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# Synthesis and Use of Chiral Surfactants

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A thesis
Presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfillment
of the requirements for the degree
Master of Science in Chemistry

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by
Xiaoye Yang
August 2001

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Hamid S. Kasmai

Keywords: Chiral surfactants, Dimethyl leucinol, Siloxane-based polymers, Alkyl halide, Enantiomers, Enantioselective.

Abstract

Synthesis and Use of Chiral Surfactants.

It has been previously shown that micelles formed from surfactants with chiral head groups serve to induce a chiral reaction medium, leading to enhanced enantioselectivities in the reaction products. This utilization of chiral surfactants will offer an economical alternative to traditional chial solvents while simultaneously reducing organic waste. We have successfully dimethlated S-leucinol in an 85% yield and have synthesized a hydrocarbon-based surfactant with this molecule as a head group. We have also formed polymeric surfactants that have polydimethylsiloxane as the hydrophobic portion with the (S)-dimethylleucinol as a head group. Tests of the solubility of these surfactants have been conducted. We also have done a reduction of a ketone in 95% ethanol and 1.3%-4% (w/v) surfactants, resulting in ee. 5.4%-6.6%.

DEDICATED TO MY BELOVED PARENTS

# ACKNOWLEDGMENTS

I would like to express my deepest appreciation to Dr. Tammy A. Davidson for her guidance, teaching, and support throughout this work with great patience.

I would like to thank Sarah Folk and Dr. DeSimon (University of North Carolina) for allowing me to us their instrument to carry out my research.

I wish to thank Dr. Chu-Ngi Ho, Dr. J. Wardeska, Dr. H.S. Kasmai, and Dr. R. Mohseni for their suggestions and help during my research.

I wish to acknowledge the help and encouragement from Dr. T.-S. Huang.

I also acknowledge the East Tennessee State University Research Development Committee for financial support of this work.

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# Chapter 1

# INTRODUCTION

## Surfactants

Surfactant applications are present in almost every chemical industry and can be found in every cleaning or conditioning product. Such applications include detergents, paints, dyestuffs, cosmetics, pharmaceuticals, fibers, and plastics. Moreover, surfactants play a vital role in the oil industry for enhanced and tertiary oil recovery. [1, 2]

The word surfactant derives from the contraction of the terms surface-active agent and covers a group of molecules that are able to modify the interfacial properties of the liquid (nonaqueous or aqueous) in which they are present. Such molecules have hydrophilic and hydrophobic regions in their structure as illustrated schematically in Figure 1.[3]

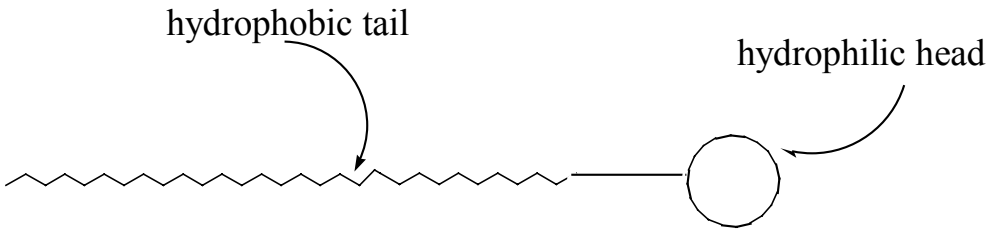



Figure 1. Structure of a surfactant

Most surfactants have a long hydrocarbon tail that can be linear or branched and interacts only very weakly with the water molecules in an aqueous environment, hence the chain is called hydrophobic tail. The hydrophilic head is a relatively small ionic or polar group that interacts strongly with the water via dipole-dipole or ion-dipole interactions.

Micellization

In dilute solutions, surfactant molecules exist as individual species in the media. And the solutions have completely ideal chemical and physical properties. As the surfactant concentration increases, chemical and physical properties of the solutions deviate from ideality by degree, and at a certain concentration, aggregation of the surfactant monomers occurs and micelles are formed. This concentration is the critical micellization concentration (CMC).[3] Figure 2 shows the pressure changing with concentration. As the concentration is increased the Osmotic pressure increases linearly, then above the CMC the rise is less pronounced. Micelles make a smaller contribution to the observed pressure than the monomers.

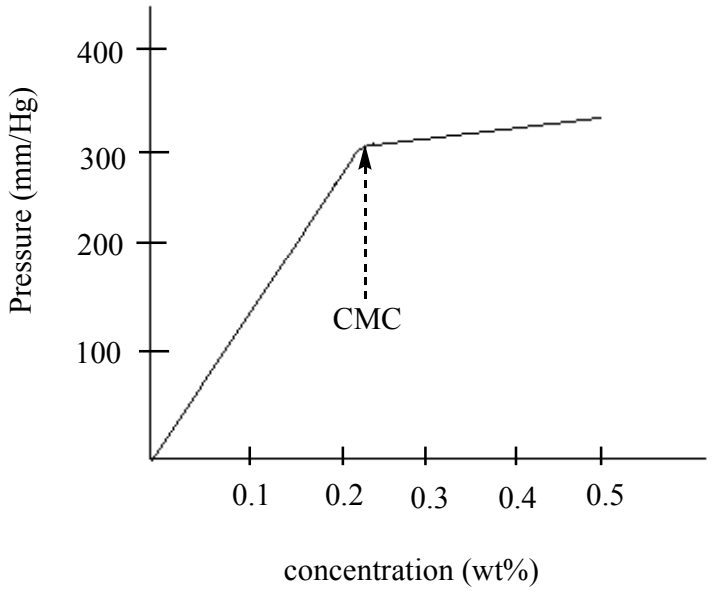



Figure 2. Osmotic pressure of sodium dodecyl sulphate solution.[2]

There are two major approaches to the theoretical description of micelle formation. In the law of mass action approach, it is considered that there is an equilibrium between monomers and micelles; the activity of the solute increases as the concentration is increased above the CMC.

For nonionized detergents the equilibrium can be written as

$$n \text{ (monomers)} \leftrightarrow \text{micelle}$$

$$K = C_{mic}/C_{mon}^{\ n}$$

where K is the equilibrium constant, and activities have been replaced by concentrations.

And for ionized detergents, the relationship becomes

$$n \text{ (long chain monomer ions )} + (n-p)(\text{counter ion}) \leftrightarrow \text{micelle}$$

$$K = C_{mic}/C_{mon}^{\ n} * C_c^{(n-p)}$$

where $C_c$ is the concentration of counterions, p of which are not bound to the micelle, e.g. the degree of ionization of the micelle.[4]

In the two-phase or pseudo-phase theory, the micelle is treated as a separate but soluble phase that begins to form at the CMC. Hence, the CMC is the saturation concentration for the monomers, and the concentration or activity of the monomers should not increase above it.

