amidinum bicarbonate salts generated from N'-dodecyl-N,N-dimethylacetamidine (A1-C_{12}) and N'-hexadecyl-N,N-dimethylacetamidine (A1-C_{16}) were insoluble and precipitated as white solids. The precipitate was filtered through a Büchner funnel, washed with ethyl ether, and dried. The product is a white solid. Neutral amidine can be regenerated by heating the salt at 60°C. N'-dodecyl-N,N-dimethylacetamidine (A1-C_{12}) is a clear colourless liquid at ambient conditions and N'-hexadecyl-N,N-dimethylacetamidine (A1-C_{16}) is an amorphous solid. N'-octyl-N,N-dimethylacetamidine (A1-C_8) was purified by distillation under reduce pressure. N'-octyl-N,N-dimethylacetamidine (A1-C_8) is a clear colourless liquid under ambient conditions. Compounds were characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR). The spectra were consistent with previous reports for A1-C_{12} and A1-C_{16} [33].

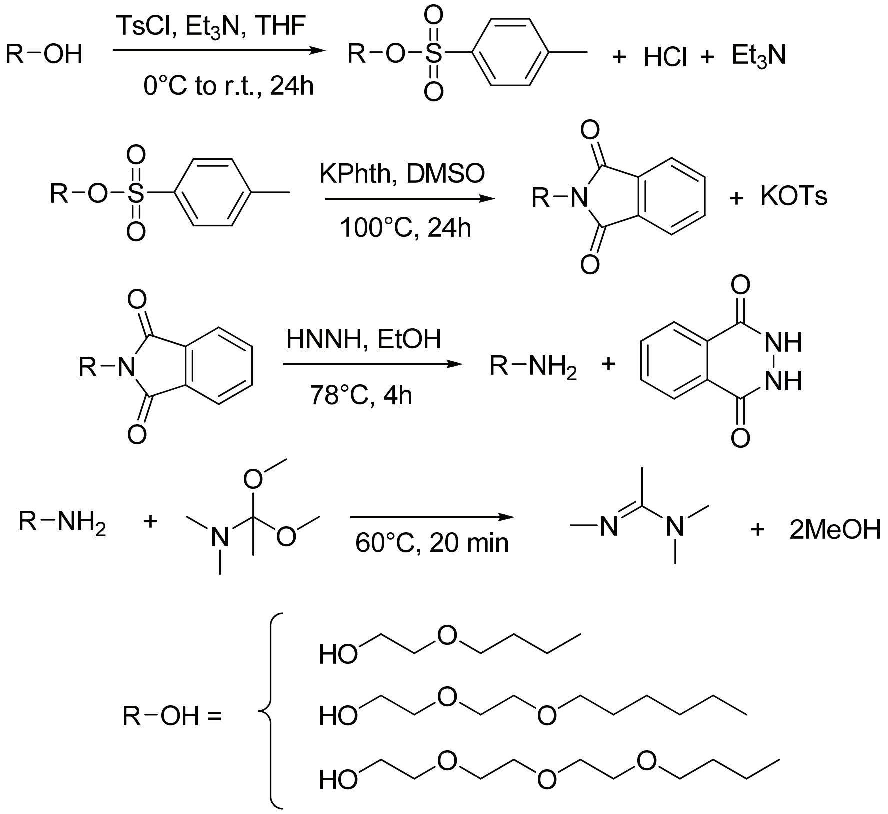
N'-octyl-N,N-dimethylacetamidine (A1-C_8): Yield: 93%. δ_H (400 MHz; $CDCl_3$) 3.17 (t, 2H), 2.88 (s, 6H), 1.88 (s, 3H), 1.48 (quint, 2H), 1.26 (b, 10H), 0.88 (t, 3H). δ_C (400 MHz; $CDCl_3$) 158.8, 50.0, 38.0, 32.4, 31.9, 31.5, 29.3, 29.7, 27.7, 22.7, 14.1, 12.4.

N'-dodecyl-N,N-dimethylacetamidine (A1-C_{12}): Yield: 96%. δ_H (400 MHz; $CDCl_3$) 3.18 (t, 2H), 2.88 (s, 6H), 1.89 (s, 3H), 1.51 (quint, 2H), 1.29 (m, 18H), 0.89 (t, 3H). δ_C (400 MHz; $CDCl_3$) 158.8, 50.2, 38.0, 32.4, 31.9, 29.4 – 29.7, 27.6, 22.7, 14.1, 12.4.

N'-hexadecyl-N,N-dimethylacetamidine (A1-C_{16}): Yield: 97%. δ_H (400 MHz; $CDCl_3$) 3.17 (t, 2H), 2.87 (s, 6H), 1.87 (s, 3H), 1.49 (quint, 2H), 1.28 (m, 26H), 0.88 (t, 3H). δ_C (400 MHz; $CDCl_3$) 158.8, 50.0, 38.0, 32.4, 31.9, 31.5, 29.4 – 29.7, 27.6, 22.7, 14.1, 12.4.

2.3.2 Second Generation Surfactants

The synthesis of second generation amidine surfactants focused on incorporating oxygen atoms in the tail in order to improve water solubility. Starting from various commercial ethylene glycol alkyl ether derivatives, the primary amine analogues were made through the Gabriel synthesis [56]. The complete synthetic pathway used is shown in Scheme 2. Polyethylene glycol alkyl ether starting materials were widely available industrial solvents. They provided a broad range of possible well-defined HLB values. Incorporation of ethylene oxide units in surfactants is a common practice in order to influence various physical properties [57].



Scheme 2 – Synthetic pathway to tail group modified amidine switchable surfactants starting from an alcohol. The alcohol is converted to a primary amine via the Gabriel synthesis and further made into an amidine by reaction with N,N-dimethylacetamide dimethylacetal.

A known amount of an alcohol was charged into a round bottom flask. Toluenesulphonyl chloride (1.0 equivalent) dissolved in tetrahydrofuran was added. The reaction mixture was cooled in an ice water bath. Triethylamine (1.2 equivalent) was slowly added to the reaction mixture dropwise. The reaction mixture was left to react overnight. A white precipitate formed and was removed after cooling by filtration through a Büchner funnel. The filtrate was transferred to a separatory funnel and washed with several portions of saturated aqueous sodium bicarbonate, distilled water, and saturated aqueous sodium chloride. The organic layer was collected, dried over magnesium sulfate, filtered, and concentrated in a rotary evaporator under reduced pressure. The remaining material is a clear faintly yellow liquid and was characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR).

Ethylene glycol tosylate hexyl ether ($TsOE_1C_6$): Yield: 84%. δ_H (400 MHz; $CDCl_3$) 7.78 (d, J = 8.1Hz, 2H), 7.32 (d, J = 8.1Hz, 2H), 4.14 (t, 2H), 3.58 (d, 2H), 3.35 (d, 2H), 2.43 (s, 3H), 1.47 (quint, 2H), 1.25 (s, 6H), 0.87 (t, 3H). δ_C (400 MHz; $CDCl_3$) 144,8, 133.0, 129.8, 127.9, 71.5, 69.4, 68.0, 31.6, 29.5, 25.6, 22.6, 21.6, 14.0.

Diethylene glycol tosylate hexyl ether ($TsOE_2C_6$): Yield: 80%. δ_H (400 MHz; $CDCl_3$) 7.78 (d, J = 7.9Hz, 2H), 7.32 (d, J = 7.9Hz, 2H), 4.15 (t, 2H), 3.67 (t, 2H), 3.55 (m, 2H), 3.49(m, 2H), 3.40 (t, 2H), 2.43 (s, 3H), 1.54 (quint, 2H), 1.27 (s, 6H), 0.86 (t, 3H). δ_C (400 MHz; $CDCl_3$) 144.8, 133.0, 129.8, 127.9, 71.5, 70.7, 70.0, 69.3, 68.7, 31.6, 29.6, 25.7, 22.6, 21.6, 14.0.

Triethylene glycol tosylate butyl ether ($TsOE_3C_4$): Yield: 82%. δ_H (400 MHz; $CDCl_3$) 7.73 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 4.10 (t, 2H), 3.62 (t, 2H), 3.52 (m, 8H), 3.39 (m, 2H), 2.39 (s, 3H), 1.50 (quint, 2H), 1.31 (quint, 2H), 0.85 (t, 3H). δ_C (400 MHz; $CDCl_3$) 144.8, 133.0, 129.8, 127.9, 71.1, 70.7, 70.6, 70.5, 70.0, 69.3, 68.6, 31.7, 21.5, 19.2, 13.9.

A known amount of polyethylene glycol tosylate alkyl ether was charged into a round bottom flask. Dimethylformamide, dried overnight using activated 4 Å molecular sieves, was added to reaction mixture (approximately 10 ml DMF per 1 g polyethylene glycol tosylate alkyl ether). Potassium phthalimide (1.1 equivalents) was dispersed in the reaction mixture. The reaction mixture was heated to 100°C and left to react overnight. The reaction mixture consisted of a white precipitate in a clear yellow solution. Dimethylformamide was removed by distillation under reduced pressure. Diethyl ether was added to the residue and the reaction mixture was placed in a refrigerator at 4°C overnight. The solids were removed by filtration through a Büchner funnel. The filtrate was concentrated in a rotary evaporator under reduced pressure, dissolved in ethyl acetate and transferred to a separatory funnel. The crude product was washed with several portions of distilled water and saturated aqueous sodium chloride. The organic layer was collected, dried over magnesium sulfate, filtered, and concentrated in a rotary evaporator at reduced pressure. The remaining material was a clear yellow liquid and was characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR).

Ethylene glycol phthalimide hexyl ether (PhthE$_1$C$_6$): Yield: 64%. δ_H (400 MHz; CDCl$_3$) 7.83 (m, 2H), 7.72 (m, 2H), 3.88 (t, 2H), 3.66 (t, 2H), 3.43 (t, 2H), 1.49 (t, 2H), 1.20 (s, 6H) 0.81 (t, 3H). δ_C (400 MHz; CDCl$_3$) 168.3, 133.8, 132.2, 123.2, 71.0, 67.3, 37.5, 31.6, 29.5, 25.7, 22.5, 14.0.

Diethylene glycol phthalimide hexyl ether (PhthE$_2$C$_6$): Yield: 70%. δ_H (400 MHz; CDCl$_3$) 7.78 (m, 2H), 7.67 (m, 2H), 3.85 (t, 2H), 3.70 (t, 2H), 3.59 (m, 2H), 3.48 (t, 2H), 3.36 (t, 2H) 1.44 (quint, 2H), 1.20 (s, 6H), 0.82 (t, 3H). δ_C (400 MHz; CDCl$_3$) 168.3 133.8, 132.2, 123.2, 72.5, 71.5, 70.0, 67.8, 37.2, 31.6, 29.5, 25.7, 22.5, 14.0.

Triethylene glycol phthalimide butyl ether (PhthE$_3$C$_4$): Yield: 68%. δ_H (400 MHz; CDCl$_3$) 7.78 (m, 2H), 7.67 (m, 2H), 3.85 (t, 2H), 3.70 (t, 2H), 3.57 (m, 6H), 3.46 (t, 2H) 3.37 (t, 2H), 1.48 (m, 2H), 1.29 (m, 2H), 0.85 (t, 3H). δ_C (400 MHz; CDCl$_3$) 168.3, 133.8, 132.2, 123.2, 72.5, 71.1, 70.6, 70.1, 67.9, 37.2, 31.6, 19.2, 14.0.

A known amount of polyethylene glycol phthalimide alkyl ether was charged into a large round bottom flask. Ethanol (approximately 50 ml per 1 g of polyethylene glycol phthalimide alkyl ether) was added to reaction mixture. Hydrazine monohydrate (2.0 equivalents) was added. The reaction mixture was heated to reflux for 4 h. A large amount of white precipitate formed. The reaction mixture was concentrated in a rotary evaporator under reduced pressure. Diethyl ether was added to the residue and well mixed. The solids were removed by vacuum filtration through a Büchner funnel. The filtrate was concentrated in a rotary evaporator under reduced pressure. The remaining material was a clear pale yellow liquid and was characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR).

Amino ethylene glycol hexyl ether (H$_2$NE$_1$C$_6$): Yield: 81%. δ_H (400 MHz; CDCl$_3$) 3.46 (m, H), 2.89 (t, 2H) 1.86 (b, 2H), 1.59 (quint, 2H), 1.31 (m, 6H), 0.89 (t, 3H). δ_C (400 MHz; CDCl$_3$) 72.7, 70.9, 42.0, 31.8, 29.9, 26.0, 22.7, 14.0.

Amino diethylene glycol hexyl ether (H$_2$NE$_2$C$_6$): Yield: 79%. δ_H (400 MHz; CDCl$_3$) 3.52 (m, 4H), 3.44 (t, 2H), 3.38 (t, 2H), 2.78 (t, 2H), 1.85 (b, 2H), 1.51 (quint, 2H), 1.22 (s, 6H), 0.81 (t, 3H). δ_C (400 MHz; CDCl$_3$) 73.3, 71.5, 70.3, 70.0, 41.7, 31.6, 29.5, 25.7, 22.6, 14.0.

Amino triethylene glycol butyl ether ($H_2NE_3C_4$): Yield: 82%. δ_H (400 MHz; $CDCl_3$) 3.55 – 3.42 (m, 8H), 3.33 (t, 2H), 3.28 (t, 2H), 2.68 (b, 2H), 2.66 (t, 2H), 1.54 (quint, 2H), 1.37 (m, 2H), 1.23 (t, 2H), 0.89 (t, 3H). δ_C (400 MHz; $CDCl_3$) 73.1, 70.9, 70.6, 70.3, 41.8, 31.9, 19.4, 14.0.

A known amount of polyethylene glycol amine alkyl ether was charged into a round bottom flask. N,N-dimethylacetamidedimethylacetal (1.1 equivalents) was added. The reaction mixture was left to react overnight under ambient conditions. The reaction mixture was concentrated in a rotary evaporator under reduced pressure to remove methanol and unreacted N,N-dimethylacetamidedimethylacetal. N'-3,6-oxanonyl-N,N-dimethyl-acetamidine (A1-E_1C_6), N'-3,6-dioxadodecyl-N,N-dimethylacetamidine (A1-E_2C_6), and N'-3,6,9-trioxatridecyl-N,N-dimethylacetamidine (A1-E_3C_4) were clear yellow liquids at ambient conditions and were characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR).

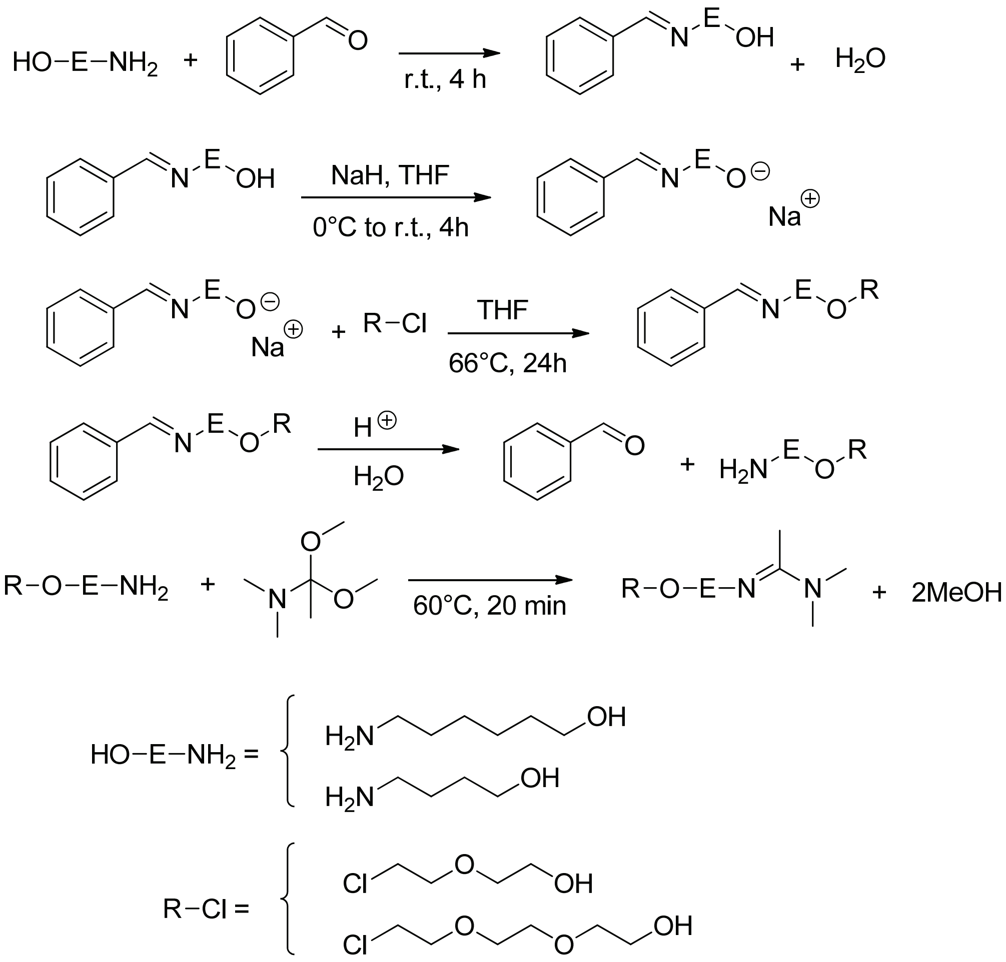
N'-3-oxanonyl-N,N-dimethylacetamidine (A1-E_1C_6): Yield: 92%. δ_H (400 Mhz; C_6D_6) 3.77 (t, 2H), 3.55 (t, 2H), 3.43 (t, 2H), 2.60 (s, 6H), 1.58 (m, 2H), 1.50 (s, 3H), 1.35 (m, 2H), 1.22 (m, 4H), 0.85 (t, 3H). δ_C (400Mhz; C_6D_6) 158.5, 73.5, 71.1, 71.0, 70.6, 50.5, 37.8, 32.3, 14.1, 12.3.

N'-3,6-dioxadodecyl-N,N-dimethylacetamidine (A1-E_2C_6): Yield: 82%. δ_H (400 Mhz; C_6D_6) 3.84 (t, 2H), 3.65 (t, 2H), 3.54 (m, 4H), 3.34 (t, 2H), 2.60 (s, 6H), 1.55 (quint, 2H), 1.50 (s, 3H), 1.33 (m, 2H), 1.22 (m, 4H), 0.86 (t, 3H). δ_C (400 Mhz; C_6D_6) 158.3, 73.7, 71.5, 71.1, 70.7, 50.7, 37.8, 32.1, 30.3, 26.3, 23.0, 14.2, 12.2.

N'-3,6,9-trioxatridecyl-N,N-dimethylacetamidine (A1-E_3C_4): Yield: 74%. δ_H (400 Mhz; C_6D_6) 3.60 – 3.50 (m, 10H) 3.39 (t, 3H), 3.34 (t, 2H), 2.82 (s, 6H), 1.82 (s, 3H), 1.50 (t, 2H), 1.30 (m, 2H), 0.85 (t, 3H). δ_C (400 Mhz; C_6D_6) 158.6, 73.6, 71.1, 71.0, 70.9, 70.7, 70.2, 50.7, 37.8, 32.3, 14.1, 12.3.

2.3.3 Third Generation Surfactants

Third generation amidine surfactants retained oxygen atoms in the tail to provide better water solubility. However, the hydrophilic polyethylene oxide moiety is situated away from the amidine moiety. This substitution was made in order to enhance the compatibility of amidine surfactants and indigenous crude oil surfactants.



Scheme 3 – Synthetic pathway to tail group modified amidine switchable surfactants starting from an omega amino alcohol. Primary amine is first protected as benzylimine. The surfactant tail is tethered on using Williamson ether synthesis. Amidine is made by reaction with N,N-dimethylacetamide dimethylacetal.

A known amount of benzaldehyde was charged into a round bottom flask flushed with argon and cooled in an ice bath. Amino alcohol (1.0 equivalent) was added. The reaction mixture was left to react for 4 h. Heat was generated. Water was removed under reduced pressure. The reaction mixture was a clear pale yellow liquid and was characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR).

Benzylidene amino hexanol ($BzNC_6OH$): Yield: 98%. δ_H (400 MHz; CDCl3) 8.26 (s, 1H), 7.72 (m, 2H), 7.41 (m, 3H), 5.09 (b, 1H), 3.61 (m, 4H), 2.76 (m, 2H), 1.57 (quint, 2H), 1.71 (quint, 2H), 1.39 (m, 4H). δ_C (400 MHz; CDCl3) 161.2, 136.1, 130.6, 128.6, 128.1, 62.6, 61.6, 32.6, 30.8, 27.1, 25.6

A known amount of sodium hydride was dispersed in tetrahydrofuran dried overnight using activated 4 Å molecular sieves. Benzylidene amino hexanol (1.0 equivalent) was added slowly to the sodium hydride dispersion. A gas was immediately generated. The reaction mixture was left to react for 2 h at room temperature. Chloro-alcohol (1.0 equivalent) was added to reaction mixture. The reaction mixture was heated to reflux for 4 h. A precipitate was formed.

The reaction mixture was concentrated in a rotary evaporator under reduced pressure. Cold diethyl ether was added to the residue. The precipitate was removed by vacuum filtration through a Büchner funnel. The reaction mixture was concentrated in a rotary evaporator under reduced pressure. The remaining material was a yellow liquid. Hydrochloric acid (1.1 equivalents) was added to the reaction mixture and heated to 60°C for 3 h. Benzaldehyde and water were removed by distillation under reduced pressure.

Sodium methoxide (1.1 equivalents) was added to the reaction mixture. A precipitate formed. Cold diethyl ether was added. The precipitate was removed by vacuum filtration through a Büchner funnel. The reaction mixture was concentrated in a rotary evaporator under reduced pressure. The residue was a clear yellow liquid and was characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR).

Amino-3,6-dioxatridecanol ($H_2NC_4E_3$): Yield: 64%. δ_H (400 MHz; $CDCl_3$) 7.36 (s, 2H), 3.46 – 3.66 (m, 9H), 2.56 (t, 2H), 1.45 (quint, 2H), 1.36 (quint, 2H), 1.26 (b, 4H). δ_C (400 MHz; $CDCl_3$) 77.5, 72.7, 71.0, 61.6, 41.5, 33.2, 32.6, 26.6, 25.5.