Both the approaches to the representation of micellization are useful, but neither is a formally correct description, and the choice of approach is often a matter of convenience.[4]

Micellar Structure

The surfactant's amphiphilic natures allow for self-aggregation into small vesicles termed micelles. In polar solvents, such as water, monomers assemble to form a micelle in such a way that the polar head groups project outwards into the polar bulk solvent and their hydrocarbon tails huddle in the core of the micelle. This way, the hydrophobic tails are shielded from water as seen in Figure 3.

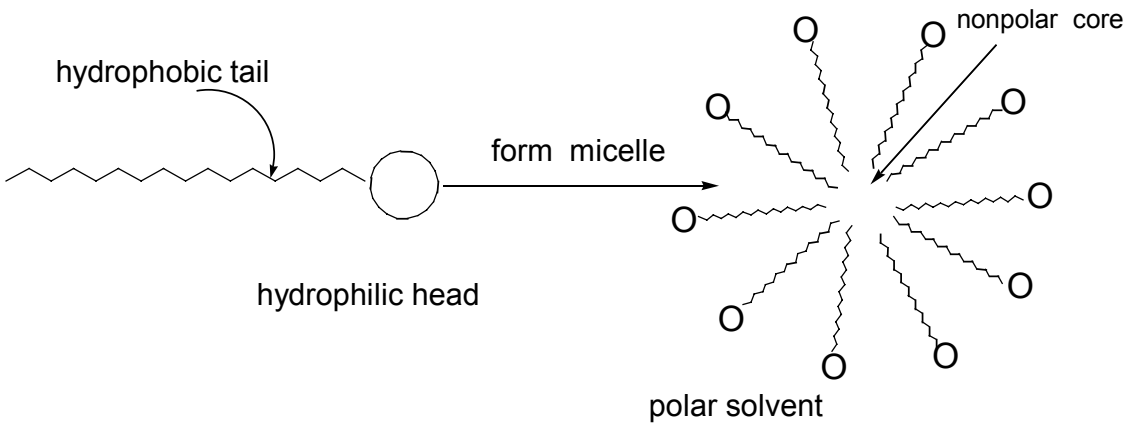



Figure 3. Formation of micelle

Aggregates can also occur in nonpolar solvents. These systems are called reverse micelles or inverted micelles as shown in Figure 4. Head groups of surfactant monomers are located inside to form a polar core and hydrocarbon tails are projected toward the bulk solution to form the outside shell of the micelle. If there is any water in the solution, it will be entrapped in the core. Reverse micelles are able to solubilize a relatively large amount of water in their cores, and this capacity can allow them to solubilize water-soluble substances in a nonpolar solvent. For example, it has been reported that water can be solubilized in carbon dioxide, a non-polar solvent, when the appropriate surfactant is chosen.[5]

The surface activity of the surfactant is determined by the nature and ratio of lipophilic and hydrophilic groups and by the spatial arrangement. This dual nature of the surfactant is responsible for the properties of micellization, surface activity, and solubilization. When the surfactant concentration is close to CMC, micelles are small. As the surfactant concentration

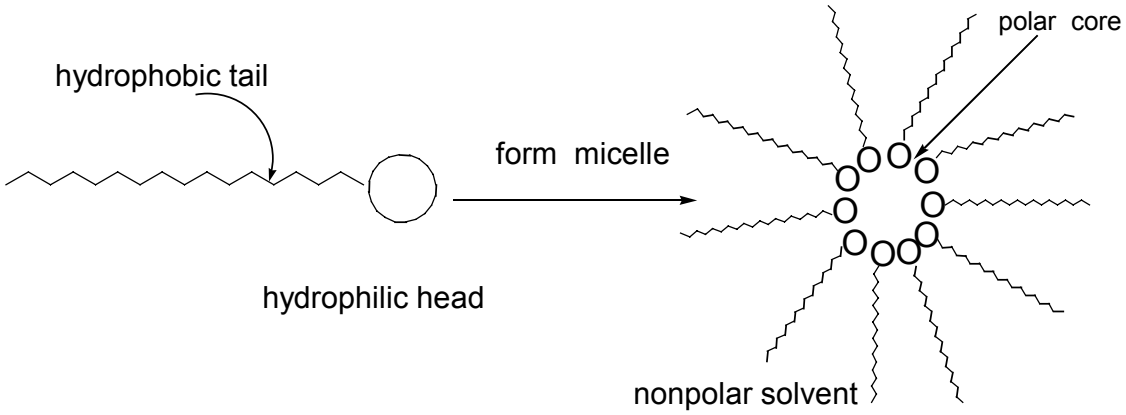



Figure 4. Formation of reverse micelle

increases they become larger, and after a certain concentration they elongate and convert into rodlike micelles. The presence of salt or organic additives can also lead to this conversion or affect the conversion concentration.[3]

Solubilization

One of the most important processes leading to micellar effects on reactions is the solubilization of substrates in micellar interiors. This solubilization is defined as "a particular mode of bringing into solution substances that are otherwise insoluble in a given medium, involving the previous presence of a colloidal solution whose particles take up and incorporate within or upon themselves the otherwise insoluble material".[6] It is, therefore, possible to solubilize water-insoluble substances or to increase the solubilities of slightly soluble ones in aqueous micellar solutions. Otherwise, polar substances can be solubilized in different regions of reversed micelles depending on the nature of both the micelles and solutes. Because the solvent

molecules can penetrate beyond the polar head groups, solute in the solvent phase can interact both with the polar head groups and with nonpolar chains of the surfactants.

The micellar phase may be referred to as amphiphatic. It has affinity for both nonpolar and polar species. Thus, micellar cores behave like an organic phase and the hydrophobic forces play a critical role in the solubilization process. Reverse micelles have the opposite function. For example, one can use the solubilization of polar substances in reverse micelles in order to extract polar substances from their aqueous solutions in contact with an organic phase containing surfactant micelles.[3]

The solubilization of substances in micellar media leads to a dynamic equilibrium of solute between micelles and the bulk phase. Several factors affect solubilization of which the structure of the surfactant and solute, temperature, and addition of electrolytes and non-electrolytes are probably the most important.

Siloxane Surfactants

Siloxane surfactants consist of a permethylated siloxane group coupled to one or more polar groups. They have certain unique properties: their hydrophobic group is silicone, so that they are able to lower surface tension to ≈20 dyn/cm compared with ≈ 30 dyn/cm for typical hydrocarbon surfactants and cause them to be surface active in both aqueous and nonaqueous media.[7] They also are similar to hydrocarbon surfactants in many ways. Critical micellization concentrations (CMC) vary with molecular structure in the same way –within a homologous series, proportionately larger hydrophobic groups lead to smaller CMC values. They both show similar patterns of self-association in aqueous solution, forming aggregates and liquid crystal

phases of the same types and following the same trends with molecular structure. Figure 5 shows the molecular origin of the principal difference between hydrocarbon and siloxane surfactants.

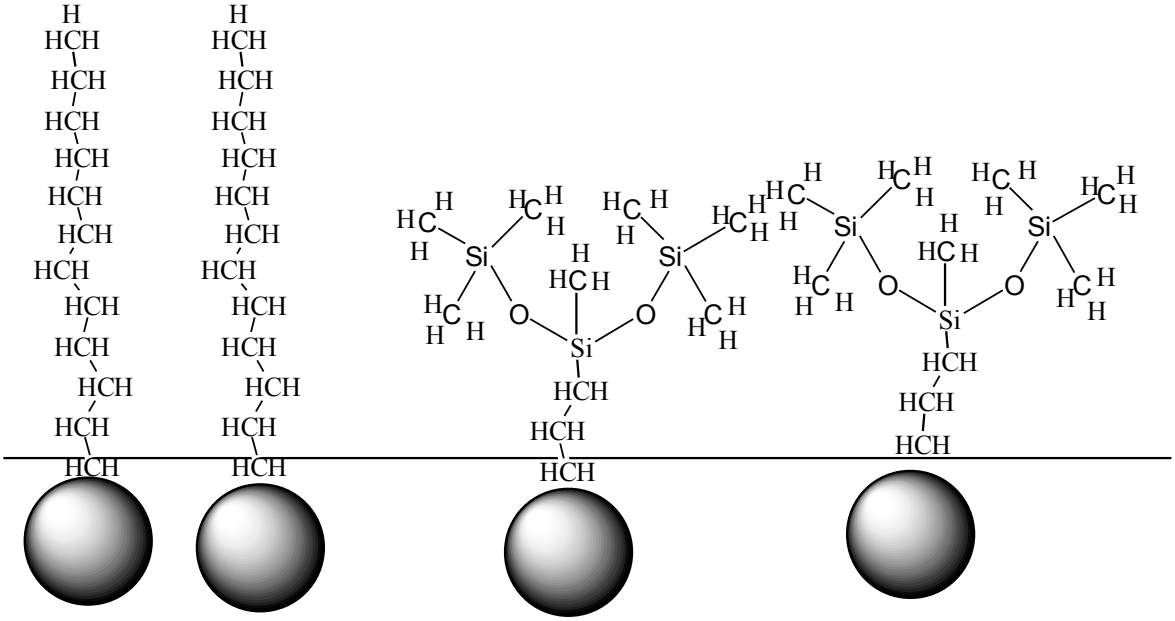


Figure 5. Comparison of the surface character of hydrocarbon and siloxane surfactants.

The –O-Si-O-Si- backbone serves as a flexible framework, while the methyl groups are the cause of the surface-active character of siloxane surfactants. Compared with hydrocarbon surfactants, siloxane surfactants have about 20 dyn/cm of the surface energy of a methyl-saturated surface. Because most hydrocarbon surfactants consist of alkyl, or alkylaryl hydrophobes, containing mostly $–CH_2-$ groups that pack loosely at the air-liquid interface, the surface energy of hydrocarbon surfactants is about 30 dyn/cm or higher.[7] Due to siloxane surfactants' range of properties, they have a variety of uses in applications where other types of surfactants are relatively ineffective. For instance, siloxane surfactants are only one of two polymeric materials that demonstrate high solubility in $CO_2$ at easily accessible temperatures and pressure ($T<100^oC$

and P<500bar). The other is amorphous or low-melting fluoropolymers.[5] In our research, polydimethylsiloxane (PDMS) is one of the surfactants of interest.

## Chiral Molecules

Of much recent interest to the pharmaceutical industry and food and drug administration is the production and sale of "chiral drugs", meaning drugs that contain a single enantiomer. Enantiomers are a type of stereoisomers that are nonsuperimposable mirror images of each other. Molecules that have the property of being nonsuperimposable on their mirror image are said to be chiral or to possess "handedness".[8, 9] Chiral molecules can show their different handedness in many ways, including the way they affect human beings.

Such is the case with the anti-inflammatory agent ibuprofen, Figure 6, the major component of Advil. Only the (S) isomer is effective, while the (R) isomer has no anti-inflammatory action. Although the (R) isomer is gradually converted to the (S) isomer in the body, a medicine based on the (S) isomer alone takes effect more quickly than the racemate.

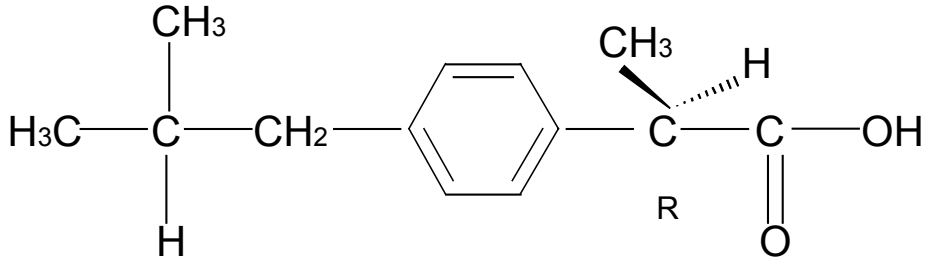



Figure 6. Structure of Ibuprofen

In some enantiomers, R and S have similar activities. But for most enantiomers, they have completely different activities, such as penicillamine, Figure 7. The (S) isomer is a highly potent

therapeutic agent for primary chronic arthritis: the (R) isomer instead has no therapeutic action, but is highly toxic.

Some enantiomers' different activities already have caused many tragedies, such the drug Thalidomide, Figure 8. It was an extremely popular drug during 1950 to 1963 that was used to

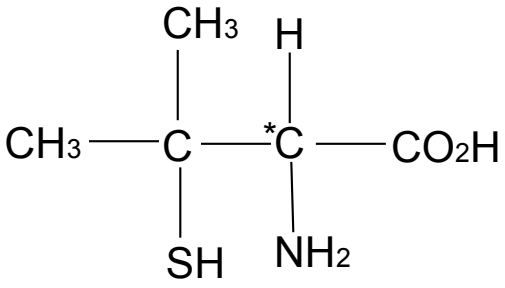



Figure 7. Structure of Penicillamine

alleviate the symptoms of morning sickness in pregnant women. In 1963, it was discovered that thalidomide was the cause of horrible birth defects in many children born. Actually, just one of the thalidomide enantiomers had the effect of curing morning sickness. The other that was also present in the drug (in an equal amount) was the cause of abnormalities and the drug was withdrawn from the market and its availability highly restricted.