A known amount of the amine was charged into a round bottom flask. N,N-dimethylacetamide-dimethylacetal (2.0 equivalents) was added. The reaction mixture was left to react overnight under ambient conditions. The reaction mixture was concentrated in a rotary evaporator under reduced pressure to remove methanol and unreacted N,N-dimethylacetamide-dimethylacetal. The remaining material was a clear yellow liquid and was characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR).

N'-7,10,13-trioxatridecyl-N,N-dimethylacetamidine (A1-C_4E_3): Yield: 87%. δ_H (400 MHz; C_6D_6) 3.71 – 3.47 (m, 5H), 3.31 (t, 2H), 3.26 (t, 2H), 3.20 (t, 2H), 2.72 (s, 6H), 1.81 (m, 2H), 1.71 (m, 2H), 1.59 (s, 3H), 1.58 (b, 2H), 1.48 (m, 2H), 1.24 (m, 2H). δ_C (400 MHz; C_6D_6) 157.6, 71.5, 71.2, 71.1, 70.3, 61.1, 50.2, 48.2, 36.7, 33.0, 30.4, 28.0, 26.9.

2.4 Summary

Amidine type cationic switchable surfactants were synthesized including A1-C_8, A1-C_{12}, A1-C_{16}, A1-E_1C_6, A1-E_2C_6, A1-E_3C_4, and A1-C_4E_3. The modified structures included ethylene oxide units in the tail to increase water solubility. Surfactants with different hydrophile-lipophilic balance were available by virtue of the commercial availability of the alcohol precursors.

2.5 Future Work

Third generation amidine surfactants were effective in stabilizing O/W emulsions of the heavy crude oil. Phase separation after carbon dioxide treatment was also improved when compared to results attainted with sodium carbonate; both separated water and crude oil contained less residual oil and water, respectively. The surfactant performance can be further improved by tuning the HLB of surfactant by modifying the lengths of both hydrophilic and lipophilic regions now that the correct orientation has been established.

Further modification of the substituent tail groups could also lead to improved performance. Commercial demulsifiers include block copolymers of propylene oxide and ethylene oxide. An amidine with analogous structure, Figure 14, may be an effective demusifier. Correct orientation and balance of hydrophilic and lipophilic groups would allow stabilization of a heavy crude oil emulsion.

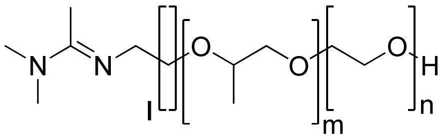
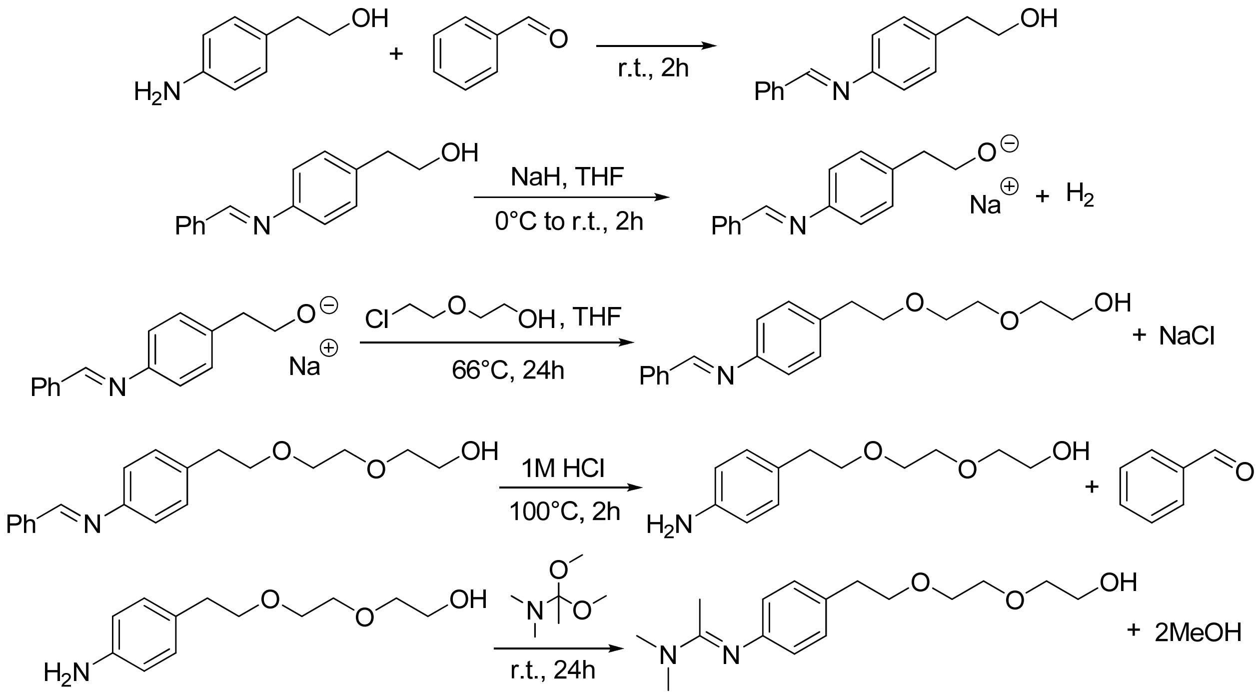


Figure 14 – Future amidine switchable surfactant target for heavy crude oil transport emulsions based on poplyproylene polyethylene block co-polymer demulsifiers.

Concurrent work on amidine switchable surfactant head structures determined that the base strength of the amidine moiety is dependent on its electronic structure. Electron rich groups such as aromatic systems decreased the basisty of the amidine. The study also found that surfactants derived from alkyl aniline were the most promising demulsifiers. The surfactant target provided in Scheme 4, N'-p-(3,6,9-trioxanonyl)phenyl-N,N-dimethyl-acetimidamide (A5-E_3) combines the improved tail and head structures. This synthetic pathway uses commercially available starting materials in order to streamline synthesis.



Scheme 4 – Synthetic pathway to next generation surfactants with both improved water solubility and demulsification ability.

Chapter 3 – Transport Emulsions

Heavy crude oils with kinematic viscosity in excess of 10000 cSt at 40°C cannot be easily transported in pipelines due to prohibitive costs [58]. The generation of an emulsion in water creates a low viscosity mixture with high crude oil content. Heavy crude oil dispersed in a low viscosity fluid such as water can be transported through conventional pipelines [11, 47, 49]. However, after such pipelining, the separation of the oil from the water is desired. With Orimulsion®, such separation is not achieved and the fuel, unfortunately, has a significant water content when it is burned. A heavy crude oil emulsion prepared using switchable surfactants could be destabilized with the appropriate trigger. Successful application of switchable surfactants would improve separation of heavy crude oil from the low viscosity mixture. Eliminating the need for heated pipelines and diluents would reduce the cost of heavy crude oil production.

3.1 Experimental

3.1.1 Materials

Five crude oil samples were provided by Chevron Energy Technology Company. A detailed analysis of each crude oil sample was also provided. Samples included two Venezuelan extra heavy crude oils (Sample I and Sample II), North Sea crude oil (Sample III), Californian heavy crude oil (Sample IV), and bituminous oil from Alberta (Sample V). A summary of crude oil analysis provided in Table 6.

Table 6 – Analysis of various crude oil samples provided by Chevron Energy Technology Company.

Property	Crude Oil Sample				
	I	II	III	IV	V
API gravity (°)	9.4	7.7	19.5	10.9	8.1
Specific gravity	1.004	1.017	0.937	0.994	1.014
Viscosity at 40°C (cSt)	18925	65689	129	9398	–
Viscosity at 100°C (cSt)	653.1	687.2	11.22	234.7	193.6
Water Content (ppm)	0.46	453	542	80	5100
TAN[‡‡] (mg_{KOH}/g)	1.26	3.49	1.65	3.03	2.28
TBN[§§] (mg_{HCl}/g)	2.31	3.15	<0.4	<0.5	<0.5
Asphaltene content (wt%)	13.6	8.7	0.01	4.67	7.14
Carbon content (wt%)	83.2	84.2	87.5	85.1	83.0
Hydrogen content (wt%)	10.4	10.4	12.1	11.1	10.3
Nitrogen content (wt%)	0.7	0.7	0.2	0.9	0.5
Sulphur content (wt%)	4.9	4.2	0.7	2.1	4.3

[‡‡] Total acid number: the amount of potassium hydroxide required to neutralize a crude oil sample. This number is indicative of the acidity of the crude oil. The molecular weight of potassium hydroxide is 56.11g/mol.

[§§] Total base number: the amount of hydrochloric acid required to neutralize a crude oil sample. This number is indicative of the basicity of the crude oil. The molecular weight of hydrochloric acid is 36.46g/mol.

Deionized water was used in all experiments. Water was purified using a Millipore MilliQ® Ultrapure Water purification system.

3.1.2 Making Crude Oil Emulsions

The emulsification apparatus is illustrated in Figure 15 and consisted of an overhead IKA Power Control-Visc overhead stirrer with an IKA R2305 four-blade propeller and a constant-temperature heating jacket attached to a lab jack. Heating water was provided by a Haake D1 circulator bath. The emulsification vessel consisted of a 150 ml tall-form Berzelius beaker. During emulsification, the stirrer was placed as close to the bottom as possible.

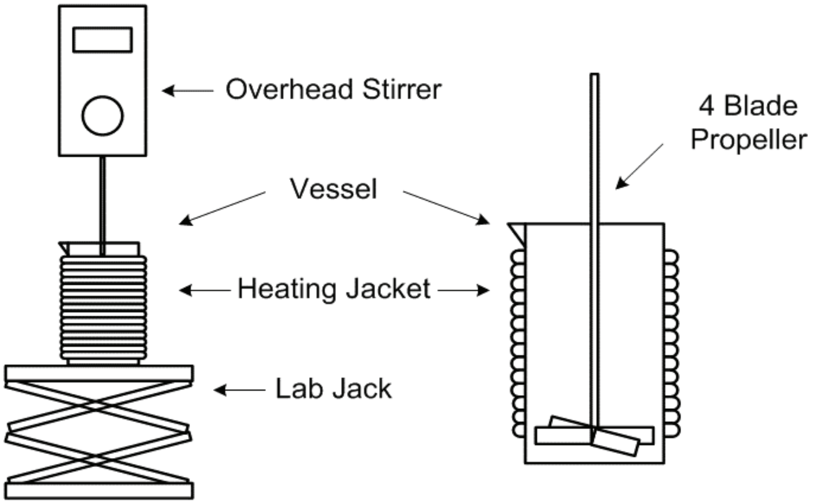


Figure 15 – Diagram of the device used to generate heavy crude oil emulsions with a cross sectional view to illustrate the stirrer type and position.

Crude oil with lower viscosity does not require preheating. Emulsions of crude oil with lower viscosity were prepared at ambient temperature. Heavy crude oil must be heated to be handled easily. Heavy crude oil was preheated to 100°C in an oven. Heated crude oil was well mixed before use. Deionized water was preheated to 60°C in a water bath.

Approximately 30 g of preheated deionized water was transferred into a 150 ml tall form beaker. The surfactant was dissolved in the deionized water. The beaker was placed inside a heating jacket and mixed using the overhead stirrer. Preheated crude oil was weighed and slowly poured into the deionized water while being stirred initially at 300 – 500 rpm. The crude oil was periodically weighed until approximately 70 g crude oil was added to deionized water. The emulsion was stirred at 2000 rpm for 5 min.

The surfactant concentration was calculated as a weight percentage based on the amount of crude oil. Surfactant concentration calculations were therefore independent of the water content.[***] Unless otherwise noted, emulsions were made using approximately 3 parts water and 7 parts crude oil by mass.

3.1.3 Emulsion Continuous Phase

The continuous phase of an emulsion was determined by using the drop test. A drop of the emulsion was placed in a large Petri dish containing either toluene or deionized water. The emulsion drop dispersed instantly in either the water or the toluene depending on the continuous phase of the emulsion. For example, if the continuous phase was water, then the drop dispersed instantly when added to water. The

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[***] An emulsion of 70 ml crude oil and 30 ml water with 0.100 g of surfactant would have a surfactant concentration of 1430 ppm.

identification of the continuous phase was also confirmed under microscopy where oil droplets appear opaque and water appears transparent.

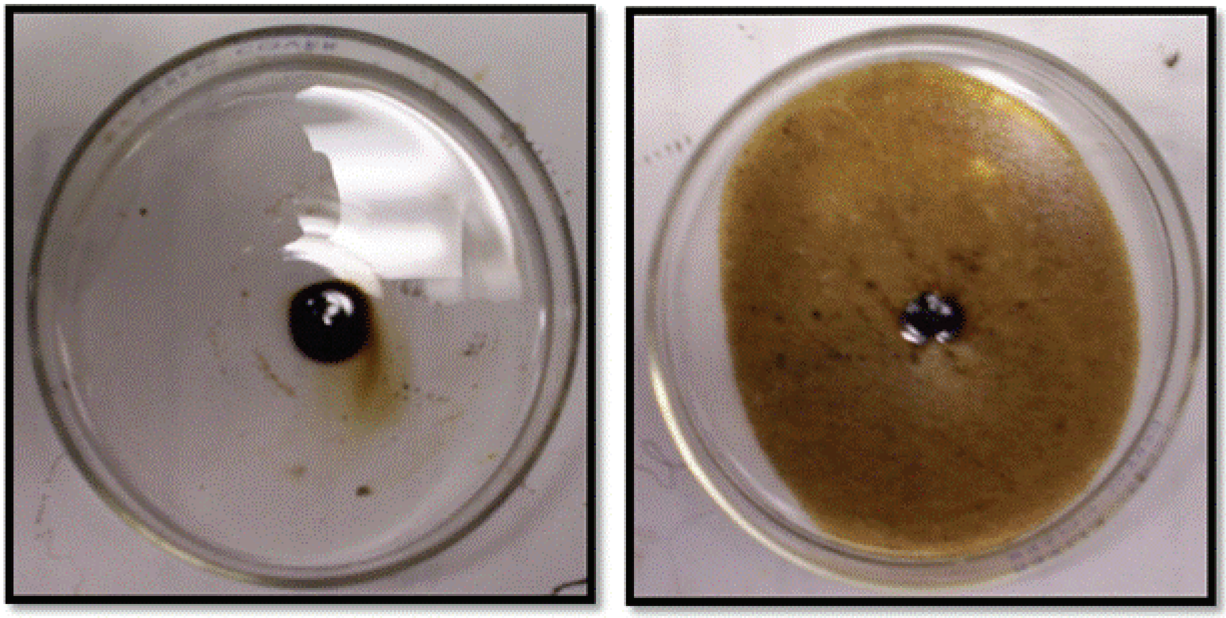

Figure 16 – Drop test performed on an O/W emulsion droplet. O/W emulsion droplet does not disperse in toluene [LEFT] but disperses well in deionized water [RIGHT].

3.1.4 Emulsion Stability

The stability of an emulsion was evaluated visually. Samples were prepared and transferred into Corning 15 ml centrifuge tubes. Centrifuge tubes were stored at ambient conditions and checked periodically for phase separation. Phase separation was determined to have occurred if multiple phases were visible. In most cases, phase separation lead to two physically distinctive phases: high viscosity oil and low viscosity water. Stability for O/W emulsions is reported using qualifiers described in Table 7.

Table 7 – Qualifiers used to describe the stability of O/W emulsions of heavy crude oil.

Stability	Description
unstable	Phase separation evident immediately after agitation is stopped
hours	Phase separation evident after no less than 1 h after agitation is stopped
days	Phase separation evident after no less than 24 h after agitation is stopped
weeks	No visible signs of phase separation after no less than 14 days.

3.1.5 Kinematic Viscosity

Viscosity was measured using factory calibrated Cannon Zeitfuchs® cross-arm glass viscometers. The emulsion sample and a glass viscometer were pre-heated to a specific temperature inside a Cannon CT-500 constant temperature bath (±0.01°C). A small amount of sample was poured into the glass viscometer. The time required for the sample to flow between markings in the glass viscometer was used to calculate the viscosity using factory-calibrated viscometer constants.

3.1.6 Water Content

Water content for heavy crude oils with boiling points well above 100°C was determined gravimetrically. The amount of water present in a sample was determined by weighing the sample before and after removal of water. Samples were dried by evaporating water in an oven at 100°C overnight. A minimum of three replicates were measured for each sample. Virgin heavy crude oil samples were tested to determine the total amount of volatiles present including water. The results are presented in Table 8.

Table 8 – Total volatile content of various crude oil samples determined at 100˚C.

Crude Oil Sample	Volatile Content (%)
I	4.5 ± 0.6
II	2.9 ± 0.3

Collection of separated phases from destabilized emulsions was often difficult due to the similarity in density between heavy crude oil and water as well as the high viscosity of the separated oil. Pockets of trapped water, shown in Figure 17, were often formed when carbon dioxide was used to destabilize emulsions of heavy crude oil and water. To determine the contaminants in each phase after carbon dioxide-induced separation, the emulsion was prepared and transferred to a large test tube. Gaseous carbon dioxide was added through a long 18 gauge needle. The regulator pressure was set between 5 and 10 psi. A wooden applicator stick was inserted to break up water pockets. Oil samples were taken from the material adhered to applicator sticks. Water samples were decanted from the separated oil.

Figure 17 – Water separation after CO_2 treatment of an O/W emulsion stabilized with naturally occurring surfactants activated with Na_2CO_3. Water pockets trapped in the heavy viscosity separated crude oil are indicated by arrows.

3.2 Pipeline Scheme A

Pipeline Scheme A is illustrated in Figure 18. This scheme is based on previous research with light crude oil [33]. An amidine surfactant in the ionic form was used to stabilize an emulsion of light crude oil in water. An inert gas such as nitrogen or air was used to return the amidine surfactant to the neutral form. The emulsion, which was no longer stabilized by the neutral amidine surfactant, separated quickly. The amidine surfactant in the neutral form was also found to be an effective demulsifier [33]. Although this system has only been used for light crude oil, an equivalent system would be ideal for generating reversible transport emulsions of heavy crude oil.

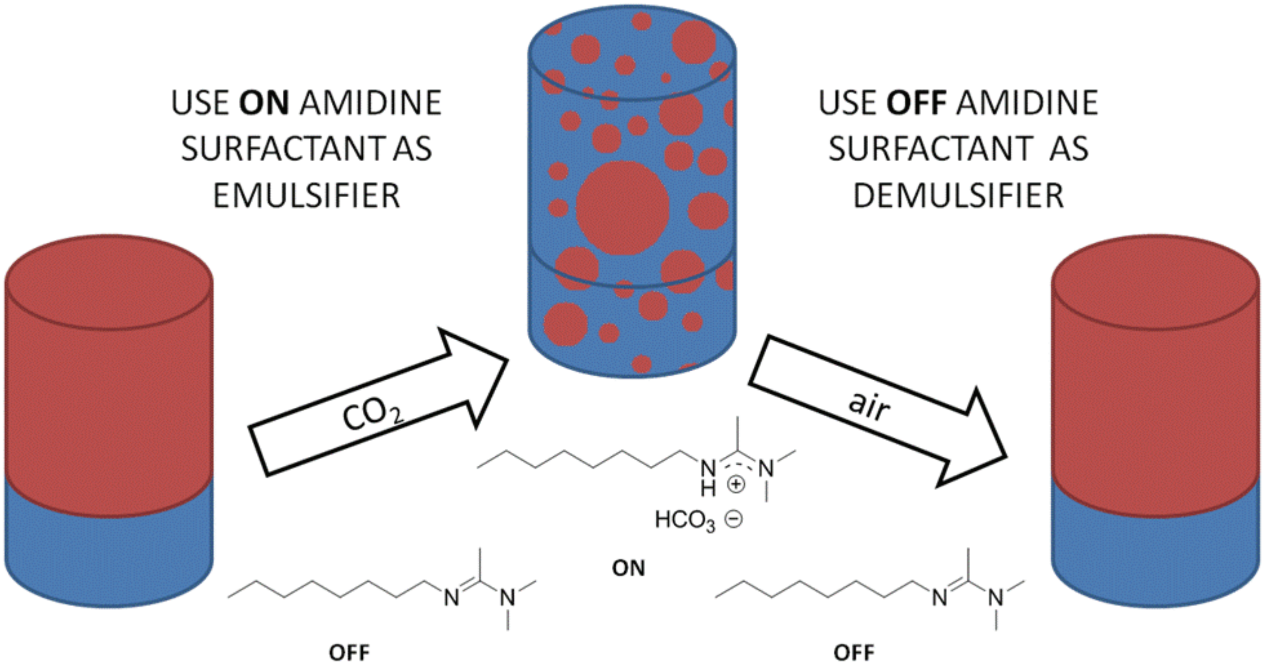

Figure 18 – Illustration of Pipeline Scheme A. A switchable surfactant is treated with carbon dioxide. The ionic amidine surfactant then stabilizes an emulsion of crude oil in water. After the pipelining is complete, the surfactant is made neutral using air to displace the carbon dioxide. The neutral surfactant then destabilizes the crude oil emulsion leading to phase separation of the oil from the water.

Various amidine surfactants were tested in order to evaluate Pipeline Scheme A for transport of stabilized low viscosity emulsions of heavy crude oil. Switchable surfactants were made ionic before emulsification by addition of carbon dioxide through a needle placed against the side of the emulsification vessel. Surfactants were well mixed before addition of crude oil. Constant carbon dioxide bubbling was maintained during emulsification in order to sustain a saturated carbon dioxide environment.

Delivery of carbon dioxide was difficult due to the viscosity of the crude oil mixture. Emulsification of heavy crude oil was completed at 60°C. N,N-dimethylacetamidine switchable surfactants are known to lose carbon dioxide at approximately 60°C [33]. Continuous carbon dioxide bubbling may not be sufficient to keep surfactant in the ionic form at this temperature. The hydrochloride salt of the amidine surfactant was prepared and tested in order to resolve this uncertainty.

3.2.1 First Generation Surfactants

No emulsion stabilized using first generation amidine switchable surfactants in the presence of carbon dioxide exhibited significant viscosity reduction.

3.2.1.1 Venezuelan Oil (Sample I and Sample II)

First generation surfactants A1-C_8, A1-C_{12}, and A1-C_{16} were unable to stabilize O/W emulsions with 70% crude oil in the presence of carbon dioxide. Water was incorporated into the crude oil after prolonged mixing. Both hydrochloride salts of A1-C_{12} and A1-C_{16} stabilized W/O emulsions. The hydrochloride salt of A1-C_8 failed to stabilize any emulsion.