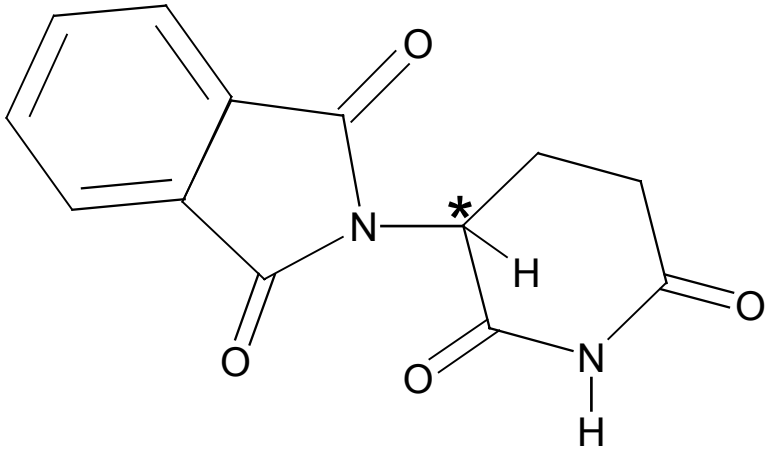



Figure 8. Structure of Thalidomide

From the above three cases and many others, we can see that synthesizing chiral compounds has become increasingly more important to chemical researchers.

Enantioselective Syntheses

If a reaction that leads to the formation of enantiomers produces a preponderance of one enantiomer over its mirror image, the reaction is said to be enantioselective. A chiral reagent, solvent or catalyst must assert an influence on the reaction. In nature, where most reactions are enantioselective, enzymes lead the chiral influences. Enzymes not only have the ability to cause reactions to take place more quickly but also have the ability to cause a dramatic chiral influence on a reaction. Many enzymes have also found use in organic chemistry experiments, where organic researchers use them to bring about enantioselective reactions. Specificity is one of the most important properties of an enzyme, but it also means that enzymes cannot be used broadly in the organic chemistry laboratory. Chemical catalysts have the similar role with enzymes.[10] Chemical catalysts require extremely exacting reaction conditions, which currently prohibits wide use. Chiral solvents or chiral reagents are other ways to influence a reaction. They have additional limitations due to the volatile organic solvents used in organic synthesis, as well as the expense of using large amounts of chiral reagents and chiral solvents during reactions.

The Separation of Enantiomers

Since the Noble Prize was awarded to Cram, Lehn, and Pederson in 1987 for their molecular recognition theory [11], the separation of enantiomers has become a major method to isolate chiral compounds. One of the procedures for separating enantiomers is based on allowing a racemic mixture to react with a single enantiomer of some other compound. The procedure,

called resolution, changes a racemic form into a mixture of diastereomers. Diastereomers can be separated by conventional means since diastereomers have different melting points, different boiling points, and different solubilities. Using chiral media in chromatography is also widely used to resolve enantiomers. The most common methods include high performance liquid chromatography (HPLC) and electrophoresis etc.[12, 13, 14] However, both methods involve a considerable amount of time and financial expense.

In the last few years, new applications of chiral micellar media have been reported in both chiral synthesis[15, 16] and separation research[17, 18]. Chiral micellar media are believed to be able to offer a viable clean alternative to more traditional methods of accomplishing many organic reactions. Micelles can concentrate the reactants within their small volumes; stabilize substrates, intermediates, or products; and orient substrates. Thus, they can alter the reaction rate, mechanism, and stereochemistry of a process. Furthermore, they can be prepared at low cost, particularly when using synthons from the chiral pool. They can be applied to a range of different reactions; they are more robust than enzymes, and they are recyclable. Third, the use of chiral surfactants can offer an economical alternative to traditional chiral solvents while simultaneously reducing organic waste.

Recently, chiral surfactants have been widely used in the separation of enantiomers. However, there are relatively few reported applications of chiral surfactants in enantioselective synthesis. Although it is at an early stage in its development, this field exhibits considerable promise.

Our research involves using micelles formed from chiral surfactants to influence the stereochemistry of organic reactions. We have synthesized siloxane-based surfactants with a water-soluble chiral head group and leucine-derived alkyl surfactants.

## Gel Permeation Chromatography

Natural polymers have been an integral part of human existence since people first appeared on earth. Our physical well being is due to the polymers in our bodies; we are clothed, sheltered, and fed with polymers; we use polymers to record our activities. Although polymers are so important to us, they were not at the forefront of organic chemistry research until the early part of the twentieth century. The nature of a polymer's molecular weight distribution (MWD), a key property needed to describe the behavior of polymers, was not understood until gel permeation chromatography appeared.[19]

Gel permeation chromatography (GPC), also called size exclusion chromatography (SEC), is the generic name given to the liquid chromatographic separation of macromolecules by molecular size, and it is a non-destructive mode of separation. Essentially a maze for molecules, the particles of the column packing have various sized pores and pore networks so that solute molecules are retained or excluded on the basis of their hydrodynamic molecular volumes, sizes, and shapes. In this section, we focus on the high-performance GPC.

### Theory of GPC

The primary purpose and use of the GPC technique is to provide molecular weight distribution (MWD) information about a particular polymeric material. A stylized separation of an ideal mixture of two sizes of macromolecules is presented in Figure 9. In the first frame, the sample is shown immediately after injection on the head of the column. A liquid mobile phase is passed through the column at a fixed flow rate, setting up a pressure gradient across its length. In the next two steps the sample polymer molecules pass into the column as a result of this pressure

gradient. The particles of the stationary phase are porous, with controlled pore size. The smaller macromolecules are able to penetrate these pores as they pass through the column, but the larger ones are too large to be accommodated and remain in the interstitial space. The smaller molecules are only temporarily retained and flow down the column until they encounter other particle pores to enter. The larger molecules flow more rapidly down the length of the column because they cannot reside inside the pores for any period of time. Finally, in the fourth step the two molecular sizes are separated into two distinct chromatographic bands. A mass detector installed at the end of the column responds to their elution by generating a signal peak for each band as it passes through whose size is proportional to the concentration. A real SEC sample chromatogram typically shows a continuum of molecular weight components contained unresolved with a single peak.[20]

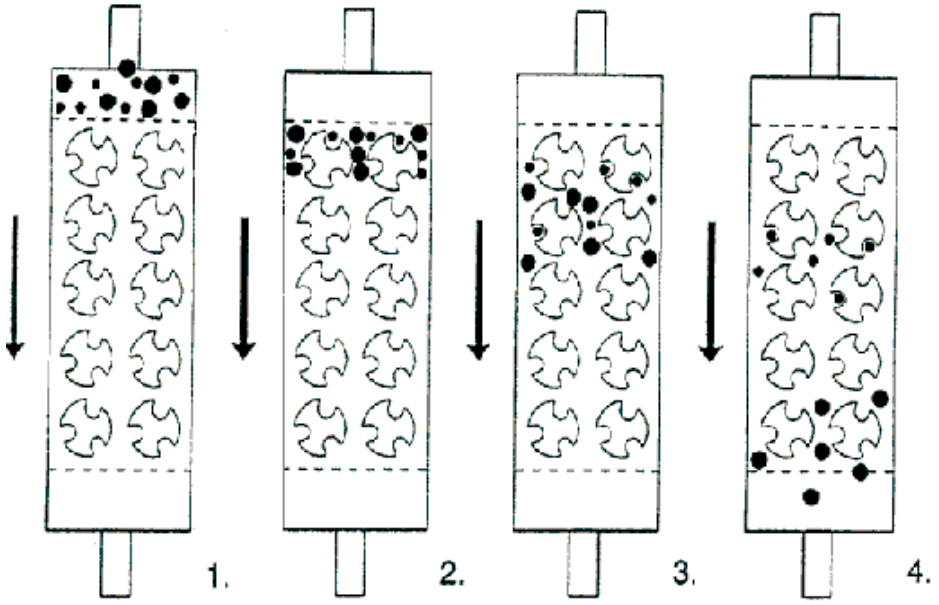



Figure 9. GPC separation of two macromolecular sizes: 1. sample mixture before entering the column packing; 2. sample mixture upon the head of the column; 3. size separation begin; 4. complete resolution.[20]

Retention Behavior

The efficiency of the separation process is a function of the dependence of the retention (or elution) volume $V_R$ on the molar mass M, and a reliable relationship between the two parameters must be established. The relationship is described as

$$V_R = V_M + KV_S$$

where $V_R$ is the volume of effluent that flows from a column between the sample injection and its emergence in the effluent; $V_M$ is the void volume of the mobile phase (that is, the unbound solvent in interstices between the solvent loaded porous particles), as estimated by the elution of a totally excluded solute; Vs is the total internal pore volume. K is the partition coefficient, as given below.

$$K = (V_R - V_M)/Vs$$

K can be stated as a fraction of the internal pore volume that is accessible to the solute. Totally excluded molecules elute in one void volume; that is, $V_R = V_M$ and K = 0. While for small molecules, which can enter all the pores of the packing, $Vs = V_M + V_S$ and K=1. Intermediate-size molecules elute between these two limits, and K ranges from 0 to 1.

To obtain molecular weight distribution (MWD), the mass of the polymer being eluted must be measured. This can be achieved continuously using refractive index, UV or IR detectors, which will give a mass distribution as a function of $V_R$.[21, 22] The elution times are then compared to a calibration curve generated from narrow molecular weight standards. For most GPC applications, the standards of choice are polystyrene.

# CHAPTER 2

# EXPERIMENTAL

## Instrumentation

GPC data were collected on a Waters Chromatograpy system consisting of a Waters 610 Fluid Unit, Waters 2410 Refractive Index Detector , and Waters 600 controller.

NMR spectra were collected on a JEOL Eclipse-400MHz Spectrometer.

IR spectra were collected on a Mattson Genesis II FTIR$^{TM}$ Spectrometer.

GC data were taken on a Varian 3800 Gas Chromatograph.

Data on enantiomeric purity were collected using a O.C.RUDOLPH & SONS INC. Model 62 Polarimeter.

UV Spectrometer (Cary 1E) was used for measuring CMC of leucine-derived surfactants.

## Materials

Hexamethylcyclotrisiloxane ($D_3$) was obtained from Acros. Sec-butyl lithium (1.3M in cyclohexane), S-leucinol (96%), 1-chloro-hexadecane (95%), 1-bromo-hexadecane (97%), and sodium borohydride (99%) were obtained from Aldrich. Tetrahydrofuran (THF) and 2-pentanone were obtained from Fisher. 3-Chloropropyldimethylchlorosilane and 3-chloropropy-lmethyldichlorosilane were obtained from Gelest.

## Poly(dimethysiloxane) (1).

Pretreatment: Hexamethylcyclotrisiloxane ($D_3$) was purified via vacuum sublimation. Cyclohexane was dried by adding $H_2SO_4$ in a 2:1 ratio and stirred 24 hours. The cyclohexane

was decanted and distilled from $CaH_2$. Tetrahydrofuran (THF) was distilled from solution under an argon atmosphere prior to use. A stock solution of $D_3$ was made by dissolving hexamethyl-cyclotrisiloxane (99.15 g) in dry cyclohexane (250 mL).

Polymer (1000 g/mol): A round bottom flask, which was sealed with a rubber septum with a magnetic stirring bar inside, was cooled to room temperature by purging argon. After the flask was cooled to room temperature, stock $D_3$ solution (20 mL, 0.379 g/mL) was added via dry syringe under argon protection. Anion initiator sec-butyllithium (7.93 mmol) was added via dry syringe. The mixture was stirred for two hours at room temperature. Then, THF (2.6 mL) was added and the mixture was allowed to stir at room temperature for 48 hours. After 48 hours, half of the mixture was transferred to another round bottom flask by dry syringe. Chlorosilane terminating reagent (3.96 mmol) was added to the first flask for the one –tail polymer via a dry syringe. Dichlorosilane terminating reagent was added to the second flask in the same moles as chlorosilane for the two-tail polymer. The one-tail and two-tail polymers were then washed with cold methanol, and residual solvent was removed using a rotovap and vacuum. A colorless liquid was obtained (1-tail polymer, 2.92 g , 62%; 2-tail polymer, 2.41 g, 51%). $^1$H NMR: $\delta$=3.50 (2H, t, $CH_2$Cl, J=7Hz); $\delta$=1.82 (2H, m, $CH_2CH_2$Cl); $\delta$=0.92 (3H, t, $CH_3$); $\delta$=0.91 (3H, d, $CH_3$); $\delta$=0.045 (68H, m, $SiCH_3$).

Polymers of different molecular weights were made by adjusting the amount of initiator, THF, and terminator. $D_3$(20 mL) was used as a starting amount. A series of different molecular weights- -1000 g/mol, 2000 g/mol, 5000 g/mol, 10,000 g/mol, 25,000 g/mol- -were prepared by using this method. Table 1 shows the amounts of initiator and terminator agents.