3.2.1.2 North Sea Oil (Sample III)

First generation surfactants A1-C_8, A1-C_{12}, and A1-C_{16} were unable to stabilize O/W emulsions with 70% crude oil in the presence of carbon dioxide. W/O emulsions were generated after prolonged mixing. The hydrochloride salt of A1-C_8 was able to stabilize an O/W emulsion but the emulsion was unstable and phase separation was evident immediately after stirring was discontinued.

3.2.2 Second Generation Surfactants

No emulsion stabilized using second generation amidine switchable surfactants in the presence of carbon dioxide exhibited significant viscosity reduction.

3.2.2.1 Venezuelan Oil (Sample I and Sample II)

Second generation surfactants A1-E_1C_6, A1-E_2C_6, and A1-E_3C_4 did not stabilize O/W emulsions with crude oil Sample I or Sample II when carbon dioxide was added during emulsification. Water was again incorporated after prolonged mixing. The hydrochloride salt of A1-E_3C_4 stabilized an O/W emulsion but the emulsion was unstable and phase separation was immediately evident after stirring was discontinued.

3.2.2.2 North Sea Oil (Sample III)

A1-E_3C_4 stabilized O/W emulsions in the presence of carbon dioxide. The emulsions were unstable and phase separation was evident after agitation was discontinued. Both A1-E_1C_6 and A1-E_2C_6 stabilized W/O emulsions. The hydrochloride salts of A1-E_3C_4 stabilized an O/W emulsion but the emulsion was unstable and phase separation was immediately evident after stirring was discontinued.

3.2.3 Third Generation Surfactants

No emulsion stabilized using third generation amidine switchable surfactants in the presence of carbon dioxide exhibited significant viscosity reduction.

3.2.3.1 Venezuelan Oil (Sample I and Sample II)

In the presence of carbon dioxide, A1-C_4E_3 did not stabilize an O/W emulsion. Water was incorporated after prolonged mixing. The hydrochloride salt of A1-C_4E_3 stabilized W/O emulsions.

3.2.3.2 North Sea Oil (Sample III)

In the presence of carbon dioxide, A1-C_4E_3 stabilized an O/W emulsion. The emulsion was unstable and started to separate immediately after agitation was discontinued. Water was incorporated after prolonged mixing. Hydrochloride salt of A1-C_4E_3 stabilized W/O emulsions.

3.2.4 Summary

The addition of carbon dioxide in general did not help promote the formation of O/W emulsions of heavy crude oil. W/O emulsions were generated with crude oil Sample I and II. Although O/W emulsions were generated with crude oil Sample III, none were stable for more than 1 day. A summary of emulsions prepared using various surfactants is provided in Table 9 and Table 10. The behaviour of amidine surfactants in presence of carbon dioxide was not consistent with the behaviour of the equivalent amidine hydrochloride salt. Pipeline Scheme A cannot be used with heavy crude oil using amidine type switchable surfactants.

Table 9 – Emulsions of various heavy crude oil generated using various amidine switchable surfactants in the presence of carbon dioxide in accordance to Pipeline Scheme A.

Crude Oil Sample	Surfactant (3000 – 8000ppm)						
	A1-C_8	A1-C_{12}	A1-C_{16}	A1-E_1C_6	A1-E_2C_6	A1-E_3C_4	A1-C_4E_3
I	W/O	no emulsion	no emulsion	W/O	W/O	W/O	W/O
II	W/O	no emulsion	no emulsion	W/O	W/O	W/O	W/O
III	O/W unstable	O/W unstable	W/O	W/O	O/W unstable	O/W unstable	O/W unstable

Table 10 – Emulsions of various heavy crude oil generated using various amidine hydrochloride salts.

Crude Oil Sample	Surfactant (3000 – 8000ppm)			
	A1-C_8·HCl	A1-C_{12}·HCl	A1-C_{16}·HCl	A1-E_3C_4·HCl
I	O/W unstable	no emulsion	W/O	W/O
II	O/W unstable	no emulsion	W/O	W/O
III	O/W unstable	O/W days	O/W days	O/W days

3.3 Pipeline Scheme B

Pipeline Scheme B is illustrated in Figure 19. Crude oil contains indigenous molecules with surface active properties. These surfactants can be activated by treatment with alkali such as sodium hydroxide or sodium carbonate [8, 49, 50]. The activated indigenous crude oil surfactants were found to react with carbon dioxide.

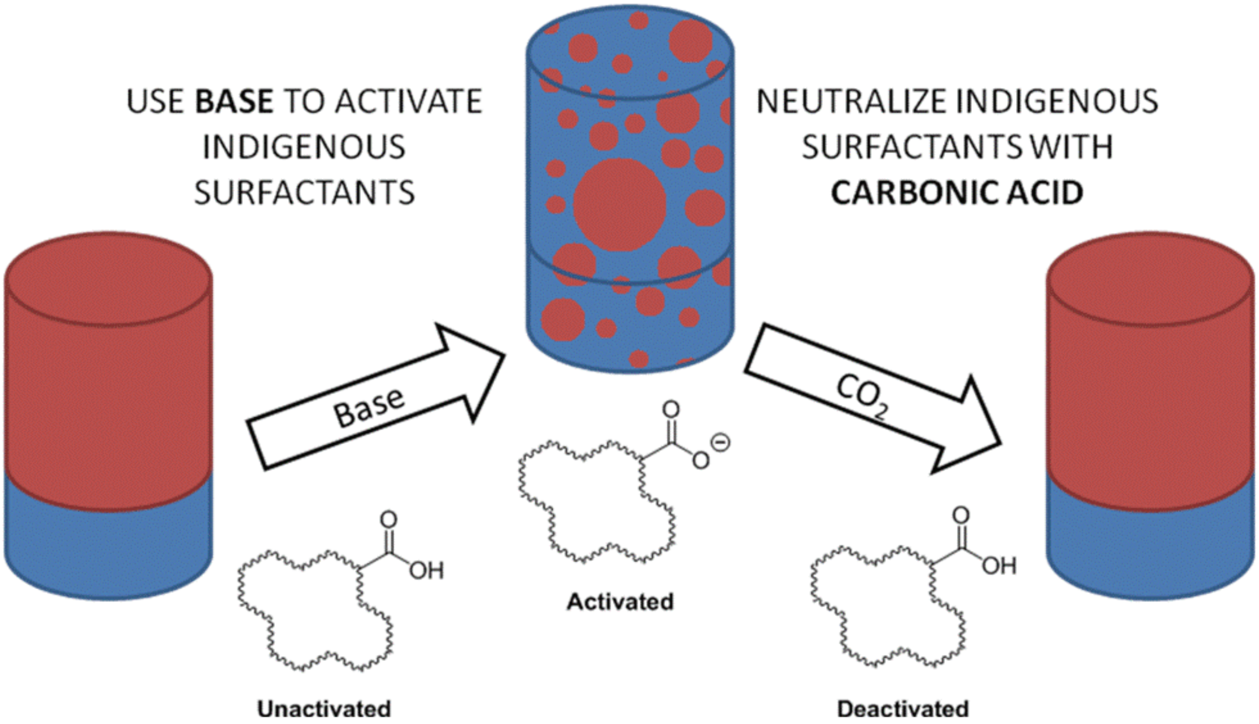

Figure 19 – Illustration of Pipeline Scheme B. Indigenous surfactants found in crude oil are activated by the addition of base. The activated surfactants then stabilize a crude oil in water emulsion. After the pipeline is done, the indigenous surfactants are deactivated by addition of carbon dioxide leading to separation of oil and water.

Various bases were tested in order to evaluate Pipeline Scheme B for transport of stabilized low viscosity emulsions of heavy crude oil. Water-soluble bases were well mixed in the aqueous layer before emulsification. No carbon dioxide was added during emulsification.

3.3.1 Emulsification with Various Bases

Low viscosity heavy crude oil emulsions were generated by activating indigenous crude oil surfactants with sodium hydroxide and sodium bicarbonate. Results were similar to previous literature. The viscosity reduction achieved was similar to previous accounts [8, 49, 50] . Additionally, the emulsions stabilized by activated crude oil surfactants were destabilized with carbon dioxide. Phase separation occurred immediately after carbon dioxide was added. Water-soluble organic bases such as DBU, and A1-E_2 were also found to be effective. A summary of emulsions prepared using various bases is provided in Table 11.

Table 11 – Emulsions of various heavy crude oil stabilized using a base as additive in accordance to Pipeline Scheme B.

Crude Oil Sample	Base (3000 - 4000ppm)		
	Na_2CO_3	DBU	A1-E_2
I	O/W weeks	O/W weeks	O/W weeks
II	O/W weeks	O/W weeks	O/W weeks
III	O/W weeks	O/W weeks	O/W weeks

The properties of emulsions generated with DBU, A1-E_2, and Na_2CO_3 are similar. No visible phase separation was observed after two weeks at 60°C. Emulsions of crude oil

Sample III were brown in appearance. Emulsions of crude oil Sample I and II were black in appearance. The viscosity of emulsions of crude oil Sample I and II stabilized with Na_2CO_3 and DBU were measured to be between 300 – 350 cSt at 20˚C.

3.3.2 Phase Separation with CO_2

The addition of carbon dioxide to an emulsion stabilized by activated indigenous surfactant caused immediate phase separation. Upon separation, an increase in viscosity was evident. In the case of crude oil Sample III, the emulsion colour changed from brown to black (see Figure 20). Similar results were achieved using 1.0 equivalent of hydrochloric acid with respects to amount of added base instead of carbon dioxide.

Figure 20 – O/W emulsion of crude oil Sample III in water. Samples untreated after emulsification [LEFT] and treated with CO_2 [RIGHT]. Photographs were taken after four weeks at room temperature.

Phase separation did not occur after emulsion samples were treated with air. The effect of hydrochloric acid, carbon dioxide, and air on emulsion stability is summarized in Table 12. In addition, an O/W emulsion was generated with a non-ionic surfactant, IGEPAL CO-720[†††] and treated with hydrochloric acid, carbon dioxide, and air. No immediate change in emulsion stability was observable. No water separation was evident after two weeks at 60°C. Carbon dioxide did not have an observable effect on an emulsion stabilized with a non-ionic surfactant.

[†††] IGEPAL CO-720 is nonylphenol polyethyleneoxide with EO number between 10.5-12.0; HLB of 14.

Table 12 – The effect of carbon dioxide, concentrated hydrochloric acid, and air on the stability of crude oil emulsions stabilized with various bases and non-ionic surfactant.

Surfactant/Base	Crude Oil Sample	Concentration (ppm)	Treatment		
			HCl	CO_2	Air
IGEPAL CO-720	I	7000	–	no effect	no effect
IGEPAL CO-720	II	11000	–	no effect	no effect
Na_2CO_3	I	2700	immediate	immediate	no effect
Na_2CO_3	II	2400	immediate	immediate	no effect
Na_2CO_3	III	3100	immediate	immediate	no effect
DBU	I	4500	immediate	immediate	no effect
DBU	II	4200	immediate	immediate	no effect
DBU	III	3300	immediate	immediate	no effect
A1-E_2	I	4200	immediate	immediate	no effect
A1-E_2	II	4300	immediate	immediate	no effect
A1-E_2	III	4600	immediate	immediate	no effect

Free flowing water was removed by decanting. The amount of residual crude oil in free water separated after carbon dioxide-treatment was found to be different for various bases. Organic bases performed better than sodium carbonate, leaving the separated oil with less water and the separated water with less oil (see Table 13).

Table 13 – Carbon dioxide-induced phase separation of emulsions stabilized by activated indigenous surfactants using various bases.

Crude Oil Sample	Base	Concentration (ppm)	Residual Contamination (%)	
			Water in Oil[‡‡‡]	Oil in Water
I	Na_2CO_3	2700	21 ± 3	2 ± 0
	DBU	4500	15 ± 4	2 ± 0
	A1-E_2	4200	12 ± 3	1 ± 1
II	Na_2CO_3	2400	15 ± 3	5 ± 0
	DBU	4200	15 ± 2	2 ± 0
	A1-E_2	4300	11 ± 3	2 ± 1

3.3.3 Protonation with CO_2

Carbon dioxide was successfully used to break heavy crude oil emulsions. The activated indigenous surfactants were believed to have been protonated by carbonic acid formed in the aqueous phase when carbon dioxide gas was bubbled into the emulsion. The ability of carbonic acid to protonate indigenous surfactants, which are believed to be more acidic acids, was evaluated using model compounds.

[‡‡‡] This value is corrected for the amount of volatiles found in virgin oil samples (4.5% for crude oil Sample I and 2.9% for crude oil Sample II).

Sodium salts of cyclohexanecarboxylic acid, benzoic acid, lauric acid, and methyl-4-hydroxycyclohexanecarboxylate were prepared by treating the acid with 1.0 equivalents of sodium hydroxide. White solids were recovered after evaporating water in a vacuum oven at 60°C. A measured amount of each salt was dissolved in 150 ml water. The aqueous solutions were clear and transferred to individual separatory funnels with 100 ml of toluene. Carbon dioxide gas was bubbled into the biphasic mixture for 1 h. The organic phase was separated. Toluene was removed using a rotary evaporator under reduced pressure. The mass of the remaining residue was measured. The process was repeated with argon gas.

The extraction of carboxylic acid from an aqueous solution of the corresponding sodium salt was enhanced by the presence of carbon dioxide (see Figure 21). An inert gas, argon, was used as control. Carbonic acid greatly increased the amount of material recovered in the organic phase.

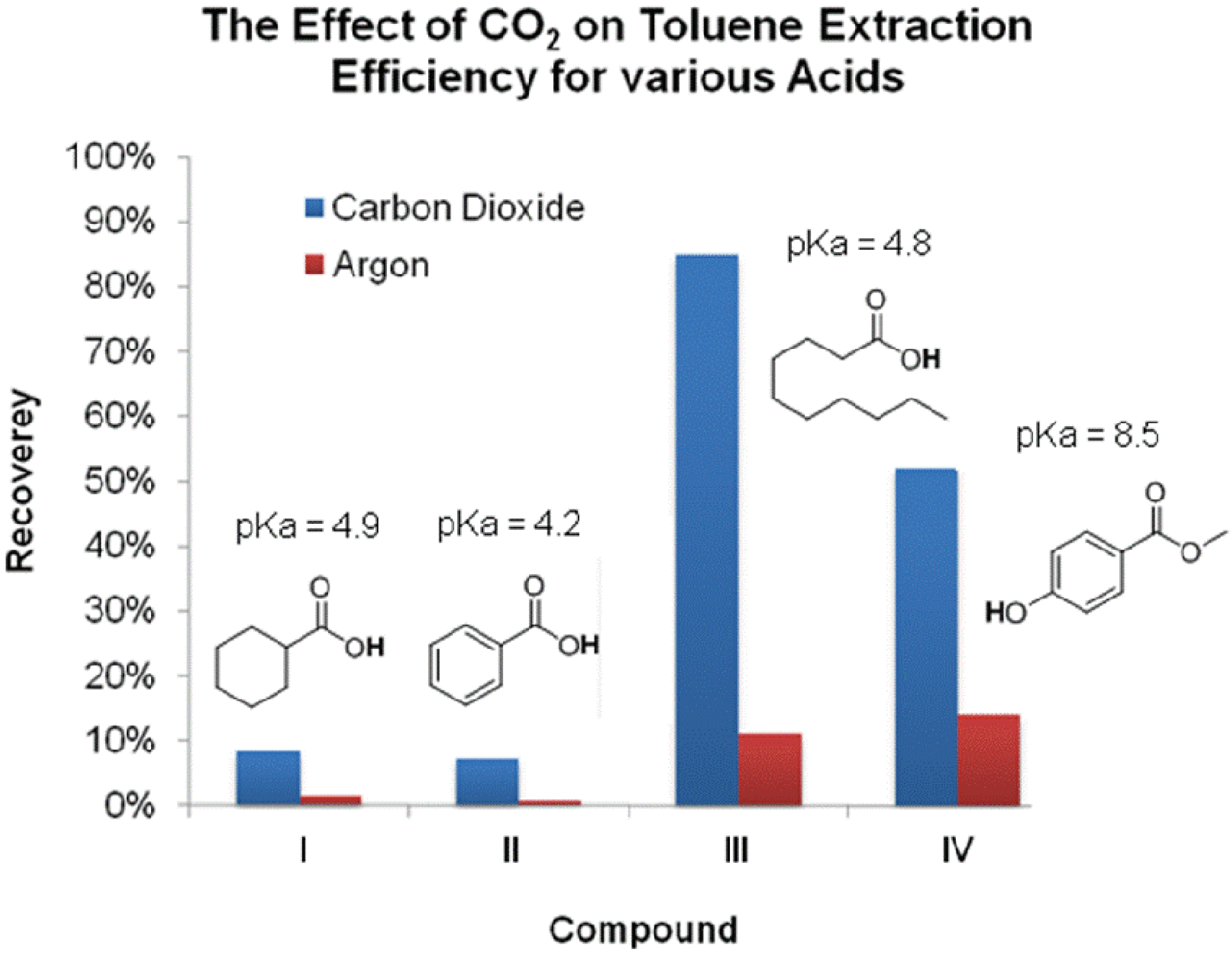

Figure 21 – Recovery of acid from aqueous solution of corresponding sodium salt was enhanced by presence of carbon dioxide.

3.3.4 Summary

Low viscosity heavy crude oil emulsions were generated by activating indigenous crude oil surfactants with a base such as sodium hydroxide or sodium bicarbonate. Additionally, the emulsions stabilized by activated crude oil surfactants were destabilized with carbon dioxide. Phase separation occurred immediately. Water-soluble organic bases such as DBU, and A1-E_2 were found to be effective. After destabilization by carbon dioxide, the separated oil and water from emulsions stabilized using organic base additives were found to contain less contaminants than those stabilized using sodium carbonate. That is, the separated water contained less crude oil and the separated crude oil contained less water.

3.4 Pipeline Scheme C

Pipeline Scheme C is illustrated in Figure 22. Water-soluble amidine bases such as DBU and A1-E_2 were found to activate indigenous crude oil surfactants leading to stable O/W emulsions (see Section 3.3). The water separated after carbon dioxide-treatment of emulsions stabilized using a basic additive was not clear and contained residual crude oil. Final clarification took months at room temperature. Amidine surfactants are capable of activating indigenous surfactants but are also themselves surface-active. A final demulsification step would be possible using an amidine surfactant instead of a regular non-surfactant water-soluble base.

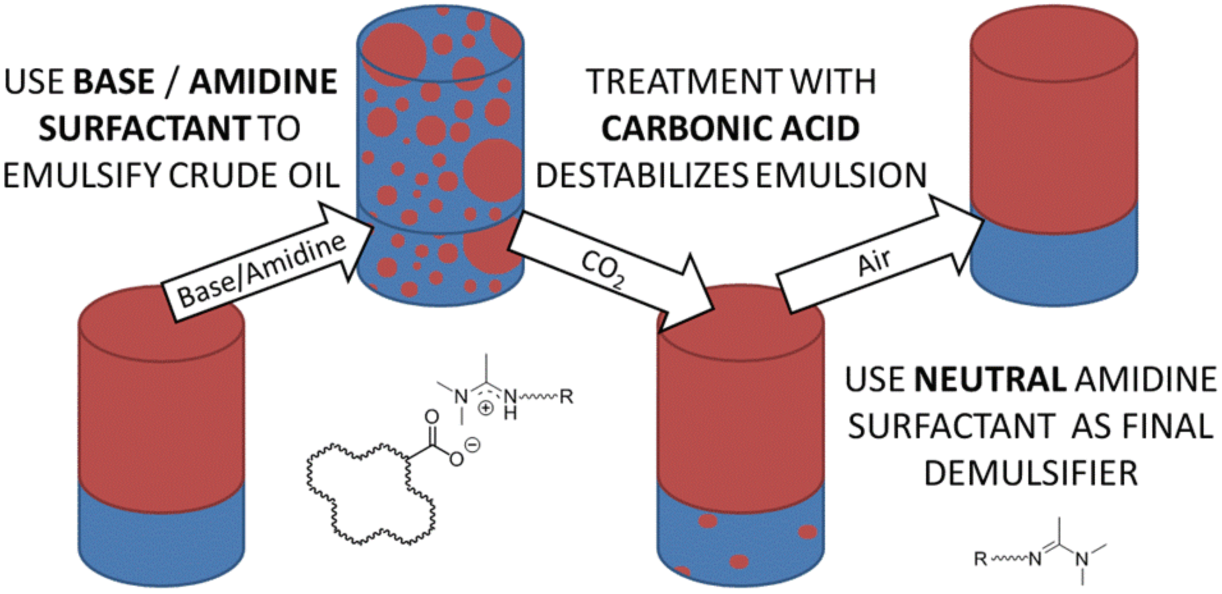

Figure 22 – Illustration of Pipeline Scheme C. The indigenous surfactants found in crude oil are activated by the addition of an amidine. The activated surfactants then stabilize a crude oil in water emulsion. After pipeline transport is complete, the indigenous surfactants are deactivated by the addition of carbon dioxide, leading to separation of the oil from the water. The amidine surfactant is then reverted back to its neutral form by the addition of an inert gas such as nitrogen or air. The neutral amidine surfactant then further demulsifies the emulsion.

After destabilizing the emulsion with carbon dioxide, the separated water containing the ionic amidine surfactant was treated with an inert gas such as nitrogen or air in order to return the amidine surfactant to the neutral form. The neutral amidine surfactant increased rate of demulsification and improved the clarity of the separated water. Various amidine surfactants were tested in order to evaluate Pipeline Scheme C for transport of stabilized low viscosity emulsions of heavy crude oil.

3.4.1 First Generation Surfactants

No emulsion stabilized using first generation amidine switchable surfactants in the absence of carbon dioxide exhibited significant viscosity reduction.

3.4.1.1 Venezuelan Oil (Sample I and Sample II)

In the absence of carbon dioxide, first generation surfactants, A1-C_8, A1-C_{12}, and A1-C_{16} were unable to stabilize O/W emulsions with 70% crude oil in the presence of carbon dioxide. Water was incorporated into the crude oil after prolonged mixing.