Table 1. Amounts of initiator, THF and terminating agents

| Molecular weight | 1000 | 2000 | 5000 | 10,000 | 25,000 |
|---|---|---|---|---|---|
| Initiator | 7.93 mmol | 3.97 mmol | 1.6 mmol | 0.8 mmol | 0.32 mmol |
| THF | 2.6 mL | 2.3 mL | 2.1 mL | 2.06 mL | 2.02 mL |
| 1-tail terminating reagent | 3.96 mmol | 1.99 mmol | 0.8 mmol | 0.4 mmol | 0.14 mmol |
| 2-tail terminating reagent | 3.96 mmol | 1.99 mmol | 0.8 mmol | 0.4 mmol | 0.14 mmol |

(2S)-N,N-Dimethyl-2-amino-4-methyl-1-pentanol (2)[23, 24, 25]

A 100 mL three-neck round flask was equipped with a magnetic stirrer and a reflux condensor. (2S)-amino-4-methyl-1-pentanol (3.9 mL, 30 mmol), 88% formic acid (5.25 mL, 121.8 mmol) and 9ml water were added into the flask, the mixture was stirred, and then 37% formaldehyde (9.6 mL, 120 mmol) was added dropwise. The reaction mixture was heated to 100$^{O}$C. After reflux was continued for 8 hours, the solution was cooled to room temperature and 30ml 5M aqueous NaOH was added. Then, the solution was extracted with diethyl ether (3x30 mL). The organic phase was washed with 20ml of 5M NaOH and then 30ml brine and 30ml distilled water. Then the organic phase was dried over sodium sulfate. The solvent was removed in vacuum to yield a pale yellow oil (2S)-N,N-dimethyl-2-amino-4-methyl-1-pentanol (3.71 g, 85%). IR: Vmax/cm$^{-1}$ 3421 (OH), 2950s, 1467s, 1367m, 1052s; $^{1}$H NMR (400MHz, $CDCl_3$); δ=3.42 (1H, m, 1-*H*H); δ=3.15 (1H, t, 1-H*H*); δ=2.59 (1H,m, 2-H); δ=2.16 (6H, s, N*Me*$_2$); δ=1.42 (3H, m) and δ=0.82 (6H, d, CH(*CH*$_3$)$_2$). $^{13}$C NMR (100MHz, $CDCl_3$); δ=62.39 (C-1); δ=61.20 (C-2); δ=39.81 (2xN*C*H3); δ=32.96 (C-3); δ=25.34 (C-4); δ=23.68 (C-5); δ=22.01 (CH-*C*H$_3$).

(2S)-N-Hexadecyl-N,N-dimethyl-(1-hydroxy-4-methyl-1-pentyl)-2-ammonium bromide.(3)[26, 27]

In a 100-mL three-neck round flask equipped with a magnetic stirrer and a reflux condensor (2S)-N,N-dimethyl-2-amino-4-methyl-1-pentanol (2.9 g, 20 mmol), 1-bromohexa-decane ( 6.30 g, 20 mmol) and absolute ethanol (10 mL) were stirred under anhydrous conditions. The mixture was refluxed 15 hours at 80$^{O}$C, then it was cooled to room temperature. Diethyl ether (75 mL) was added to precipitate the quaternary amine. The precipitate was filtered under gravity, and the pale yellow solid was purified by recrystallization from ethyl acetate (1.73 g, 19%). IR: Vmax/cm$^{-1}$ 3295br (OH), 2928s, 2210s, 1469s, 1380m, 1050s; $^{1}$H NMR (400MHz $CDCl_3$); δ=3.57 (1H, dd, 1-*H*H); δ=3.40 (1H, t, 1-H*H*); δ=3.28 (2H, m, $NCH_2$); δ=2.75 (1H, m, 2-H); δ=2.32 (6H, s, $NMe_2$); δ=1.85 (2H, m); δ=1.41 (2H, m) δ=1.27 (25H, m, 4H, and 12x$CH_2$); δ=1.08 (3H, d, $CHCH_3$); δ=1.03 (3H, d, $CHCH_3$); δ=0.89 (5H, m, $CH_2CH_3$).

(2S)-N-Hexadecyl-N,N-dimethyl-(1-hydroxy-4-methyl-1-pentyl)-2-ammonium chloride.(4)[26][27]

In a 100ml three-neck round flask equipped with a magnetic stirrer and a reflux condensor. (2S)-N,N-dimethyl-2-amino-4-methyl-1-pentanol (2.9 g, 20 mmol),1-chlorohexadecane ( 6.35 g, 20 mmol) and absolute ethanol (10 mL) were stirred under anhydrous conditions. The mixture was refluxed 24 hours at 80$^{O}$C, and then it was cooled to room temperature. Ethanol was removed by a rotovap and vacuum. The weight of the crude product was 7.7g. IR: Vmax/cm$^{-1}$ 3325br (OH), 2920s, 1610m, 1469s, 1390m, 1020s; $^{1}$H NMR (400MHz $CDCl_3$); δ=3.57 (1H, dd, 1-*H*H); δ=3.40 (1H, t, 1-H*H*); δ=3.28 (2H, m, $NCH_2$); δ=2.75 (1H, m, 2-H); δ=2.32 (6H, s, $NMe_2$); δ=1.85 (2H, m); δ=1.41 (2H, m) δ=1.27 (25H, m, 4H, and 12x$CH_2$); δ=1.08 (3H, d, $CHCH_3$); δ=1.03 (3H, d, $CHCH_3$); δ=0.89 (5H, m, $CH_2CH_3$).

Attaching the tertiary amine to the siloxane polymer (5)

In a 100-mL three-neck round flask equipped with a magnetic stirrer and a reflux condensor. (2S)-N,N-dimethyl-2-amino-4-methyl-1-pentanol (0.24 g, 1.6 mmol), 1000g/mol 1-tail siloxane polymer (1g) and absolute ethanol (5 mL) were stirred under anhydrous conditions. The mixture was heated for 72 hours at $50^{O}$C, then cooled to room temperature. Ethanol was removed by a rotovap and vacuum. The crude product was 1.1g. $^{1}$H NMR (400MHz $CDCl_3$); δ=3.5 (3H, m); δ=3.20 (1H, t); δ=2.67 (1H, m); δ=2.23 (6H, s); δ=1.77 (2H, m);δ=0.90 (6H, dd); δ=0.045 (68H, m, $SiCH_3$).

The tertiary amine was attached to a series of different weight polymers by similar methods. The ratios of polymers and dimethyl leucinol are shown in Table 2.