3.4.1.2 North Sea Oil (Sample III)

In the absence of carbon dioxide, A1-C_8 was able to stabilize an O/W emulsion of crude oil Sample III. The emulsion showed signs of phase separation after two hours. A1-C_{12} and A1-C_{16} were unable to stabilize an O/W emulsion.

3.4.2 Second Generation Surfactants

Only water-soluble second generation surfactants, A1-E_2C_6 and A1-E_3C_4, were able initially to stabilize an emulsion of 70% crude oil in the absence of carbon dioxide. The emulsions were unstable. Only emulsions of heavy crude oil Sample III stabilized using A1-E_3C_4 were stable for two weeks.

3.4.2.1 Venezuelan Oil (Sample I and Sample II)

In the absence of carbon dioxide, both A1-E_2C_6 and A1-E_3C_4 were able to stabilize O/W emulsions of crude oil sample I and II. A1-E_2C_6 was also capable of stabilizing W/O emulsions of crude oil Sample I. The O/W emulsions stabilized using A1-E_2C_6 and A1-E_3C_4 were unstable and phase separation was evident less than 12 h.

3.4.2.2 North Sea Oil (Sample III)

In the absence of carbon dioxide, all second generation surfactants were able to initially stabilize an O/W emulsion of crude oil Sample III. The emulsion stabilized by A1-E3C4 was stable for two weeks while the emulsions stabilized with A1-E_2C_6 and A1-E_1C_6 were stable for less than 12 h.

3.4.3 Third Generation Surfactants

Third generation surfactants successfully stabilized low viscosity emulsions of heavy crude oil for two weeks.

3.4.3.1 Venezuelan Oil (Sample I and Sample II)

A1-C_4E_3 stabilized an O/W emulsion of heavy crude oil Sample I and II. The emulsions were stable for two weeks. The viscosity of the 70% crude oil emulsions were reduced to 150 – 200 cSt at 60˚C.

3.4.3.2 North Sea Oil (Sample III)

A1-C_4E_3 stabilized an O/W emulsion of heavy crude oil Sample III. The emulsions were stable for two weeks.

3.4.4 Phase Separation with CO_2

Addition of carbon dioxide caused immediate phase separation for emulsions stabilized using activated indigenous surfactants. The amount of residual crude oil in the free separated water was found to be different for various bases (see Table 14). Second and third generation amidine surfactants also performed better than sodium carbonate leaving the separated oil with less water and the separated water with less oil.

Table 14 – Carbon dioxide-induced phase separation of emulsions of crude oil Sample II generated by water-soluble amidine surfactants A1-E_3C_4, A1-E_2C_6, and A1-C_4E_3.

Base (3000 – 6000 ppm)	Residual Contamination (wt%)	
	Water in Oil [§§§]	Oil in Water
Na_2CO_3	15 ± 5	5 ± 0
A1-E_3C_4	10 ± 2	<1%
A1-E_2C_6	11 ± 2	<1%
A1-C_4E_3	13 ± 2	1%

3.4.5 Demulsification

Many compounds are known to speed the process of phase separation. Amidine type structures have been shown in literature to enhance demulsification of various emulsions

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[§§§] This value is corrected for the amount of volatiles found in virgin oil samples (4.5% for crude oil Sample I and 2.9% for crude oil Sample II).

[59-62]. The addition of A1-C_8 to a Petri dish containing water with emulsified crude oil caused fast separation. Water clarity was significantly improved within 24 h (see Figure 23). The emulsion treated with A1-C_8 was a dilute O/W emulsion of 1 wt% crude oil Sample II stabilized with Na_2CO_3.

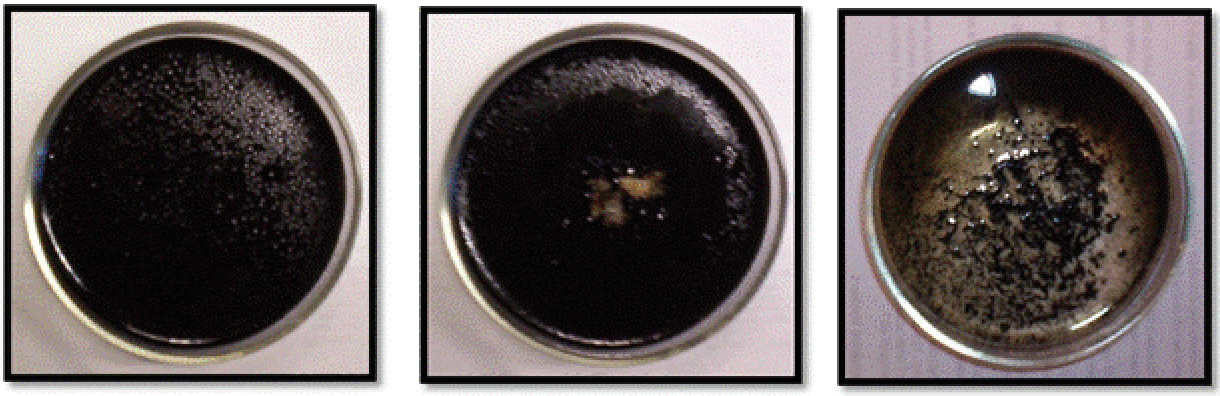


Figure 23 – Dilute oil in water emulsion was broken with a few drops of the neutral form of A1-C_8. Pictures taken before addition [LEFT], after 5 min [CENTRE], and after 24 h [RIGHT].

A survey of various amidine surfactants as demulsifiers was completed. Samples were prepared with 1 – 2 wt% demulsifier. The demulsifier was added to water prepared with 1% crude oil Sample II stabilized with Na_2CO_3. Demulsification was tracked visually over the course of several days. Photographs of the process at various time intervals are presented in Figure 24.

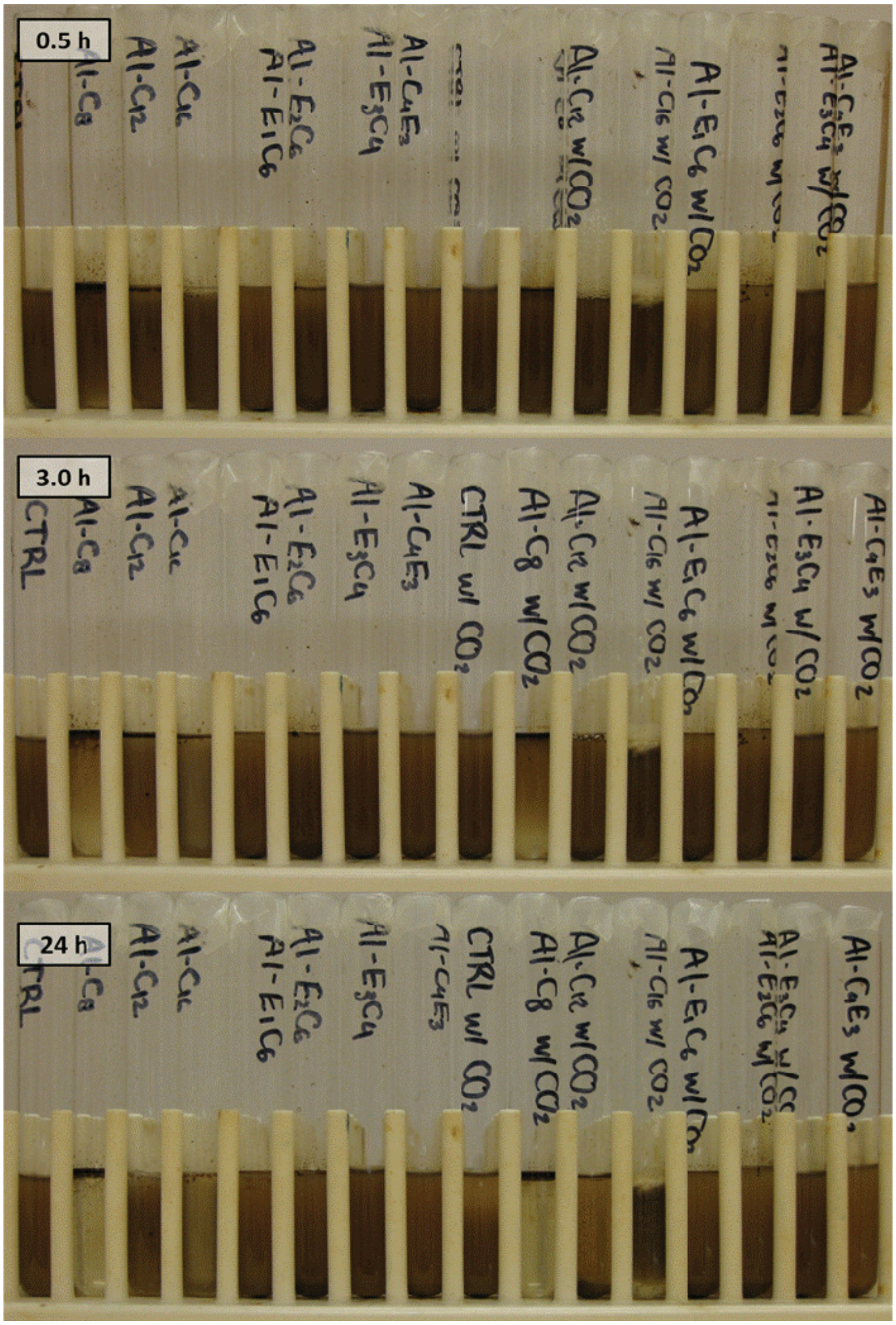


Figure 24 – Demulsification of dilute crude oil in water emulsions using various amidine switchable surfactants in both ionic and neutral forms. Demulsifiers tested include (from left to right): no surfactant, A1-C_8, A1-C_{12}, A1-C_{16}, A1-E_1C_6, A1-E_2C_6, A1-E_3C_4, A1-C_4E_3, no surfactant with CO_2, A1-C_8 with CO_2, A1-C_{12} with CO_2, A1-C_{16} with CO_2, A1-E_1C_6 with CO_2, A1-E_2C_6 with CO_2, A1-E_3C_4 with CO_2, and A1-C_4E_3 with CO_2.

A1-C_8 was the best demulsifier. The beginning of oil separation was visually evident in less than 1 h. The bicarbonate form of A1-C_8 was also effective but slower with onset of separation visually evident after 2 h. After 24 h, the water in both samples was clear without any visible residual oil contamination. The neutral forms of A1-C_{12} and A1-C_{16} were also effective demulsifiers. Onset of separation occurred after approximately 3 h. The ionic forms of A1-C_{12} and A1-C_{16} were not as effective, although an improvement in water quality was evident after 24 h.

Separated water was recovered from an emulsion of crude oil Sample II destabilized with carbon dioxide; the emulsion was originally stabilized by A1-C_4E_3. Samples of this separated water were treated with air, A1-C_8, or additional A1-C_4E_3. Air was supplied through a syringe. Photograph of samples provided in Figure 25. A1-C_8 was the superior demulsifier in this situation. The separated water was clear after 24 h.

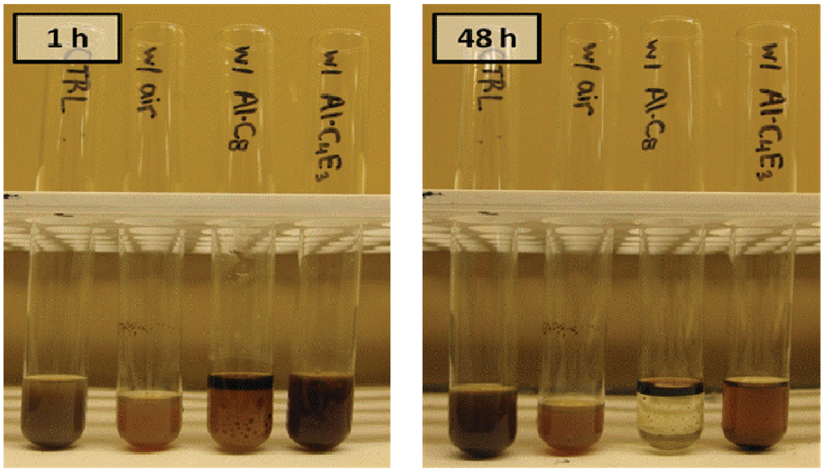


Figure 25 – Water quality after intinal phase separation triggered by carbon dioxide. Treatment of water recovered after CO_2 induced phase separation of an emulsion of crude oil Sample II stabilized with A1-C_4E_3. Samples were treated with (from left to right): nothing, air, A1-C_8, or A1-C_4E_3.

3.4.6 Summary

Water soluble amidine surfactants were found to activate indigenous crude oil surfactants. O/W emulsions with various levels of stability were made from heavy crude oil. They were found to lead to better phase separation. Separated water contained less emulsified oil. Water content of separated oil was also reduced. The stability of heavy crude oil emulsions stabilized with A1-C_4E_3 satisfied the two week specification. Amidine surfactant compatibility was achieved by interchanging the relative position of hydrophilic and hydrophobic moieties. A summary of emulsions prepared using various surfactants is provided in Table 15.

Table 15 - Emulsions of various heavy crude oil generated using various amidine switchable surfactants in the absence of carbon dioxide in accordance to Pipeline Scheme C.

Crude Oil Sample	Surfactant (3000ppm – 8000ppm)						
	A1-C_8	A1-C_{12}	A1-C_{16}	A1-E_1C_6	A1-E_2C_6	A1-E_3C_4	A1-C_4E_3
I	W/O	W/O	W/O	W/O	W/O O/W	O/W hours	O/W weeks
II	W/O	W/O	W/O	W/O	O/W hours	O/W hours	O/W weeks
III	O/W hours	W/O	W/O	O/W hours	O/W hours	O/W weeks	O/W weeks

3.5 Discussion

3.5.1 Indigenous Surfactants

The presence of indigenous surfactants in heavy crude oil presented problems to the original pipeline scheme, which was therefore abandoned. Addition of carbon dioxide during emulsification was detrimental to emulsion stability in the presence of basic additives such as sodium carbonate or amidine surfactant. The simultaneous activation of indigenous surfactants by the basic amidine surfactants and deactivation of indigenous surfactants by carbon dioxide lead to unstable emulsions. The two concurrent incompatible processes are believed to be the cause of the general inconsistency of the results of Pipeline Scheme A.

Pipeline Schemes B and C, on the other hand, took advantage of the indigenous surfactants in the oil, by having them activated by addition of base. The activated surfactants were then able to stabilize emulsions of heavy crude oil and water. The stabilized O/W emulsions containing approximately 70% crude oil exhibited significant viscosity reduction. Both inorganic bases (*e.g.* NaOH and Na_2CO_3) and water-soluble organic bases (*e.g.* DBU, A1-E_2, and Et_3N) were effective in stabilizing O/W emulsions of heavy crude oil in water.

The choice of base can influence the properties of the stabilized emulsion such as the emulsion continuous phase. In order to stabilize an O/W emulsion of heavy crude oil, a water-soluble base is required. The solubility and partition coefficient of selected bases are presented in Table 16. All the bases listed in Table 16 expect for choline hydroxide were able to activate indigenous surfactants in the heavy crude oil and stabilized O/W emulsions.

Table 16 – Absolute and relative solubility of various bases.

Base	pK_{aH}	Solubility (g/L)	Partition (log P)
NaOH	13.5	1110	–
Na_2CO_3	10.3	300	–
Et_3N	10.7	85	1.45
DBU	12.0	high	1.25
CholineOH	13.9	650	-3.77

3.5.2 Carbon Dioxide

Crude oil emulsions stabilized by activated surfactants separated immediately after treatment with carbon dioxide, suggesting that the stabilization mechanism was neutralized by carbon dioxide. Addition of hydrochloric acid caused a similar reaction leading to immediate phase separation. Addition of other gases such as argon, nitrogen, and air did not trigger phase separation.

Carbon dioxide in aqueous solution forms carbonic acid. Carbonic acid reacted with the activated surfactants reversing the effect of the base. The sudden swing in properties of the surfactants destabilized the emulsion and lead to phase separation. Indigenous surfactants in the crude oil are contained in the heavier asphaltenic crude oil fractions.

Compounds in this crude oil fraction contain acidic functional groups such as phenols and carboxylic acids. The acidity of compounds representative of asphaltenic acidic groups and select bases are presented in Table 17.

The destabilization of the emulsion was caused by changes in the interfacial properties through neutralization of certain activated indigenous surfactants with carbonic acid. Carbonic acid is a weak acid generated from gaseous carbon dioxide in aqueous solutions. The pKa of carbonic acid in water is 6.3 while the pKa of most carboxylic acids falls between 4.0 and 5.0. The presence of an organic phase facilitates this process since the protonated acid is much less soluble in the aqueous phase. The protonation of acidic groups with carbonic acid is possible due to the difference in solubility of the anionic and neutral forms of the surfactants.

Table 17 – Acidity of select compounds in water.

Compound	Acidity (pK_a)	Basicity (pK_{aH})
1,5-Dinitrophenol	3.9	–
Benzoic acid	4.2	–
Acetic acid	4.8	–
Phenol	10.0	–
Sodium hydroxide	–	13.5
Sodium carbonate	–	10.2
Triethylamine	–	10.7
DBU	–	12.0

3.5.3 Amidine Surfactants

Amidines are sufficiently basic to activate the indigenous surfactants in heavy crude oil samples. When this occurs, there are two surface active compounds: the ionic amidine switchable surfactants and the activated indigenous crude oil surfactants (see Figure 26).

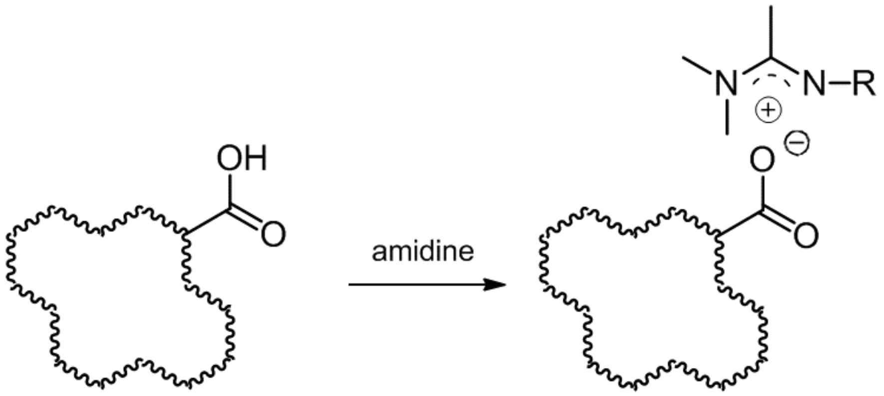


Figure 26 – Activation of indigenous crude oil surfactants. Addition of amidine base in presence of indigenous acidic surfactants creates two surface active species.

The influence of the indigenous surfactants is crucial for determining the success of the emulsification. Amidine surfactant hydrochloride salts cannot activate the indigenous crude oil surfactants. As a result, amidinium chloride salt generated emulsions were different from those generated with untreated amidine. Only the hydrochloride salts of A1-C_{12} and A1-C_{16} were able to stabilize O/W emulsions of crude oil Sample III (Table 18)

Table 18 – Emulsions of 70% crude oil Sample III generated with hydrochloride salt of surfactants displayed improved stability over emulsion generated with neutral amidine surfactant.

Surfactant (3000 – 8000 ppm)	Preparation	
	none	with HCl
A1-C_8	O/W hours	O/W unstable
A1-C_{12}	O/W hours	O/W days
A1-C_{16}	O/W hours	O/W days

Table 19 – Various emulsions of 70% crude oil generated with neutral and hydrochloride salt of A1-E_3C_4.

Crude Oil Sample	Surfactant (3000-8000ppm)	
	A1-E_3C_4	HCl•A1-E_3C_4
I	O/W unstable	W/O
II	O/W unstable	W/O
III	O/W hours	n/a

The effect of activated indigenous crude oil surfactants must be considered when using an amidine switchable surfactant with crude oils known to contain significant amounts of acidic compounds.

3.5.3.1 First Generation Amidine Surfactants

First generation surfactants suffered from poor water solubility at ambient conditions. A1-C_{12} and A1-C_{16} were essentially insoluble in water. A1-C_8 displayed poor water solubility in neutral form but was slightly soluble as the bicarbonate salt. First generation amidine surfactants in their neutral form could not generate O/W emulsions of heavy crude oil Sample I and II. The stabilized W/O emulsions did not exhibit a significant viscosity reduction.

In the absence of activated indigenous surfactants, the ionic form of A1-C_8 was unable to stabilize any emulsion of water with the heavy crude oils. The ionic form of A1-C_{12} and A1-C_{16} stabilized W/O emulsions of crude oil Sample I and II but W/O emulsions are not desired for viscosity reduction. O/W emulsions of crude oil Sample III were stabilized with the ionic forms of A1-C_{12} and A1-C_{16}.

3.5.3.2 Second Generation Amidine Surfactants

Second generation surfactants were tailored to have various degrees of aqueous solubility. A1-E_3C_4 was soluble in water even in neutral form. A1-E_1C_6 displayed poor solubility and was immiscible with water even as the bicarbonate salt. Although A1-E_2C_6 and A1-E_3C_4 were able to generate an O/W emulsion in certain situations, no second generation amidine surfactant was able to stabilize an O/W emulsion containing 70% heavy crude oil for two weeks. Phase separation started after agitation ceased.

In the absence of activated indigenous surfactants, the ionic form of A1-E_1C_6, A1-E_2C_6, and A1-E_3C_4 formed W/O emulsions with heavy crude oil Sample I and II. The ionic form of A1-E_3C_4 also formed a W/O emulsion with crude oil Sample III.

3.5.3.3 Third Generation Amidine Surfactants

The inability of all second generation surfactants to stabilize heavy crude oil emulsions, despite the wide range of water solubility, was likely due to incompatibility with activated indigenous crude oil surfactants. Third generation amidine surfactants were designed to correct this by changing the surfactant configuration. The hydrophilic moiety was placed away from the amidine moiety. The resulting surfactant, A1-C_4E_3, was able to generate stable heavy crude oil emulsions.

In the absence of activated indigenous surfactants, the ionic form of A1-C_4E_3 generated a W/O emulsion with crude oil Sample I and II and an O/W emulsion with crude oil Sample III.

3.6 Summary

Low viscosity emulsions of heavy crude oil were generated by activating indigenous crude oil surfactants with water-soluble bases such as Na_2CO_3, DBU, Et_3N, and A1-E_2. The emulsions containing 70 wt% heavy crude oil were visually stable under ambient conditions for over two weeks. Immediate phase separation was found to occur with the addition of carbon dioxide. Free water was easily separated from the high viscosity crude oil. Water-soluble organic bases exhibited improvements in the quality of phase separation compared to inorganic bases. Amidine surfactants with appropriate structure were also capable of stabilizing heavy crude oil emulsions.

Activating indigenous crude oil surfactants using amidine surfactants with low water solubility was ineffective in generating low viscosity heavy crude oil emulsions. Water-soluble amidine surfactants A1-E_2C_6 and A1-E_3C_4 suffered from poor emulsion stability and separated within hours. Amidine surfactant with reversed orientation of hydrophilic and lipophilic regions, A1-C_4E_3, was able to stabilize emulsions of all tested heavy crude oil samples for over two weeks. The addition of carbon dioxide to an emulsion stabilized with A1-C_4E_3 caused immediate phase separation. Recovered oil and water had lowered amount of contamination when compared to separated emulsion stabilized with Na_2CO_3.

3.7 Future Work

The results of the investigation must be confirmed by vigorous engineering tests under more realistic conditions. Many of the difficulties encountered in the current investigation involved equipment and the difficulties associated with working with heavy crude oil.

The method of addition of carbon dioxide may play an important role in improving phase separation. The availability of gaseous carbon dioxide at ambient conditions is significantly greater in water than in crude oil. This is punctuated by the difference in viscosity of the two materials with the virgin heavy crude oil well over 100 cSt at 100˚C.

In order for process water to be discharged, considerable treatment is required to reduce the level of oil contamination. Although A1-C_4E_3 performed well in demulsification testing, having been able to clarify a dilute emulsion stabilized by sodium carbonate, the superiority of first generation amidine switchable surfactants in the demulsification of crude oil is unmatched. In order to take advantage of both the emulsion-stabilizing ability of A1-C_4E_3 and the excellent demulsifying ability of the first generation amidine surfactants, the modified hybrid pipeline scheme illustrated in Figure 27 was proposed. The amidine surfactant in this case contains a sensitive linker between the hydrophobic and hydrophilic regions. Once the link is severed, a first generation type amidine with superior demulsification capacity is produced. The severed hydrophilic moiety would be dissolved in the aqueous phase and be no longer surface active.

The sensitive linker can be made using various strategies. An acid labile group would be ideal especially if carbonic acid can be used to accelerate the rate of hydrolysis. Among available linkers, the hydrolysable ester linkage is well understood. Ester groups have been introduced into surfactant molecules in order to speed up hydrolysis as well as biodegradation in the environment. A possible synthetic pathway is illustrated in Scheme 5.

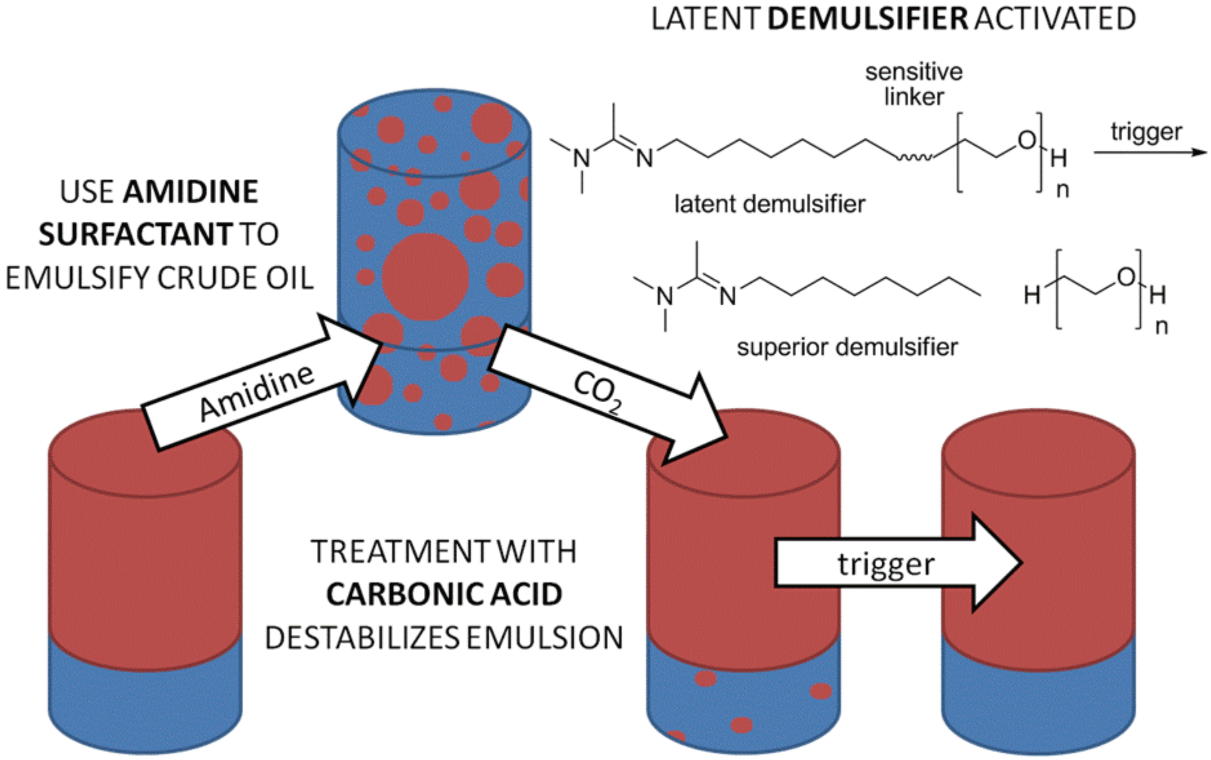
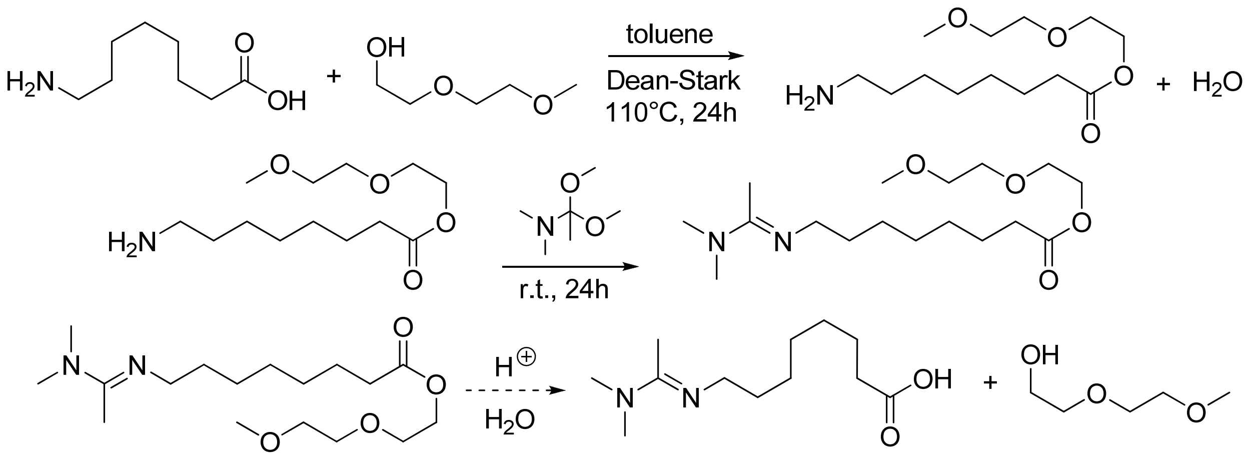


Figure 27 – Illustration of mproved pipeline scheme. Indigenous surfactants found in crude oil activated by addition of amidine surfactant designed with latent demulsifier. Activated surfactants stabilize crude oil in water emulsion. Indigenous surfactants deactivated with addition of carbon dioxide leading to separation. The amidine surfactant's sensitive linker is severed to produce powerful demulsifier.



Scheme 5 – Possible synthetic pathway to a cleavable switchable cationic amidine type surfactant.

Chapter 4 – Anionic Switchable Surfactants

Truly reversible switchable surfactants must meet minimum performance specifications. The various forms of the surfactant must have significantly different levels of surface activity in order to cause useful changes in surface properties such as surface tension, contact angle, and emulsion stability. The neutralization of a surfactant's electrostatic charge is sufficient. Other effective strategies include inducing conformational changes in surfactant structure. Furthermore, the surfactant must be able to change forms reversibly in order to be considered switchable.

The cationic switchable surfactants developed previously in the Jessop group rely on carbon dioxide to switch between cationic and neutral forms. In order for this process to be reversible, the acid (cationic) form must be capable of reacting with bicarbonate while the base (neutral) form must capable of reacting with carbonic acid. The strength of the base is directly related to the equilibrium between the two surfactant forms [63].

While cationic surfactants have many uses, anionic surfactants are more commonly used. The range of applications of anionic surfactants is considerably wider than that of cationic surfactants [64]. For that reason, it became clear that the development of switchable surfactants that are anionic in the more active form should be a priority. Towards the end of my research time, I began preliminary tests of that concept. Because there was insufficient time to complete the development of the anionic surfactants, the material in this chapter should not be considered comprehensive or complete and is meant only to provide a brief account of on-going research into switchable surfactant technology. Nevertheless, the results were considered sufficiently encouraging that their description here was judged worthwhile.

In previous work with crude oil, indigenous surfactants were activated using a water soluble base to stabilize low viscosity emulsions (see Section 3.3). Furthermore, the emulsions stabilized in this fashion were broken with carbon dioxide gas. The carbonic acid formed by carbon dioxide is believed to have neutralized the activated surfactants (see Section 3.5.2). This phenomenon was the basis for the development of the anionic carbon dioxide-responsive switchable surfactants to be described in this chapter. Examples of the anionic switchable surfactants are illustrated in Figure 28.

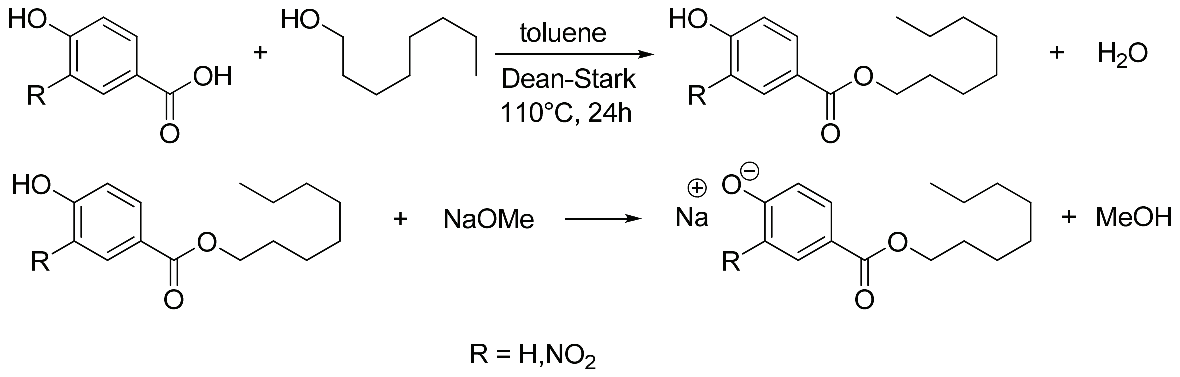


Figure 28 – Various anionic switchable surfactant systems.

Carboxylate soap, prepared by saponification of fatty animal or plant material using alkali, was used by ancient civilizations such as Babylon [65]. They have mostly been replaced today by synthetic derivatives. Synthetic phosphate and sulfate surfactants exhibit enhanced performance but suffer from environmental problems such as persistence due to low rates of biodegradation [66] and eutrophication [67]. Carboxylate soaps are much stronger bases than their phosphate or sulfate counterparts. This fact is important, as the reaction with carbon dioxide in water, illustrated in Figure 28, is essentially a neutralization reaction with carbonic acid. The acidity of various acids is presented in Table 20. Carbonic acid is a comparatively weak acid. Carboxylic acids are more acidic than carbonic acid when considering only their aqueous acid dissociation constants (pKa). The greater acidity suggests that the carboxylate salts would be difficult to protonate with carbonic acid. However, the presence of a secondary phase increases the amount of protonated material (see Section 3.3.3).

Table 20 – Acidity in water of various acids commonly found in surfactant structures [68, 69].

Compound	Acidity (pK_a)
Carbonic acid	6.4
Acetic acid	4.8
Methyl phosphate	1.5, 6.3
Methyl sulfate	− 2.6
Hydrochloric acid	− 4

The solubility behaviors of ionic and non-ionic compounds are generally very different. A polar solvent such as water dissolves ionic compounds with much greater efficacy. The difference in surface activity of an anionic compound and its uncharged conjugate acid may yield a switchable surfactant system.

The calculated HLB of various carboxylic acid surfactants in both ionic and neutral state is presented in Table 21. HLB is calculated using the following equation [70]:

$$\text{HLB} = 7 + \sum(\text{hydrophilic group number}) - \sum(\text{hydrophobic group number})$$

The HLB of the neutral form of surfactants listed in Table 21 generally suggests that the acids would serve as W/O type emulsifier while the HLB of the ionic form generally suggests that the salts would serve as an O/W type emulsifier. Switching between the two forms is therefore expected to cause dramatic changes in surface properties such as emulsion stability, contact angle, and surface tension.

Table 21 – Calculated HLB of both ionic and neutral form of various fatty acid switchable surfactants [70].

Tail Group Structure	Calculated HLB	
	R–COOH	R–COONa
$CH_3(CH_2)_{16}$	1.0	18.0
$CH_3(CH_2)_{14}$	2.0	19.0
$CH_3(CH_2)_{12}$	3.0	19.9
$CH_3(CH_2)_{10}$	3.9	20.9
$CH_3(CH_2)_8$	4.9	21.8
$CH_3(CH_2)_6$	5.8	22.8
$CH_3(CH_2)_{11}O(C_6H_4)$	1.7	18.7
$CH_3(CH_2)_7\ O(C_6H_4)$	3.6	20.6

4.1 Experimental

4.1.1 Materials

Chemicals, reagents, solvent, and other material were used as received without further purification or treatment unless otherwise specified. Deionized water was supplied from a Millipore MilliQ® Ultrapure Water purification system. The air supply was provided through an in-house compressor. A cotton filter was used to remove contaminants from the air supply. Sources of chemical reagents, solvents, and other chemical agents are summarized in Table 22.

Table 22 – Chemical reagents and solvents used during investigation.

Compound	Supplier	Lot No.
Sodium hydroxide	BDH	119073/67054
Sodium methoxide, 30wt%	Acros Organics	A016706101
Sodium octanoate, 99%	Sigma-Aldrich	088K0169
Lauric acid, 98%	Fluka	1390026
Myristic acid, 98%	Fluka	1349933
Palmitic acid, 98%	Sigma-Aldrich	81550
Stearic acid, 95%	Sigma-Aldrich	05217DJ
p-Octyloxybenzoic acid, 98%	Sigma-Aldrich	1390026
p-Dodecyloxybenzoic acid, 98%	Sigma-Aldrich	16520EA
2-Butoxyethoxy acetic acid, 98%	TCI America	F1LO1
Octanol, 99%	Sigma-Aldrich	014542DO

Compound	Supplier	Lot No.
Potassium permanganate, 99%	Sigma-Aldrich	75897LJ
Hydrogen peroxide, 35wt%	Sigma-Aldrich	31593MJ
n-Heptane, 100%	Fisher	076690
Toluene, HPLC grade	Fisher	091486
Carbon dioxide 4.0	Praxair	n/a
Argon 4.8	Praxair	n/a

4.1.2 Surface Tension

Surface tension was determined using the du Noüy ring method [71] and the capillary rise method [72]. In the former method, a Fisher Semiautomatic Model 21 Tensiometer was used to measure the force required to lift a platinum-iridium alloy ring of known dimensions through an interface. Samples were placed in a small crystallization dish. The force at the point of detachment and film rupture is related to surface tension through the relationship illustrated in Figure 29. The latter method is based upon the fact that in a narrow capillary tube, adhesion to the glass surface causes a liquid to either be seemingly drawn in or pushed out. A graduated glass capillary tube of known bore size was immersed into a solution contained in a glass cylinder. The capillary was held perpendicular to the liquid surface using a rubber stopper. The equilibrium height difference is related to surface tension through the relationship illustrated in Figure 29.

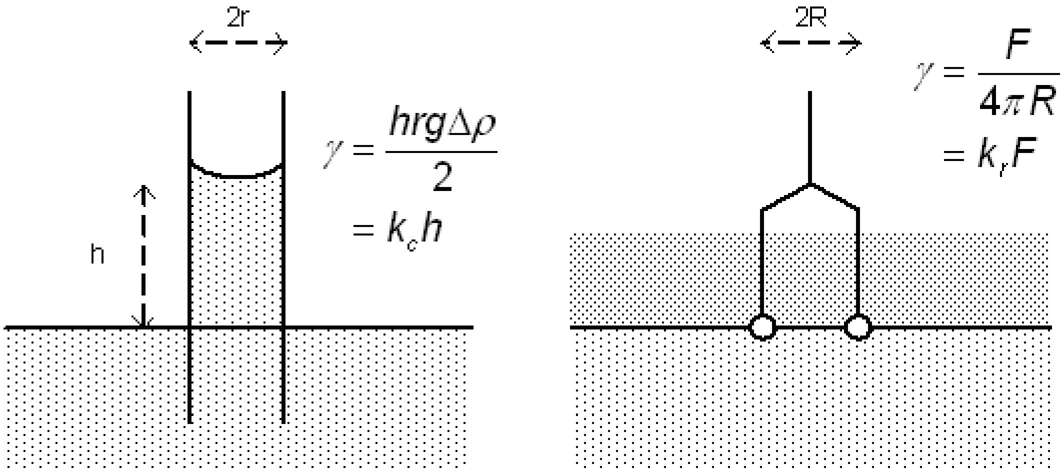


Figure 29 – Various methods used to masure surface tension. Surface tension measure using the capillary method [LEFT] and the du Noüy ring method [RIGHT]; g is the gravitational force constant, Δρ is difference in density between liquid and gas, and F is the upwards force acting on ring.

The apparatus was placed in a glove-bag attached to either an argon gas or carbon dioxide gas cylinder. A very small positive gas pressure was maintained inside of the glove-bag. In some cases, a very long period of time was required in order to reach equilibrium. Measurements were only taken with clear solutions devoid of visible suspended material. Air stones or diffusers were used in order to quickly saturate solutions.

4.1.3 Emulsion Preparation

Aqueous surfactant solutions were prepared in volumetric flasks and well mixed before use. Emulsions were prepared in 25 mm glass test tubes. The organic material was added to aqueous surfactant solution and agitated using a Scientific Industries Vortex

Genie 2 at the highest setting for a specified amount of time. The vortex mixer provided the energy required to emulsify immiscible phases.

Surfactant concentrations are reported as a weight percent based on total emulsion volume (% w/v). Surfactant concentration is therefore dependent on both the amount of water and organic material.[****]

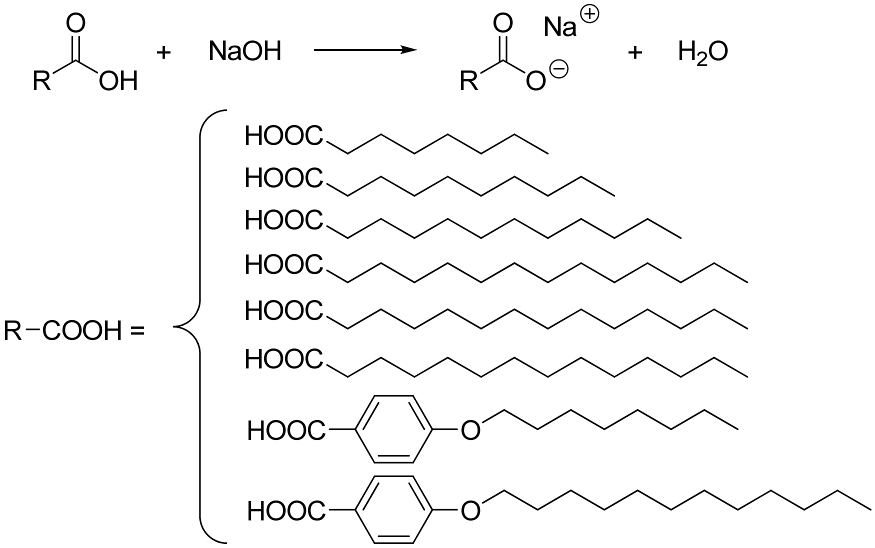
Solutions were treated with carbon dioxide, argon, or air, by bubbling the gas directly into the solution through an 18-gauge syringe needle. Gases were not pre-heated.

4.2 Surfactant Synthesis

4.2.1 Sodium Carboxylate Salts

Sodium salts of various fatty acids were prepared by reaction with sodium hydroxide in water. The synthetic pathway is illustrated in Scheme 6.

[****] An emulsion of 50 ml toluene and 50 ml water with 0.100 g of surfactant would have a surfactant concentration of 1000 ppm.



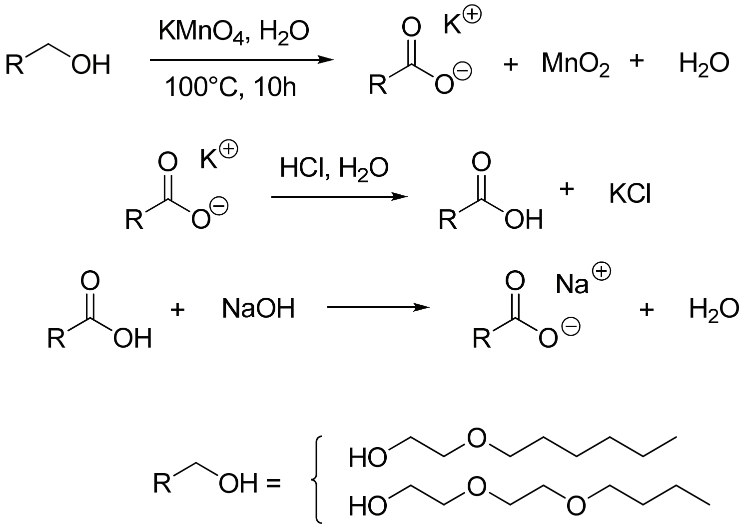
Scheme 6 – Sodium carboxylate surfactant made by treating carboxylic acid with sodium hydroxide.