Table 2. The ratios of dimethly leucinol and Siloxane-based polymer

| Polymer | Amount of polymer | Amount of leucinol | Polymer | Amount of polymer | Amount of leucinol |
|---|---|---|---|---|---|
| 1000-1_tail | 1 g | 0.2 g | 5000-2_tail | 0.5 g | 0.02 g |
| 1000-2_tail | 1 g | 0.24 g | 10000-1_tail | 0.5 g | 0.013 g |
| 2000-1_tail | 0.5 g | 0.055 g | 10000-2_tail | 0.5 g | 0.009 g |
| 2000-2_tail | 0.5g | 0.07 g | 25000-1_tail | 0.5 g | 0.0023 g |
| 5000-1_tail | 0.5 g | 0.02 g | 25000-2_tail | 0.5 g | 0.0020 g |

2-Pentanol (6)[28]

A 250-mL round flask equipped with a magnetic stirrer, 2-pentanone (28 g), ethanol (50 mL, 95%), and (2S)-N-Hexadecyl-N,N-dimethyl-(1-hydroxy-4-methyl-1-pentyl)-2-ammonium chloride were mixed. The solution was cooled in an ice bath contained in a large beaker for 15 min. While the flask was in the ice bath, sodium borohydride (2.0 g) was carefully added. After the vigorous reaction had ceased, the flask was removed from the ice bath, and allowed to stand at room temperature for 45 minutes. After 45 min, 5M sodium hydroxide solution (5 mL) was added to decompose the borate ester. Water (40 mL) was added to separate the solution to two layers. The solution was extracted with diethyl ether (3x30 mL) and dried with sodium sulfate. Diethyl ether was removed by a rotovap. Ethanol was separated from the 2-pentanol by fractional distillation. $[\alpha]^{D}_{25}$= +1.24 (C=0.372 g/mL, ethanol); ee=6.6%. $^{1}$H NMR (400MHz $CDCl_3$); δ=3.74 (H, m, 2-H); δ= 2.04 (H, s, OH); δ=1.36 (5H, m, 1-H &3H); δ=1.12 (2H, m, 4-H); δ=0.88 (3H, t, 5-H); $^{13}$C NMR (100MHz $CDCl_3$); δ=67.77 (C-2); δ= 41.52 (C-3); δ=23.40 (C-4);δ=18.97 (C-1); δ=14.08 (C-5).

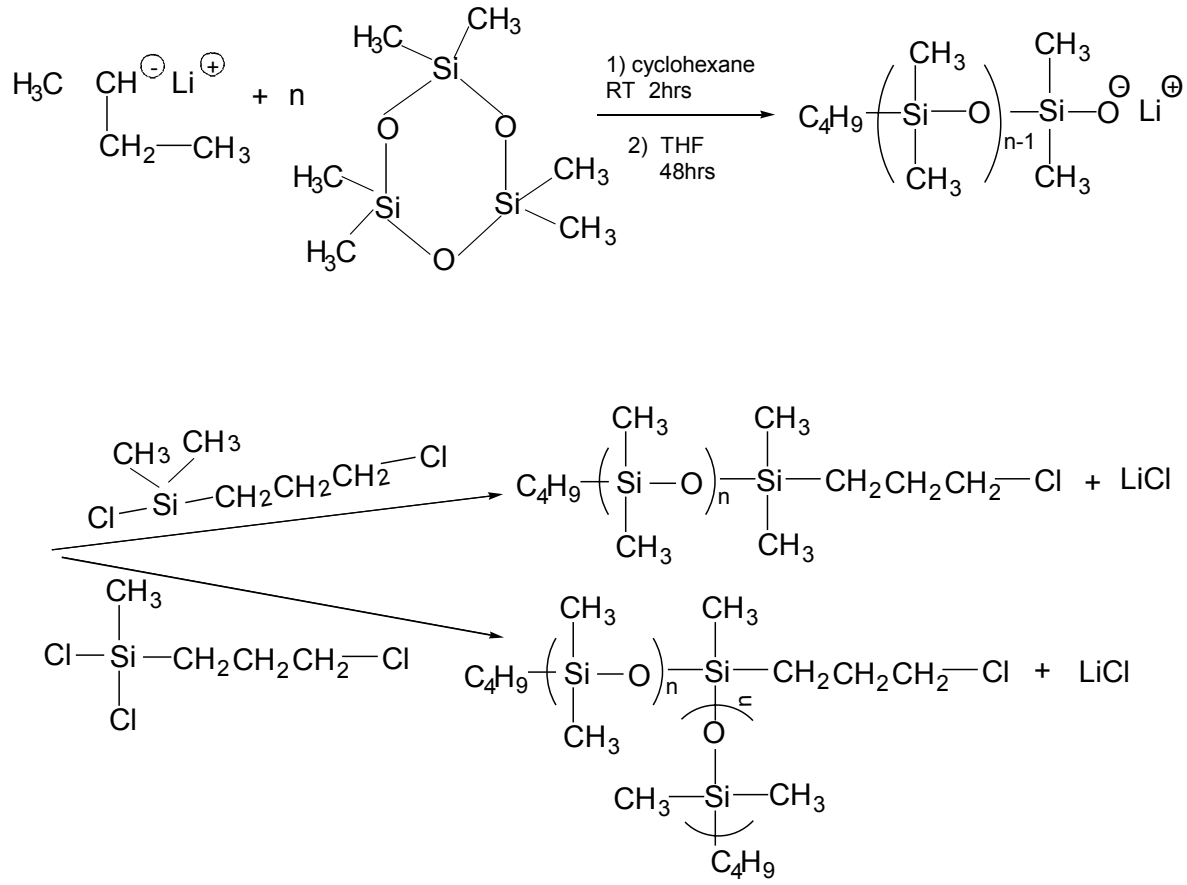
CHAPTER 3

RESULTS AND DISCUSSION

## Synthesis of Surfactants

### Synthesis of siloxane-based polymers

Poly(dimethylsiloxane) was synthesized using anionic polymerization of hexamethyl-cyclotrisiloxane (FW=222.47) initiated with sec-butyllithium at room temperature as seen in Scheme 1. After two hours, 10% THF (by total solution volume) was added as a promoting solvent and the reaction continued for 48 hours at room temperature. Termination was




Scheme 1. Synthesis of siloxane-based polymers

accomplished with 3-chloropropyldimethylchlorosilane for a single tail product and 3-chloropropyl-methyldichlorosilane for a two-tailed product. By adjusting the amount of initiator, THF, and terminator, a series of different weight siloxane-based polymers were made. Synthesis of the siloxane-based polymer produced relatively good yield and pure products in both the one-tailed as well as the two-tailed polymer categories.

Table 3. Yields of siloxane-based polymers

| 1-tailed | 1000MW | 2000MW | 5000MW | 10000MW | 25000MW |
|---|---|---|---|---|---|
| Product | 2.92 | 4.35 | 2.95 | 2.16 | 2.27 |
| Expected | 4.74 | 3.01 | 4.12 | 4.05 | 4.00 |
| %yield | 62% | 69% | 72% | 53% | 57% |
| 2-tailed | | | | | |
| Product | 2.41 | 2.25 | 2.84 | 3.14 | 2.59 |
| Expected | 4.68 | 4.32 | 4.11 | 4.04 | 4.00 |
| %yield | 51% | 52% | 70% | 78% | 65% |

Anionic initiator sec-butyllithium was used in the polymer synthesis because this kind of initiator easily controls the molecular weight of the polymer. THF is chosen as a promoter solvent to make the situation more polar so that polymer formation can occur quickly.