A known amount of fatty acid was charged into an Erlenmeyer flask. Sodium hydroxide (1.1 equivalents) dissolved in 250 ml water was added. The reaction mixture was heated to reflux for 4 hours. Sufficient water was added to make a clear solution.

Precipitation of the carboxylate salt was achieved by cooling the solution to 0°C in an ice water bath. The solids were collected by vacuum filtration and washed with several portions of cold deionized water and diethyl ether. The solids were dried overnight in a vacuum at 60°C. The solids were crushed into fine power using mortar and pestle. White amorphous solids were recovered.

4.2.2 Ethoxylated Sodium Carboxylate Salts

Sodium salts of various carboxylic acids with ethoxylated tails were prepared by reacting an alcohol with a strong oxidant. The synthetic pathway is illustrated in Scheme 7.



Scheme 7 – Synthetic pathway to tail modified carboxylate switchable surfactants starting from an alcohol. The alcohol is oxidized to a carboxylic acid using potassium permanganate.

A known amount of alcohol was charged into a round bottom flask. Potassium permanganate (3.5 equivalents) and sodium hydroxide (3.5 equivalents) dissolved in 250 ml water was added. The reaction mixture was heated to reflux for 3 h.

A black precipitate was formed. After cooling, the solids were removed by vacuum filtration through a Büchner funnel. The filtrate was acidified using concentrated hydrochloric acid (2.0 equivalents). Water was removed under reduced pressure. Precipitates were removed by vacuum filtration through a Büchner funnel. Filtrate was distilled to yield a clear slightly yellow liquid which was characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR). The spectra were consistent with literature reports [73].

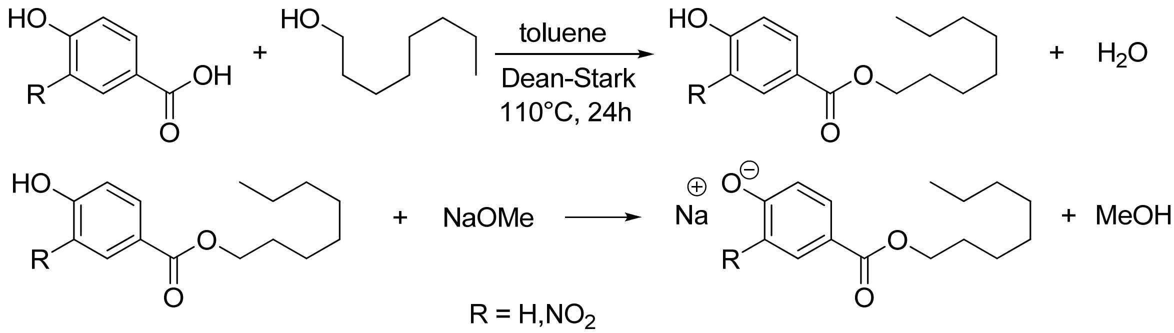
Hexyloxyacetic acid: Yield: 72%. δ_H (400MHz, $CDCl_3$) 10.4 (s, 1H), 4.12 (s, 2H), 3.52 (m, 2H), 1.61 (m, 2H), 1.22 – 1.38 (m, 6H), 0.90 (t, 3H). δ_C (400MHz, $CDCl_3$) 174.6, 72.0, 67.6, 31.5, 29.0, 25.3, 22.3, 13.6.

2-Butoxyethoxy acetic acid: Yield: 87%. δ_H (400MHz, $CDCl_3$) 11.1 (s, 1H), 4.12 (s, 2H), 3.68 (m, 2H), 3.57 (m, 2H), 3.43 (t, 2H), 1.51 (quint, 2H), 1.30 (m, 2H), 0.84 (t, 3H). δ_C (400MHz, $CDCl_3$) 174.2, 71.3, 71.1, 69.8, 68.3, 31.4, 19.1, 13.8.

A known amount of carboxylic acid was charged into an Erlenmeyer flask. Sodium hydroxide (1.1 equivalents) dissolved in minimal water was added. The reaction mixture was heated to reflux for 4 hours. Water was removed under reduced pressure to yield a clear viscous liquid.

4.2.3 Sodium Phenolate Salts

The phenolate derivatives were made by condensation of 4-hydroxybenzoic acid or 4-hydroxy-3-nitrobenzoic acid with a long chain alcohol. The synthetic pathway is illustrated in Scheme 8.



Scheme 8 – Synthetic pathway to p-alkyloxycarbonyl-phenolate switchable surfactants starting from p-hydroxy-benzoic acid derivatives.

A known amount of 4-hydroxybenzoic acid was charged into a round bottom flask. The alcohol (1.1 equivalents) was added to the reaction mixture. A Dean-Stark apparatus was attached to the reaction vessel. Sufficient toluene was added to fill the trap. The mixture was heated to reflux for two days. A toluene-immiscible liquid was trapped in the Dean-Stark apparatus.

Sodium methoxide (1.1 equivalents) was added to the reaction mixture. The reaction mixture was concentrated in a rotary evaporator under reduced pressure. The precipitate was removed by vacuum filtration. The solids were washed with additional diethyl ether and cold water. A white amorphous solid was recovered.

The solid was dissolved in deionized water and treated with excess concentrated hydrochloric acid. A white solid immediately precipitated. After cooling in an ice water bath, the solids were removed by vacuum filtration through a Büchner funnel. A light white solid was recovered and characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR). The spectra were consistent with literature reports [74].

Octyl 4-hydroxybenzoate: Yield: 96%. δ_H (400MHz, $CDCl_3$) 7.94 (d, J = 7.3 Hz, 2H), 6.87 (d, J = 7.3 Hz, 2H), 5.94 (b, 1H), 4.27 (t, 2H), 1.76 (quin, 2H), 1.43 (m, 2H), 1.28 (m, 8H), 0.87 (t, 3H). δ_C (400MHz, $CDCl_3$) 166.5, 159.8, 131.8, 122.8, 115.0, 65.0, 31.6, 29.5, 25.7, 22.6, 14.0.

A known amount of 4-hydroxy-3-nitrobenzoic acid was charged into a round bottom flask. Octanol (1.1 equivalents) was added to the reaction mixture. A Dean-Stark apparatus was attached to the reaction vessel. Sufficient toluene was added to fill the trap. The reaction mixture was heated to reflux for two days. A toluene-immiscible liquid was trapped in the Dean-Stark apparatus and removed.

Sodium methoxide (1.1 equivalents) was added to the remaining material in the flask. The reaction mixture was concentrated in a rotary evaporator under reduced pressure. The precipitate was removed by vacuum filtration. The solids were washed with additional diethyl ether and cold water. A yellow amorphous solid was recovered.

The solid was dissolved in deionized water and treated with excess concentrated hydrochloric acid. A light yellow solid immediately precipitated. After cooling in an ice water bath, the solids were removed by vacuum filtration through a Büchner funnel. A light yellow solid was recovered and characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR).

Octyl 4-hydroxy-3-nitrobenzoate: Yield: 92%. δ_H (400MHz, $CDCl_3$) 10.82 (s, 1H), 8.74 (d, J = 2.0 Hz, 1H), 8.17 (dd, J = 8.6 Hz, J = 2.1 Hz, 1H), 7.16 (t, J = 8.6 Hz, 1H), 4.26 (t, 2H), 1.71 (quin, 2H), 1.35 (m, 2H), 1.21 (b, 8H), 0.81 (t, 3H) . δ_C (400MHz, $CDCl_3$) 171.7, 158.0, 137.9, 127.2, 120.2, 65.7, 31.8, 29.2, 29.1, 28.6, 25.8, 22.7, 14.1.

4.3 Surfactant Properties

The surfactants were tested both in the presence and in the absence of carbon dioxide in order to determine if the two forms of the surfactant were readily and reversibly accessible. In addition, the surfactant's influence on a colloidal system was evaluated to determine if the shift in interfacial properties brought on by carbon dioxide was sufficient to cause significant changes to the colloidal system. The following experiments were performed in order to evaluate the critical properties of a switchable surfactant including the reversibility of the switching and the resulting changes in performance.

4.3.1 Surfactant Switching

The ability of a switchable surfactant to change forms reversibly is essential for the enhanced recycling of surfactant or process water. This reversibility was evaluated visually and confirmed by ^{1}H NMR spectroscopy.

4.3.1.1 Sodium Carboxylate Salts

At first, the reversible switching was observed visually. Saturated aqueous solutions of sodium caprylate, sodium caprate, sodium laurate, sodium myristate, sodium palmitate, sodium stearate, sodium 4-octyloxybenzoate, and sodium 4-dodecyloxybenzoate were prepared and diluted by a factor of ten[††††]. The solutions were prepared at ambient conditions. The solutions were sequentially subjected to carbon dioxide then heated to 60°C in a hot water bath and sparged with argon gas. The addition of carbon dioxide caused the solution to become cloudy and eventually form a precipitate . Heating caused the solution to become clear, even after cooling back to ambient temperature. A sample was taken after each step and the complete process for sodium 4-octyloxybenzoate is

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[††††] One part saturated solution was added to nine parts water.

presented in Figure 30. The same behaviour in water was reproduced with sodium salts of lauric acid, myristic acid, palmitic acid, stearic acid, 4-octyloxybenzoic, acid and 4-dodecyloxybenzoic acid. The acid forms of the surfactants have poor water solubility and precipitate once protonated by carbonic acid. Caprylic acid and capric acid did not switch readily. The experiment was repeated with sodium salts of hexyloxyacetic acid and 2-butoxyethoxy acetic acid. Neither compound was observed to switch readily.

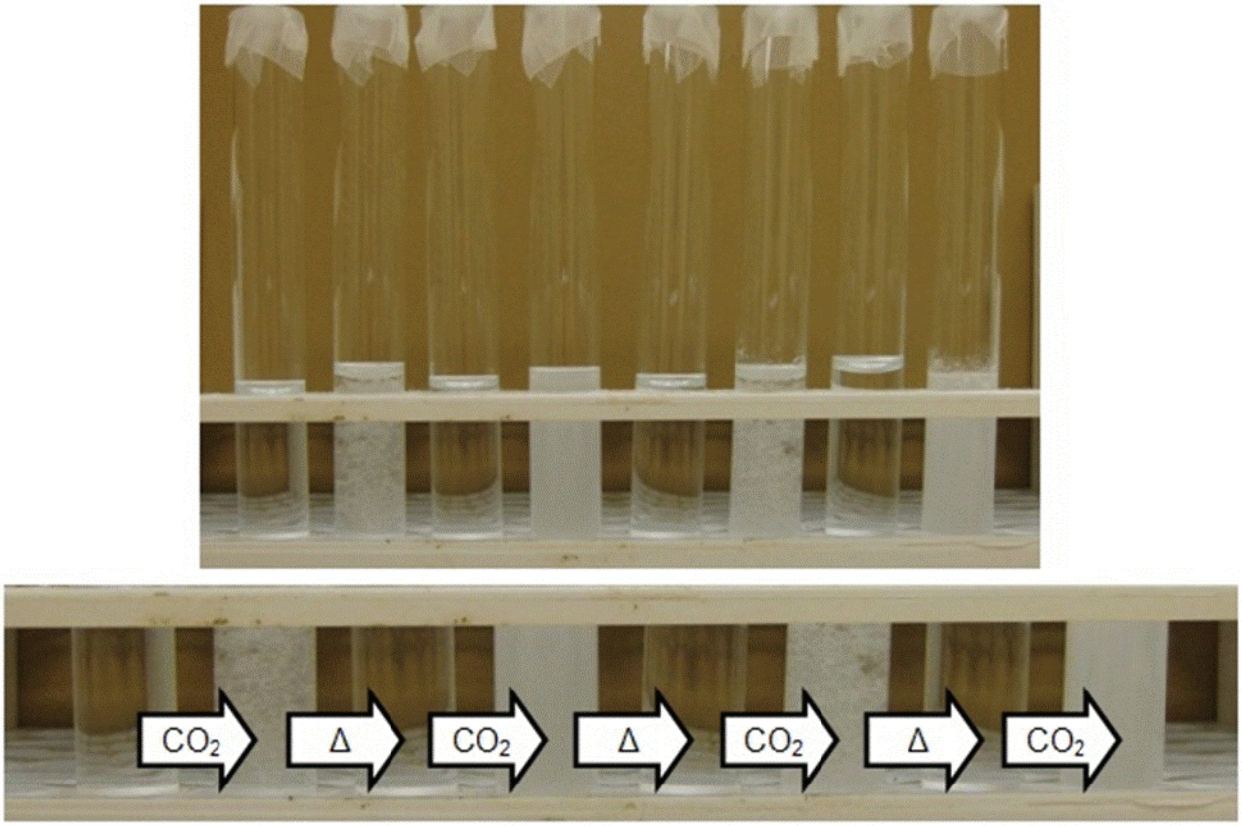
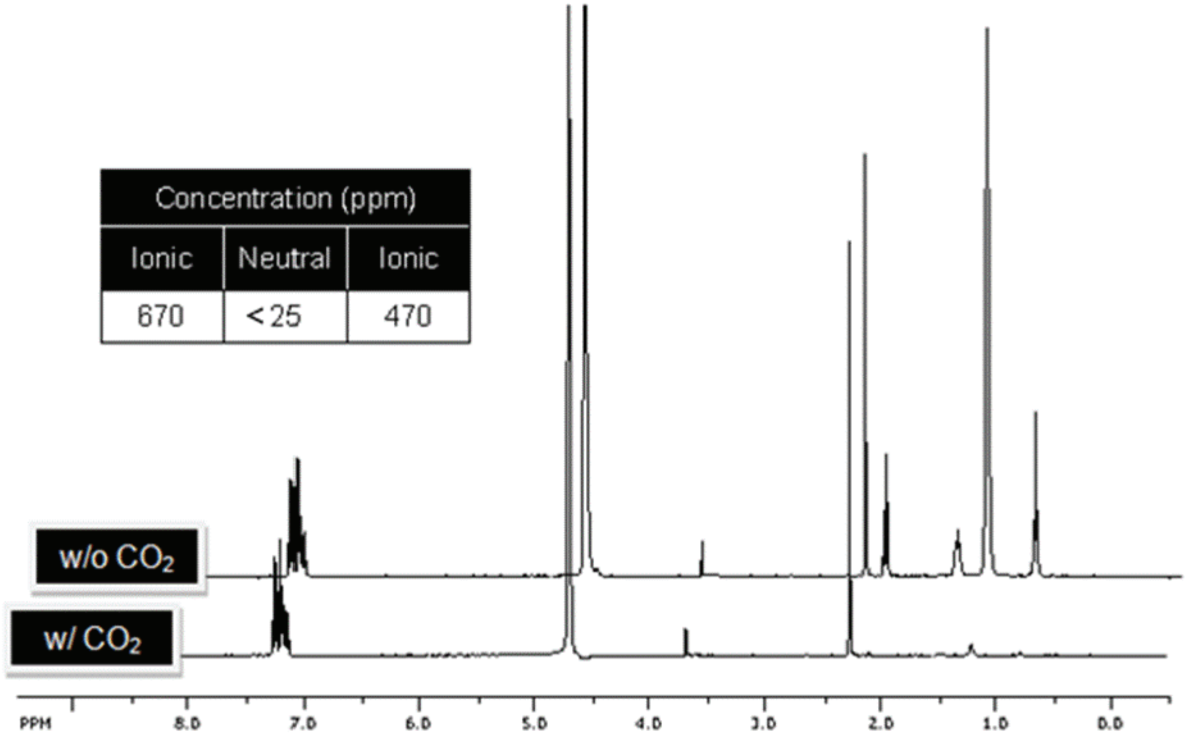


Figure 30 – Example of an anionic switchable surfactant in water. Addition of carbon dioxide to a sodium 4-octyloxybenzoate solution caused precipitation of 4-octyloxybenzoic acid. The anionic form of the surfactant was regenerated by heating in a water bath at 60°C with argon bubbling to remove dissolved carbon dioxide.

For further confirmation, the reversible switching was monitored by NMR spectroscopy. A solution of sodium laurate was prepared in deuterium oxide. An aliquot of the solution was taken before addition of carbon dioxide, after bubbling carbon dioxide into the solution for 5 min, and after heating the solution in a water bath at 60°C while bubbling argon into the solution for 5 min. Carbon dioxide caused the apparent disappearance of sodium laurate from the aqueous phase. Removal of carbon dioxide caused the sodium laurate to return. The concentrations of sodium laurate are presented in Figure 31. The concentration of sodium laurate in the aqueous phase was significantly depressed by carbon dioxide but returned after carbon dioxide was removed from the aqueous phase.



Concentration (ppm)		
Ionic	Neutral	Ionic
670	<25	470

Figure 31 – Anionic switchable surfactant evident by NMR. Disappearance of sodium laurate from aqueous phase after treatment with carbon dioxide gas. The peaks at 7.2 ppm are due to the toluene internal standard. Peaks corresponding to sodium laurate appearing below 2.2 ppm were used to determine aqueous concentration.

Switching from the anionic to the non-ionic form of the carboxylate type surfactants was possible by treating an aqueous surfactant solution with carbon dioxide gas. This process was only effective when the acid form of the switchable surfactants was poorly soluble in water. The switchable surfactant was converted back into the anionic form by heating and mixing. This process is fully reversible.

4.3.1.2 Sodium Phenolate Salts

A 1 wt% solution of nitro-4-octyloxycarbonyl phenolate was prepared in water. The solution was clear and soapy. After bubbling carbon dioxide gas into the solution for 5 min, a white solid precipitated and was identified as 4-octyloxycarbonyl phenol by ^{1}H NMR spectroscopy in $CDCl_3$. The solution was also no longer soapy. Attempts to reverse the process by removing carbon dioxide were unsuccessful. A clear solution was not formed after prolonged heating in a water bath at 60˚C and bubbling of argon. The surfactant could only be activated again using an additional equivalent of base such as sodium carbonate or sodium hydroxide. The solution is clear after additional base was added.

A 1 wt% solution of sodium 4-octyloxy-3-nitrobenzoate was prepared. The solution is clear, orange, and soapy. The solution was sequentially subjected to carbon dioxide then heated to 60°C in a hot water bath and sparged with argon gas. Carbon dioxide caused the solution to become cloudy. The solid precipitate was identified as 2-nitro-4-octyloxycarbonyl phenol acid by ^{1}H NMR spectroscopy in $CDCl_3$. Heating, mixing, and sparging with argon caused the sodium salt to reform. A sample was taken after each step and the complete process is illustrated in Figure 32.

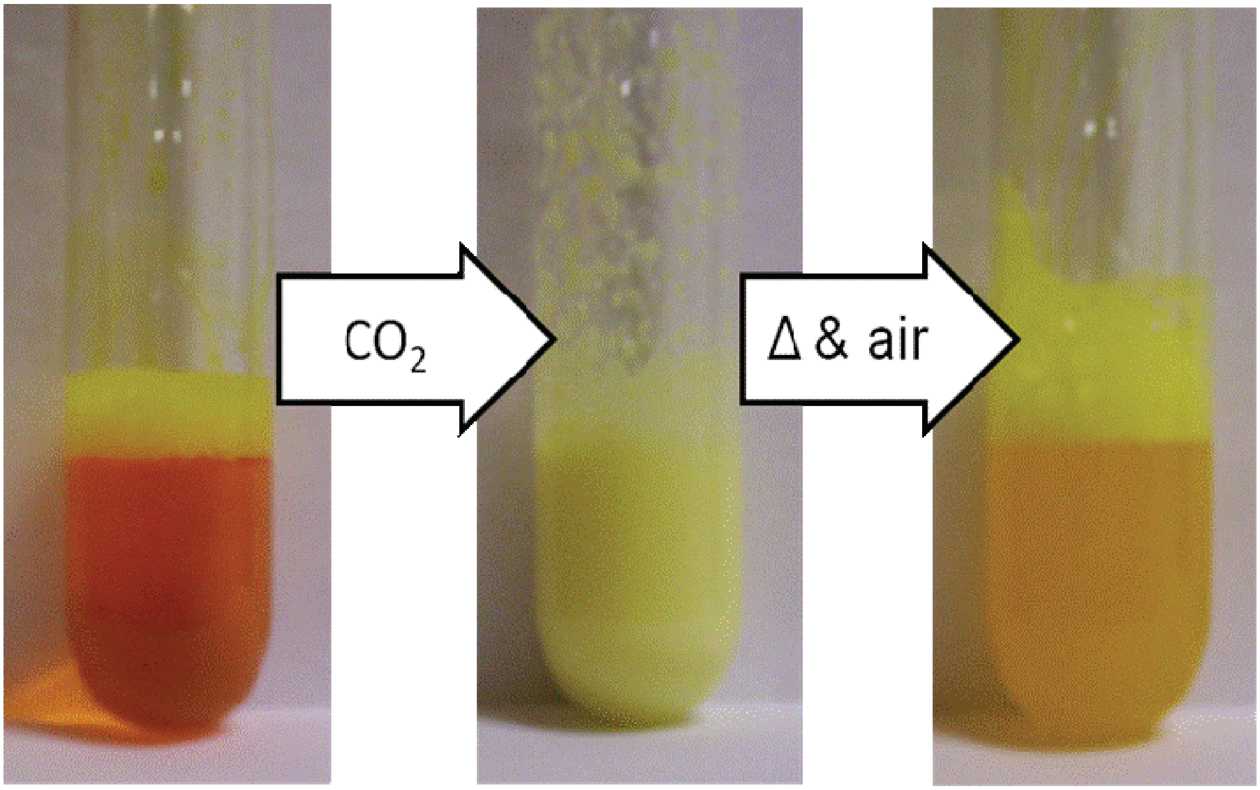


Figure 32 – Example of an anionic switchable surfactant in water. Addition of carbon dioxide to a sodium 2-nitro-4-octyloxycarbonyl phenolate solution caused precipitation of octyl-4-hydroxy-3-nitrobenzoate. The sodium salt was regenerated by heating in a water bath at 60°C argon bubbling to remove dissolved carbon dioxide.

4.3.2 Surface Tension

The surface or interfacial tension of a biphasic mixture is influenced by the presence of surface-active compounds. In the case of a switchable surfactant, where two or more forms of the surfactant exist, the interfacial tension can be controlled by switching the surfactant between its two forms. Whether this can be achieved with the new switchable anionic surfactants was evaluated by measuring surface or interfacial tension while various forms of the surfactant are present.

The effect of sodium laurate and lauric acid on the interfacial tension of n-heptane, water, and air is presented in Table 23. Surface and interfacial tension was measured using the ring method for a biphasic mixture of 50 ml of n-heptane and 50 ml of water. With the addition of carbon dioxide, a solution of sodium laurate was converted into a solution that behaved comparably to a solution of lauric acid. In these experiments, carbon dioxide was added to the biphasic mixture until both layers were clear and devoid of any insoluble material.

Table 23 – Surface tension and interfacial tension of n-heptane and water with sodium laurate switchable surfactant. Surfactant concentration was 4.3 mM.

Interface	Interfacial Tension (dynes/cm)			
	CTRL	RCOOH	RCOONa	RCOONa w/CO_2
heptane/air	23.0	22.5	–	22.3
water/air	72.6	–	33.0	72.4
heptane/water	49.4	39.7	32.8	37.3

The effect of sodium 4-octyloxybenzoate and 4-octyloxybenzoic acid on the interfacial tension of toluene, water, and air is presented in Table 24. Surface and interfacial tension was measured for a biphasic mixture of 50 ml of toluene and 50 ml of water. With the addition of carbon dioxide, a solution of sodium 4-octyloxybenzoate was converted into a solution that behaved comparably to a solution of 4-octyloxybenzoic acid. In these experiments, carbon dioxide was added to the biphasic mixture until both layers were clear and devoid of any insoluble material.

Table 24 – Surface tension and interfacial tension of toluene and water with sodium 4-octyloxybenzoic switchable surfactant. Surfactant concentration was 1.5 mM.

Interface	Interfacial Tension (dynes/cm)			
	CTRL	RCOOH	RCOONa	RCOONa w/CO_2
toluene/air	30.4	29.9	–	30.1
water/air	72.6	–	58.7	70.8
toluene/water	32.3	31.3	27.6	31.7

The change in surface activity between the anionic and neutral forms of the switchable surfactants brought on by bubbling of carbon dioxide was detected by measuring surface tension and interfacial tension. Carbon dioxide was successfully used to cause reversible changes to both the surface tension and the interfacial tension of biphasic mixtures containing a switchable surfactant. The change in surface tension did not require additional surfactants.

4.3.3 Emulsion Stability

Control of emulsion stability can be achieved by adjusting the properties of the interface [22]. This is often achieved by addition of surface active compounds in order to complement or counteract stabilization (*i.e.* lower or raise interfacial tension). Using the switchable surfactants described previously, emulsion stability may be controlled using carbon dioxide. Emulsions stabilized with anionic switchable surfactants would break once exposed to carbon dioxide. Removal of dissolved carbon dioxide by heating and/or bubbling an inert gas such as air or nitrogen would cause stability to return.

4.3.3.1 Breaking Emulsions

Emulsions made of 10 ml n-heptane and 10 ml deionized water were stabilized using various surfactants according to Table 25. The emulsions were prepared by dissolving the surfactant in the aqueous phase. The organic phase was then added and the mixture was mixed using a vortex mixer for 1 min, creating an emulsion.

Table 25 – Emulsions of n-heptane and water stabilized using various surfactants.

Sample	Surfactant	Concentration (ppm)
A	None	n/a
B	Sodium lauryl sulfate	1300
C	Sodium laurate	1200
D	Sodium p-octyloxybenzoate	600

Carbon dioxide was bubbled through a long syringe needle into each sample for approximately 30 s. Foam was initially formed. However, the amount of foam diminished after continued addition of carbon dioxide for emulsion samples stabilized with sodium laurate or sodium 4-octyloxybenzoate. The emulsion sample stabilized with sodium lauryl sulfate did not stop generating foam even after prolonged bubbling of carbon dioxide. Addition of any gas to emulsions stabilized with sodium lauryl sulfate was difficult due to loss of material through exhaust. The organic and aqueous phases of the emulsion samples containing either sodium laurate or sodium 4-octyloxybenzoate were entirely clear and each phase was distinct after settling overnight. This can be seen in photographs of samples presented in Figure 33. The emulsion stabilized using sodium lauryl sulfate did not separate after carbon dioxide bubbling. The top layer remained semi-opaque and formed a gel. This gel was stable for over two weeks.

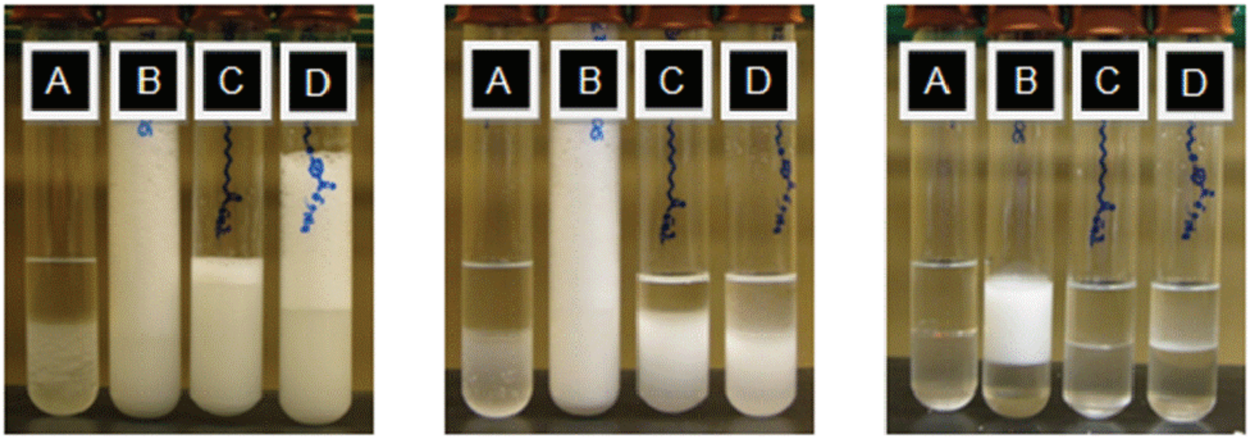


Figure 33 – Phase separation of n-heptane water emulsions. The stabilized emulsions [LEFT] were treated with carbon dioxide [MIDDLE]; complete phase separation occurred within twelve hours for switchable surfactants while SDS caused gelling in the top layer [RIGHT].

The addition of carbon dioxide to the emulsion stabilized with sodium lauryl sulfate did not cause visible phase separation. The addition of argon to an emulsion stabilized with sodium laurate also did not cause visible phase separation. In both cases, the surfactant remained in an active form stabilizing foam. The addition of carbon dioxide to an emulsion stabilized with sodium laurate caused immediate phase separation. The surfactant after reacting with carbon dioxide lost the ability to stabilize emulsions of water and heptane. Thus, carbon dioxide was successfully used to break emulsions stabilized using various switchable surfactants. The onset of phase separation occurred immediately after the addition of carbon dioxide. Broken emulsions separated into distinct layers. Carbon dioxide did not promote the breaking of emulsions stabilized with non-switchable surfactants such as sodium lauryl sulfate.

4.3.3.2 Emulsion Regeneration

A surfactant solution was made by dissolving 514 mg sodium laurate into 250 ml deionized water. Four emulsions (labelled C – F) were prepared using 10 ml of this sodium laurate solution and 10 ml n-heptane. A control sample (sample A) was made using 10 ml deionized water and 10 ml n-heptane. An additional emulsion (sample B) was made with 10 ml of 1000 ppm sodium lauryl sulfate solution and 10 ml n-heptane. Each sample was mixed using a vortex mixer for 1 min. Sample D was treated with argon through a long syringe needle for 30 s. Sample E was treated with carbon dioxide for 30 s. Sample F was treated with carbon dioxide for 30 s then warmed in a water bath at 60°C and treated with argon for another 30 s. Each sample was mixed again for 1 min and placed in a test tube rack at ambient conditions. Photographs were taken after 5 min, 20 min, 40 min, 80 min, and 180 min and are presented in Figure 34.

Emulsions containing sodium laurate were unaffected by argon bubbling but broke after similar treatment using carbon dioxide gas. The separated mixture was heated and purged with argon in order to re-generate the high HLB form of the surfactant. An emulsion of water and heptane was stabilized after this process. The stabilized emulsion was opaque and appeared white in colour.

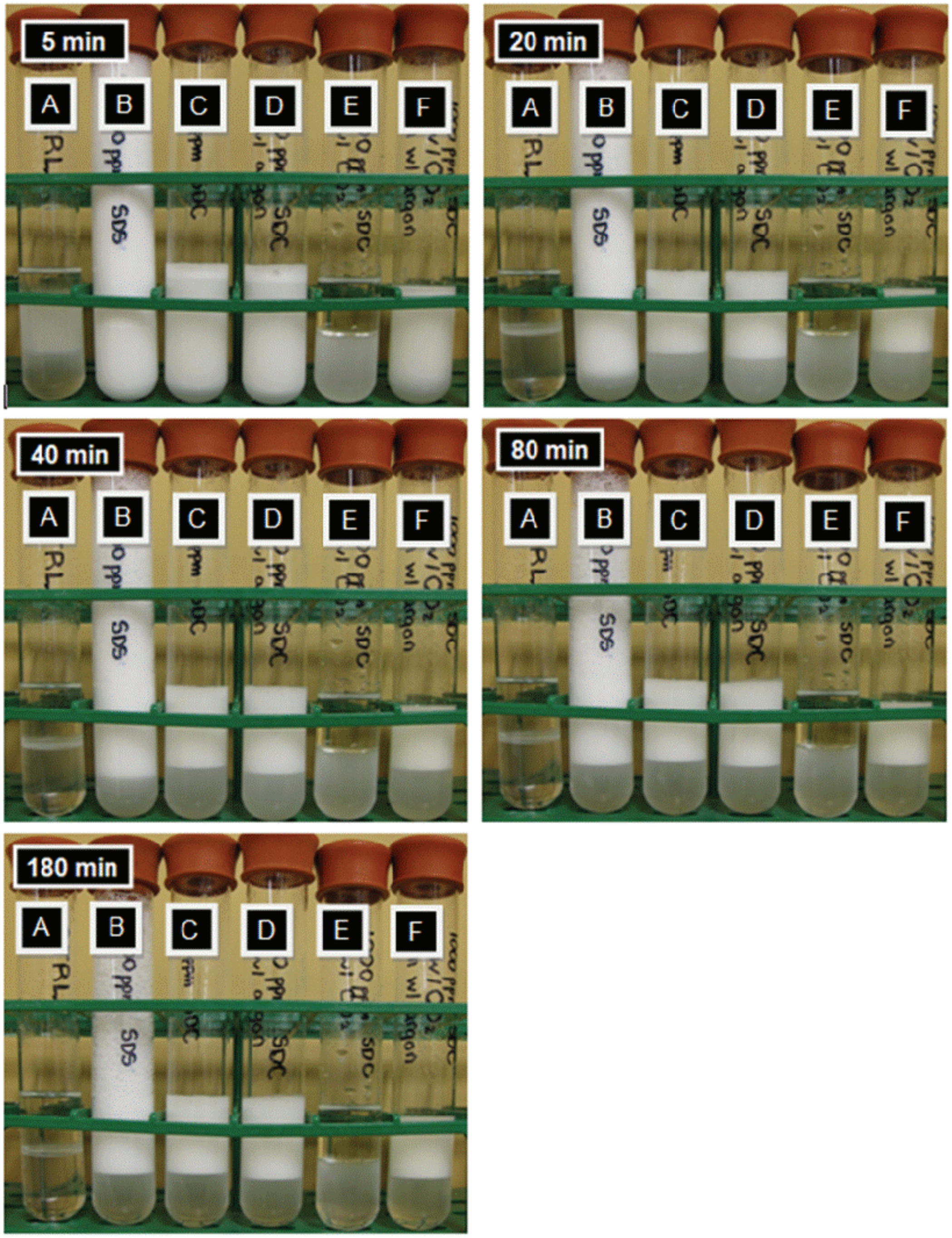


Figure 34 – Phase separation of n-heptane water emulsions. Sample A did not contain any surfactant. Sample B contained 1000 ppm sodium lauryl sulfate. Sample C – F contained 1000 ppm sodium laurate. Addition of carbon dioxide caused the emulsion stabilized by sodium laurate to separate immediately, leaving a clear organic layer (Sample E).

In the previous example, heat was used to re-generate the high HLB form of the switchable surfactant. This may not be necessary, as the un-charged form of the carboxylic acid switchable surfactants should be sufficiently acidic to react with bicarbonate in aqueous solutions. In order to confirm this, a similar experiment was performed without any heating.

Identical emulsion samples were prepared and similarly treated with argon or carbon dioxide gas (sample A – F). Heat, however, was not applied to re-generate the high HLB form of the surfactant in sample F. Instead, only argon was bubbled into the separated mixture. Photographs were taken after 5 min, 15 min, 30 min, and 45 min and are presented in Figure 35.

The emulsion in sample F was previously stabilized with sodium laurate but de-stabilized by the bubbling of carbon dioxide. The emulsion was stabilized again after argon was used to purge the phase separated mixture of dissolved carbon dioxide. The emulsion was opaque and appeared white in colour. Phase separation in emulsion sample F was evident after 15 min. This suggests that brief treatment with argon without heating is not as effective in converting surfactant back to the ionic form that stabilized emulsions. The emulsion in sample E was not purged of carbon dioxide and thus failed to form an emulsion.

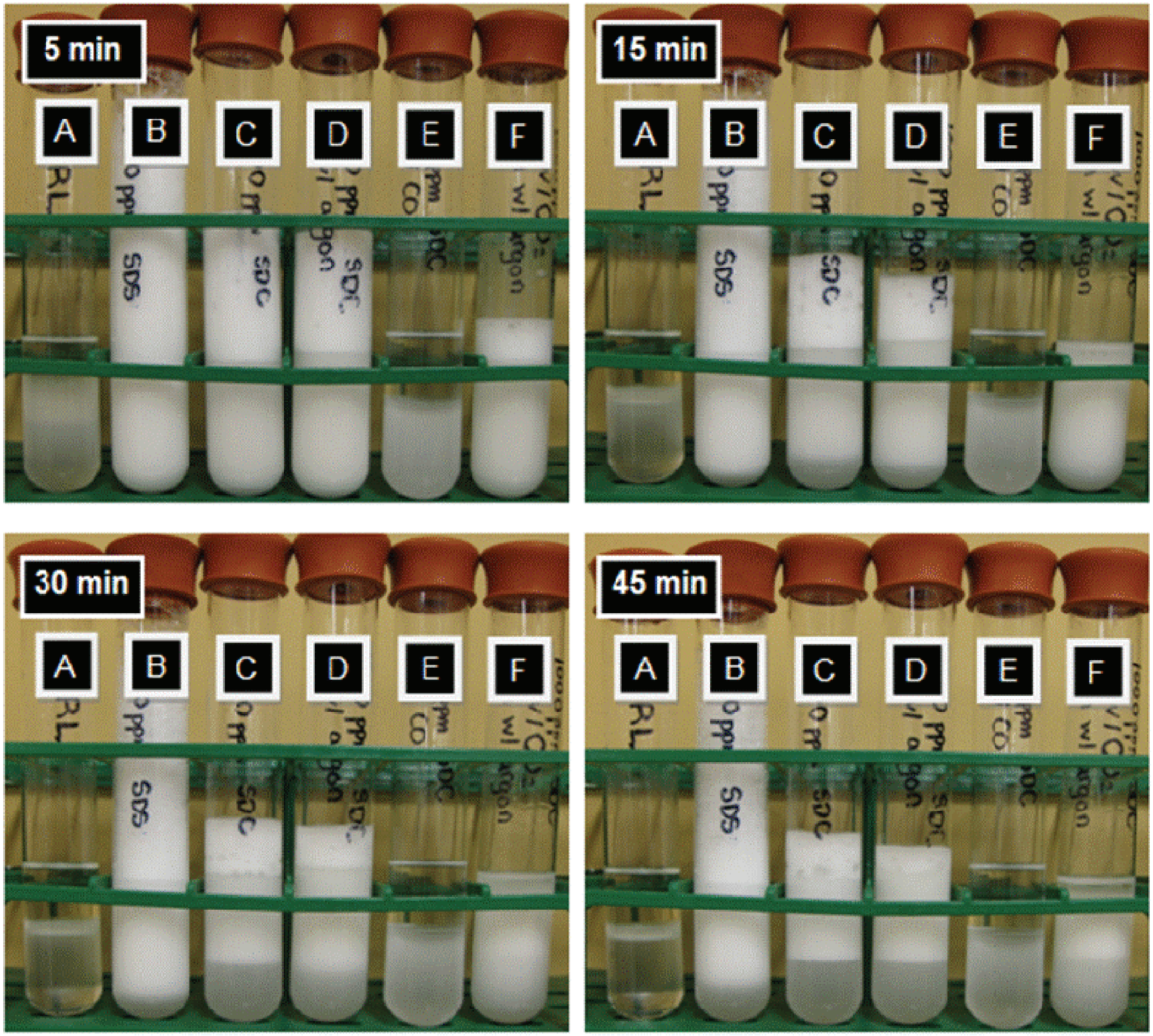


Figure 35 – Phase separation of n-heptane water emulsions. Addition of carbon dioxide caused the emulsion stabilized by sodium laurate to separate immediately, leaving a clear organic layer.

Sodium 4-octyloxybenzoate has lower water solubility in both anionic and non-ionic forms when compared to sodium laurate. Sodium 4-octyloxybenzoate exhibited similar properties as a switchable surfactant. A surfactant solution was made by dissolving 50 mg sodium 4-octyloxybenzoate into 250 ml deionized water. Four emulsions samples (labelled C – F) were prepared using 10 ml of the sodium laurate solution and 10 ml n-heptane. A control sample (Sample A) was made using only 10 ml deionized water and 10 ml n-heptane. An additional emulsion (Sample B) was made with 10 ml of 1000 ppm sodium lauryl sulfate solution and 10 ml n-heptane. Each sample was mixed using a vortex mixer for 1 min, creating emulsions. Sample C was not treated with anything and formed a stable emulsion. Sample D was treated with argon for 30 s. Sample E was treated with carbon dioxide for 30 s. Sample F was treated with carbon dioxide for 30 s then warmed in a water bath at 60°C and treated with argon for another 30 s. Each sample was mixed again for 1 min and placed in a test tube rack at ambient conditions. Photographs were taken after 5 min and 20 min and are presented in Figure 36.

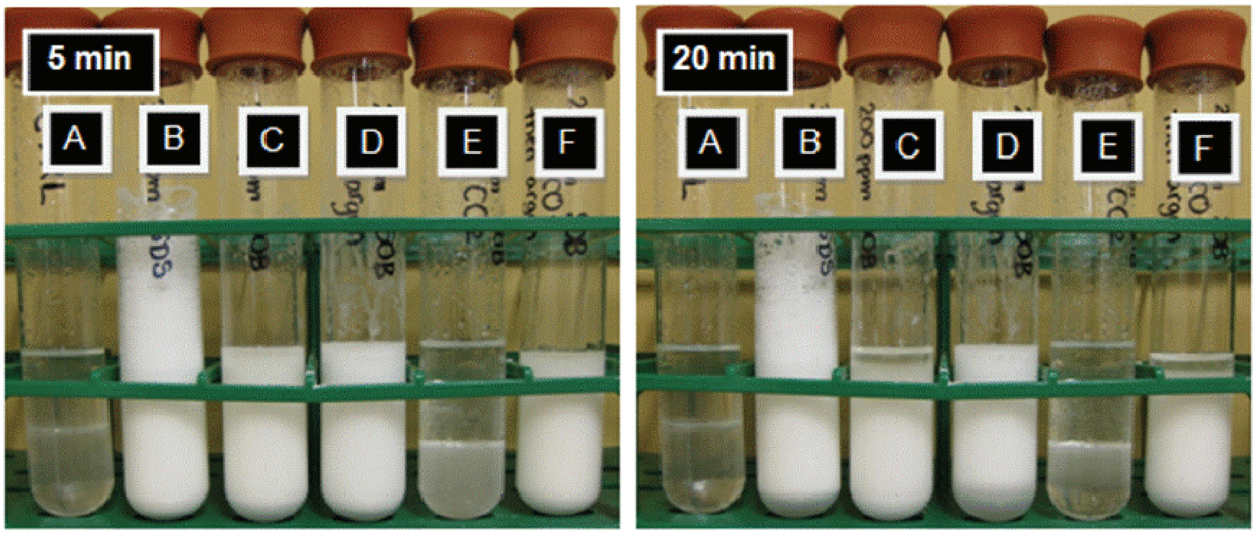


Figure 36 – Phase separation of heptane water emulsions. Addition of carbon dioxide caused the emulsion stabilized by sodium 4-octyloxybenzoate to separate immediately, leaving a clear organic layer.

The emulsion in sample F was previously stabilized with sodium 4-octyloxybenzoate but de-stabilized by bubbling of carbon dioxide. The emulsion was stabilized after argon was used to purge the phase-separated mixture of dissolved carbon dioxide. The emulsion was opaque and appeared white in colour. The emulsion in sample E was not purged of carbon dioxide and thus failed to form an emulsion.

Emulsions stabilized with sodium laurate or sodium 4-octyloxybenzoate were successfully broken using carbon dioxide gas. The broken emulsions were stabilized once again after re-generation of the high HLB form of the switchable surfactant by heating to 60˚C, bubbling with argon, and mixing.

4.4 Discussion

Treating an aqueous solution of a carboxylate, phenolate, or benzoate type anionic switchable surfactant with carbon dioxide results in a chemical reaction wherein the anion is protonated to the corresponding carboxylic acid, phenol, or benzoic acid, respectively. The anionic surfactants' ability to switch from anionic to neutral form with carbon dioxide may have been facilitated by the hydrophobic nature of the neutral form. The presence of an immiscible phase acted as a sink, allowing the weaker carbonic acid to protonate a stronger acid. This concept is illustrated in Figure 37.

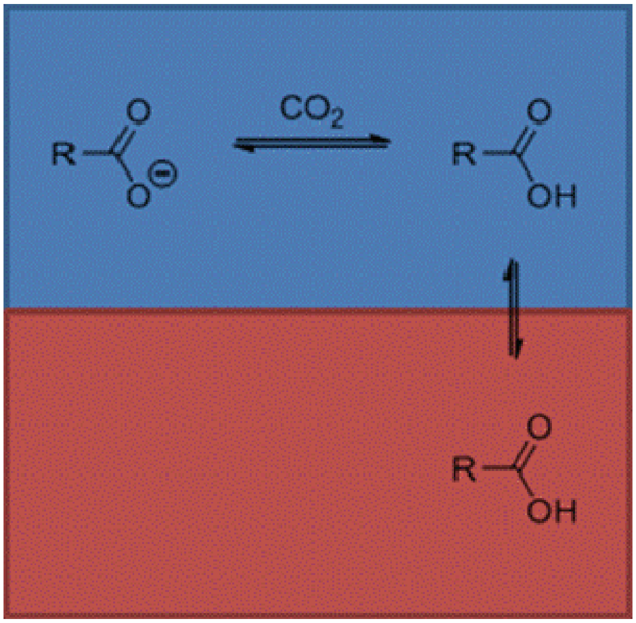


Figure 37 – Illustration of anionic siwtcahble surfactant system. Carbon dioxide is able to convert a sodium carboxylate surfactant into its neutral form despite an unfavourable equilibrium constant in the aqueous phase. The preferential partitioning of the free acid into an immiscible phase may help to push the equilibrium towards the neutral acid.

The two most important factors that made switching possible are solubility and acidity. The poor water solubility allowed carbon dioxide to lower the ionic character of a surfactant by suppressing the anionic charge. The acidity of the surfactant allowed for the reverse reaction with bicarbonate after removal of dissolved carbon dioxide gas.

4.4.1 Solubility

The hydrophobic character of a carboxylic acid is dependent on the hydrocarbon chain length and the chemical nature of any substituent. With increasing hydrocarbon chain length, the acid loses water solubility and partitions preferentially in non-aqueous solvents. The solubility of common fatty acids is presented in Table 26.

Table 26 – The absolute aqueous solubilities and relative solubilities of carboxylic acids of various length [75, 76]. Measurements were taken between 20 − 25˚C.

Compound	Carbon Number	Aqueous Solubility (g/L)	Octanol-Water Partition Coefficient (log P_{OW})
Hexanoic acid	6	9680	1.92
Caprylic acid	8	680	3.05
Capric acid	10	150	4.09
Lauric acid	12	55	4.60
Myristic acid	14	20	6.11
Palmitic acid	16	7	7.17
Stearic acid	18	3	8.23

Designing a carbon dioxide responsive anionic switchable surfactant with poor water solubility is an effective strategy when the surfactant head group is more acidic than carbonic acid. Surfactants with greater aqueous solubility experience difficulty switching to the non-ionic form in the presence of carbon dioxide. This was observed for the sodium salts of carboxylic acids with ethoxylated tails. The neutral form of the carboxylic acid surfactants derived from E_1C_6 and E_2C_6 were soluble in water. No visible precipitation occurred when carbon dioxide was bubbled into an aqueous surfactant solution at room temperature.

Solubility will determine the equilibrium concentrations of both surfactant forms in all phases. A comprehensive understanding of solubility will be essential to successful applications of the carboxylate-type switchable surfactants.

4.4.2 Acidity

In order for the anionic switchable surfactants to become truly reversible, the non-ionic form must be acidic enough to react with bicarbonate. Table 17 summarizes the acidity of various related compounds.

Carboxylic acids are very acidic and will deprotonate readily in the presence of a weak base such as sodium bicarbonate. Carboxylic acids are in fact acidic enough to be deprotonated in water at neutral pH. In this case, only the poor solubility of fatty acids prevents deprotonation and formation of a carboxylate anion.

Weaker acids such as 4-octyloxycarbonylphenol do not react with sodium bicarbonate and cannot be considered truly switchable. Once protonated by carbonic acid, 4-octyloxycarbonylphenol requires addition of a stronger base such as sodium carbonate or sodium hydroxide in order to be reconverted to a salt. The phenol switchable surfactant was made to be more acidic by installing an electron-withdrawing group. Additional resonance stabilization of the anion, provided by the nitro group, increases the acidity of the molecule. 4-Octyloxycarbonyl-3-nitrophenol reacted with sodium bicarbonate to form a water-soluble salt and thus can be considered a switchable surfactant.

4.5 Summary

Various anionic switchable surfactants were developed. The surfactants have two general forms: an ionic high HLB form and a non-ionic low HLB form. The surfactants can reversibly interchange between these two forms. The triggers for these transformations are only carbon dioxide (for the conversion to the non-ionic form) and inert gases (for the conversion to the ionic form). Additional heating accelerates the conversion to the ionic form. Examples of the switchable anionic surfactants include carboxylic acids, benzoic acids, and 4-alkylcarbonyl-3-nitophenols. Interfacial properties such as surface tension, emulsion stability, and foam stability were controlled using the anionic switchable surfactant system.

Chapter 5 – Reversible Stability Latex

Traditional methods of destabilizing latex suspensions include addition of electrolytes or lowering of the pH [77, 78]. The addition of electrolytes is irreversible and the dispersant cannot be reused without first removing the additives. Although adding base will reverse the effect on the pH, this generates a salt that again cannot be easily removed. Removing hydrochloric acid or sodium chloride from water often requires distillation, a very energy intensive process. The use of a milder method of destabilization could potentially lower the cost of production.

Latex polymer particles stabilized with anionic switchable surfactants can be destabilized by changing the nature of the surfactant. Treating latex with carbon dioxide would cause polymer particles to lose electrostatic stabilization leading to aggregation, as illustrated in Figure 38. The ability to trigger destabilization using carbon dioxide would reduce the overall cost of manufacturing and allow easiery recycling of process water. Replacing chemical additives such as hydrochloric acid would also decrease the environmental impact of making polymers by emulsion polymerization.

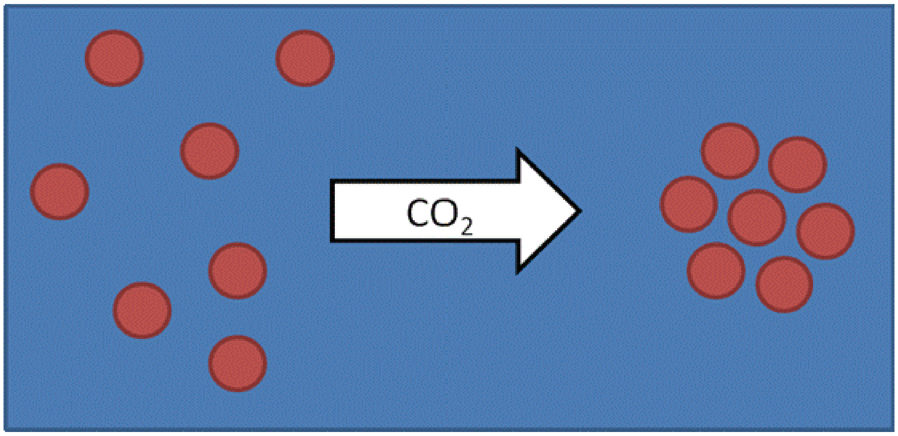


Figure 38 – Illustration of triggered particle aggregation in a latex dispersion. Colloidal polymer particles with reversible stability are capable of aggregation when an appropriate trigger is applied. For example, latex suspensions made with anionic switchable surfactant can be destabilized by the application of carbon dioxide.

In conventional latex formulations, de-stabilization is irreversible. Many latex products such as water-based coatings and paints are shipped as stabilized dispersions despite the low solids content. The transportation of water contributes to increased cost of shipping. No alternatives currently exist to solve this problem.

Using polymer particles that have reversible colloidal stability, the latex product can be prepared from polymer aggregates prior-to-use. Shipping only the concentrated aggregates would eliminate the added cost of transporting a dispersant such as water for latex paint.

Towards the end of my research time, I began preliminary tests of these concepts. Because there was insufficient time to complete the development of latex suspensions with reversible stability, the material in this chapter should not be considered comprehensive or complete and is meant only to provide a brief account of on-going research into switchable surfactant technology. Nevertheless, the results were considered sufficiently encouraging that their description here was judged worthwhile.

5.1 Experimental

5.1.1 Materials

Chemicals, reagents, solvent, and other material were used as received without further purification or treatment unless specified otherwise. Deionized water was supplied from a Millipore MilliQ® Ultrapure Water purification system. In house compressors provided air. Sources of chemical reagents, solvents, and other chemical agents are summarized in Table 27. 4-Tert-butylcatechol inhibitor was removed from styrene using an inhibitor removal column available from Sigma-Aldrich (product no. 306320).

Table 27 – Chemical reagents used to make polystyrene by emulsion polymerization.

Compound	Supplier	Lot No.
Styrene, 99%	Sigma-Aldrich	03911JJ
Inhibitor removal column	Sigma-Aldrich	93097PJ
Potassium persulfate, 98%	Acros Organics	A0203699
Carbon dioxide 4.0	Praxair	n/a

5.1.2 Particle Size and Zeta Potential

The size of polymer particles was determined using both dynamic and static light scattering methods [79]. Malvern Instruments Mastersizer 2000 was used to measure particle above 1 µm. Malvern Instruments Zetasizer Nano was used to measure particles below 1 µm. Zeta potential measurements were made using Malvern Instruments Zetasizer Nano with disposable folded capillary cells.

5.2 Emulsion Polymerization

Polymer particles were prepared by emulsion polymerization. This method has distinct advantages over bulk polymerization. The product of emulsion polymerization is stabilized latex of small polymer particles usually below 1 µm in diameter. The use of carboxylate surfactant is only historically significant as emulsion polymerization is now more commonly performed using sulfate, phosphate, and non-ionic surfactants.

Surfactant solutions were prepared by dispersing approximately 0.1 g of surfactant in 10 ml deionized water in a 25 mm diameter test tube sealed with a rubber septa and a small magnetic stir bar. The surfactant was well dispersed in an ultrasonic bath for 5 min. Uninhibited styrene (2.0 ml) was added to the reaction mixture. The Inhibitor in the styrene had previously been removed using a pre-packed inhibitor removal column. The amount of initiator specified in Table 28 was added to the reaction mixture. The test tube was then placed into a pre-heated oil bath at 70°C for 4 h and stirred at 1200 rpm.

Table 28 – Concentration of various surfactants and potassium persulfate initiator used in emulsion polymerization of styrene.

Sample	Surfactant	Amount (g)	Surfactant Concentration[‡‡‡‡] (mol%)	Initiator Concentration[§§§§] (mol%)
A	Sodium stearate	0.1020	1.9	0.6
B	Sodium palmitate	0.1010	2.1	0.4
C	Sodium myristate	0.1078	2.3	0.7

After 4 h reaction time, the sample was cooled to room temperature. The latex suspension appeared as a white solution with a distinctive bluish tint when held up to a light. The latex suspensions were stable for over one month without any visual signs of aggregation. The analysis of the latex is summarized in Table 29. The particles were very small and stabilized by electrostatic charges on the surface, as confirmed by the zeta potential.

[‡‡‡‡] The surfactant concentration is calculated based on the amount of styrene.

[§§§§] The initiator concentration is calculated based on the amount of styrene.

Table 29 – Properties of latex suspensions made by emulsion polymerization of styrene using anionic switchable surfactants.

Sample	Surfactant	Particle Diameter (nm)	Polydispersity Index	Conductivity (mS/cm)	Zeta Potential (mV)
A	Sodium stearate	38.9	0.221	0.144	- 46.8
B	Sodium palmitate	34.5	0.168	0.208	- 54.9
C	Sodium mystirate	32.9	0.201	0.214	- 47.3

5.3 Latex Destabilization and Aggregation

As described in Section 4.3.3, carbon dioxide can be used to protonate carboxylate surfactants and was destabilize of various emulsions. By analogy, it was believed that treatment of a carboxylate salt-stabilized latex suspension with carbon dioxide would destabilize the suspension and allow the polymer particles to aggregate together because electrostatic repulsion would no longer be present. The following experiments attempted to recover polystyrene particles using hydrochloric acid, sodium chloride, or only carbon dioxide gas.

A polystyrene latex suspension can be destabilized by the addition of an acid or electrolyte. Latex suspensions were prepared by emulsion polymerization of styrene using sodium stearate, sodium palmitate, and sodium mystirate, as described in Section 5.2. Approximately 3 ml of the latex suspension was diluted into 30 ml of deionized water. Addition of 5 ml 0.1 M hydrochloric acid solution to a latex suspension results in immediate aggregation. The aggregates are large and sink to the bottom. Addition of 5 ml of saturated sodium chloride solution to latex suspension also causes immediate aggregation. The aggregates are smaller and float to the surface. Destabilization of polystyrene latex containing sodium stearate is shown in Figure 39. Similar results were achieved with latex suspensions stabilized with sodium palmitate and sodium mystirate.

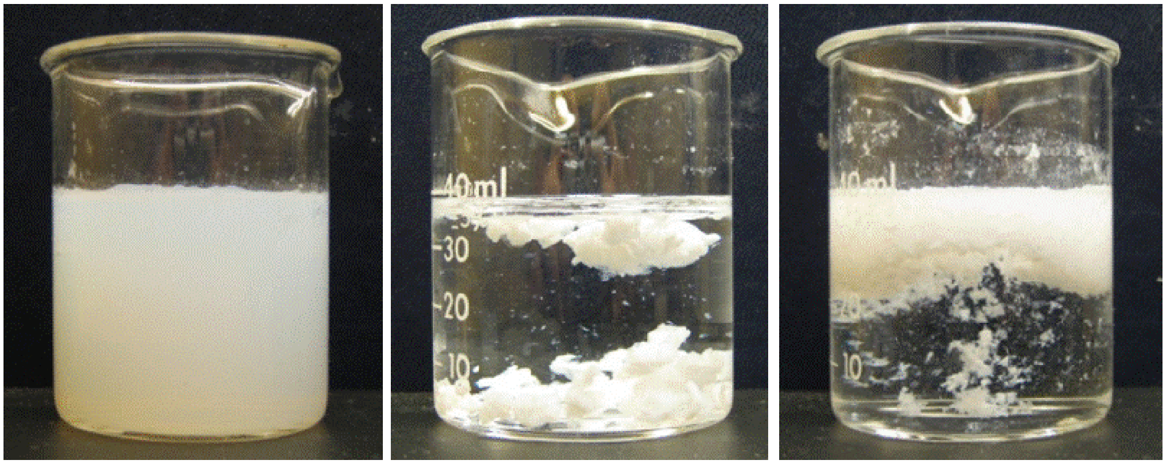


Figure 39 – Pictures of various methods used to destabilize a latex. A diluted polystyrene latex suspension [LEFT] was destabilized by conventional methods: 0.1 M hydrochloric acid solution [MIDDLE] or saturated sodium chloride solution [RIGHT].

Various latex samples were destabilized with carbon dioxide. 2.0 ml of latex suspension was placed in a fritted glass funnel containing approximately 40 ml deionized water. The fritted glass funnel served as aerator and generated large amount of small gas bubbles. Addition of carbon dioxide caused the polymer particles to aggregate and float to the surface of the water. A slurry of polymer particles floated to the surface of the solution. The particle slurry was skimmed off from the surface using a spatula or slotted spoon. The recovery process is shown in Figure 40. A very fine free flowing powder was recovered after allowing the slurry to air dry overnight.

Figure 40 – Separation and recovery of polystyrene particles from a stable latex. Treating latex with carbon dioxide caused particle aggregation. The particle aggregates floated to the surface along with the carbon dioxide bubbles. The particles were now hydrophobic and did not disperse back into solution to form a latex suspension. The particle aggregate slurry was easily separated. Air-drying slurry yielded a fine free flowing powder [INSERT].

The analysis of the particles, summarized in Table 30, revealed that much larger polymer particle aggregates had formed. The particle aggregates were approximately 100 μm in diameter. The particle aggregates were neither soluble nor suspendable in water and the zeta potential of the de-stabilized aggregates could therefore not be measured using the zetasizer instrument. The particle size distribution increased after aggregation. The aggregate slurry had a much higher solids content than the original latex dispersion..

Table 30 – Particle size analysis of styrene latex particles aggregated using the carbon dioxide flotation method.

Sample	Surfactant	Particle Diameter (µm)	Uniformity
A	Sodium stearate	113	0.595
B	Sodium palmitate	114	0.575
C	Sodium mystirate	104	0.551

In conclusion, the addition of carbon dioxide to polymer particles with switchable stability caused aggregation. The aggregates were recovered as a slurry and easily separated from the solution.

5.4 Latex Re-dispersion

The polymer aggregates may be re-dispersed as a new latex suspension if the stabilization mechanism can be restored. The polystyrene particle aggregate slurry, as described above, was diluted with deionized water heated to 60°C. The aggregates were not dried before re-dispersion. The sample was shaken and immersed in an ultrasonic bath for 5 s. The stabilized polymer latex formed from aggregated particles is shown in Figure 41. Re-dispersion of dried polymer particle aggregates was possible with additional time in ultrasonic bath.

Figure 41 – Polystyrene latex with reversible stability. Re-dispersion of polystyrene particle aggregates was accomplished by heating the solution to 60˚C and applying micro-mixing in an ultrasonic bath. The hydrophobic aggregates [LEFT] formed a stable latex [RIGHT] after re-redispersion.

Before re-dispersion, the polymer particles were clearly insoluble and stuck to the surface of the water and the sides of the glass vial. The aqueous phase was clear and did does not contain any polymer particles. The reformed latex solution is opaque. A bluish tint is visible when the latex is held up to a light source. Analysis of the latex is summarized in Table 31. The particle size distribution of the re-dispersed latex was bimodal. Electrostatic stability evidently returned to the latex after heating and mixing but not all of the particles were re-dispersed to their original particle size.

Table 31 – Size and stability of the re-dispersed polystyrene latex.

Sample	Surfactant	Particle Diameter (nm)		Polydispersity Index	Zeta Potential (mV)
A	Sodium stearate	44.2	269.1	0.511	- 45.4
B	Sodium palmitate	39.4	215.9	0.538	- 35.4
C	Sodium mystirate	35.7	250.4	0.500	- 43.2

In conclusion, polystyrene latex was successfully made by dispersing polymer aggregates into water without requiring additional surfactants. Latex stability was re-established by heating and mixing the particles in deionized water.

5.5 Discussion

In accordance to the mechanism of emulsion polymerization illustrated in Figure 11, continued chain growth is fuelled by diffusion of monomer into micelles containing live radical species. The micelles are stabilized by ionic surfactants that remain on the surface during the polymerization process. The newly formed polymer particles are surrounded by surfactant molecules that provide electrostatic stabilization.

Polystyrene particles are hydrophobic. The high molecular weight material is insoluble in water. When carbon dioxide is added to an aqueous solution containing the latex, the equilibrium between carboxylate and carboxylic acid species favours the neutral free acid. This is illustrated in see Figure 42. The poor aqueous solubility promotes the effect of carbon dioxide.

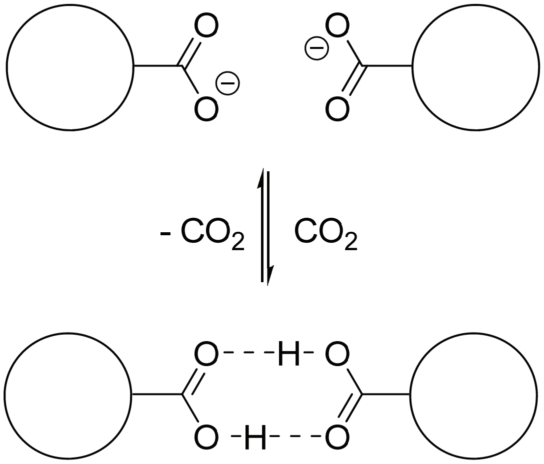


Figure 42 – The mechanism of action for reversible stability latex particles. Treating particles stabilized by anionic carboxylate groups with carbon dioxide causes protonation of carboxylate groups to carboxylic acid groups. The change effectively causes the particles to lose the electrostatic stabilization of anionic surface groups.

The re-dispersion of polymer aggregates into a latex suspension is possible due to the reversible nature of the anionic stabilization. The carboxylic acid group is more acidic than water and will form a carboxylate anion when in an aqueous solution above pH of approximately five. The difficulty lies in overcoming the inter-particle attraction of the aggregates.

Heating and mixing were effective in re-distributing the polymer aggregates into water. Once the polymer particle enters aqueous solution, the surface groups become anionic and electrostatic stabilization returns to the system as evident by measurements of zeta potential.

5.6 Summary

Polystyrene particles of 30 nm to 40 nm diameter were made by emulsion polymerization using anionic switchable surfactants. The latex suspension product was stabilized by electrostatic charges: the zeta potential was well below –30 mV. Treating the latex with carbon dioxide was found to cause aggregation. The aggregates were much larger with diameters of approximately 100 µm and were readily separated by flotation and dried into a fine free flowing powder. Re-dispersion of the aggregates was found to be possible after heating and mixing the slurry. The re-dispersed latex was found to be stabilized by electrostatic charges; the zeta potential was again well below –30 mV.

Chapter 6 – Conclusions

Surfactants are chemical compounds that influence the properties of an interface. The surface activity of a charged species can be significantly altered by eliminating the charge. Carbon dioxide gas may be used to neutralize acidic surfactants as well as induce charge in basic surfactants. For anionic switchable surfactants, the ability of carbonic acid to neutralize otherwise more acidic groups may be due to the difference in aqueous solubility between both ionic and netural forms.

Crude oil contains indigenous surfactants. Once treated with a water soluble base, low emulsion water continuous heavy crude oil emulsions are stabilized. The stable emulsions can be transported in a conventional pipeline. Neutralization of the indigenous surfactants with carbon dioxide destabilized the emulsion and caused immediate phase separation to occur. The phase separation was improved by using water soluble organic bases. A hybrid heavy crude oil pipeline system was possible due to the basic nature of the surfactant. This system was able to generate low viscosity emulsions but also retained the amidine’s demulsification potential.

A stabilized polystyrene latex was made by emulsion polymerization. The particles contain surface groups that are capable of reversibly retaining electrostatic charge. Aggregation of the particles was possible after addition of gaseous carbon dioxide. Polymer particles were readily separated from the aqueous phase by skimming the particles from the surface as a slurry. The aggregates were re-dispersed into a new suspension by heating and mixing in additional water. The re-dispersion formed a latex suspension stabilized by electrostatic surface charges.

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