Structure characterization and actual molecular weight of siloxane-based polymers were done by $^{1}$H NMR (Figure 10) and GPC. The $^{1}$H NMR shows a singlet peak at $\delta$=1.57 is due to water. Other peaks are consistent with the structure of siloxane-based polymer. Table 4 shows the actual molecular weights as calculated from $^{1}$H NMR and GPC.

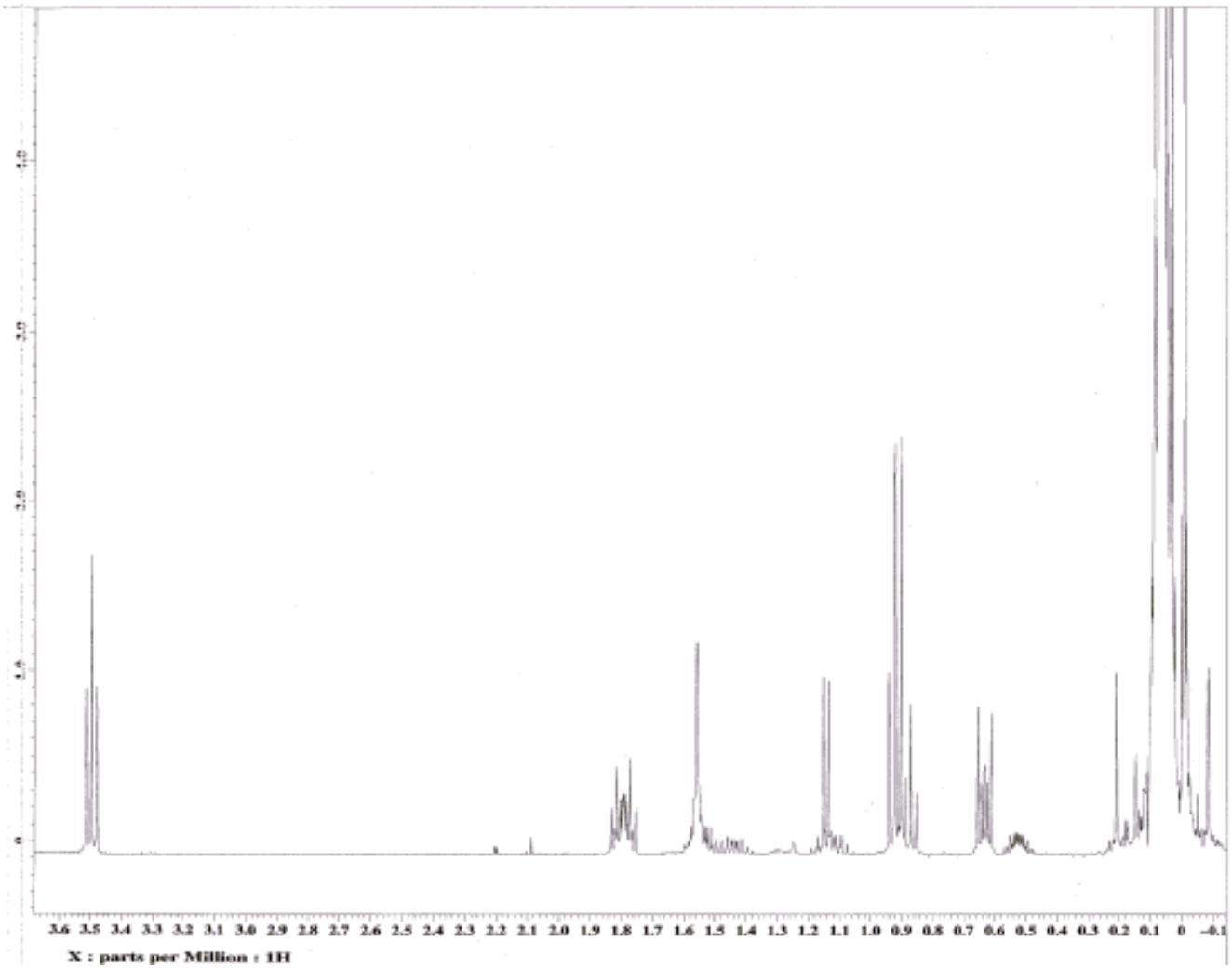



Figure 10. $^{1}H$ NMR (400 MHz, $CDCl_3$ ) of siloxane-based polymer

Table 4. Actual molecular weights from NMR and GPC

| Polymer_1tail | MW from NMR | MW from GPC | MWD | Polymer_2tail | MW from NMR | MW from GPC | MWD |
|---|---|---|---|---|---|---|---|
| 1000 g/mol | 1850 | 2846 | 1.147 | 1000 g/mol | 1924 | 2934 | 1.145 |
| 2000 g/mol | 2956 | 5766 | 1.195 | 2000 g/mol | 3852 | 5728 | 1.178 |
| 5000 g/mol | 5451 | 8815 | 1.593 | 5000 g/mol | 6794 | 9734 | 1.777 |
| 10000 g/mol | 12247 | 11759 | 2.494 | 10000g/mol | 13560 | 16761 | 2.377 |
| 25000 g/mol | 27627 | 22987 | 2.068 | 25000 g/mol | 29626 | 17651 | 1.964 |

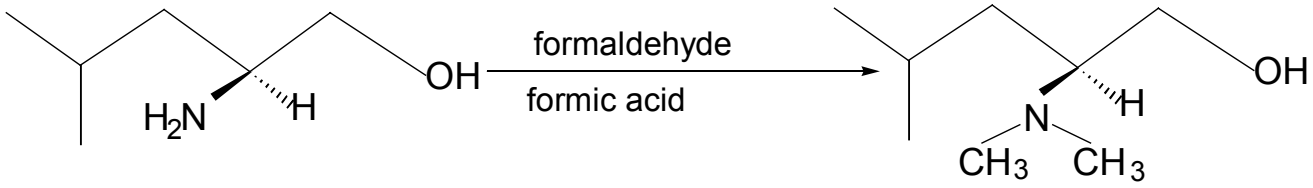
From the $^{1}$HMR and GPC, the molecular weights of 1-tail polymer appear to be larger than the molecular weights that we desired. This is likely because sec-butyl lithium very easily absorbs water and causes the concentration of initiator to dilute, so the molecular weight of polymer becomes higher than the theoretical molecular weight. Also, it is possible that the actual concentration of $D_3$ is higher than the calculated concentration due to slow evaporation of the solution. In contrast, the molecular weights of 2-tail polymers are much smaller than theoretical molecular weight due to a calculation mistake about the amount of the terminating agents.

From GPC, the molecular weight distribution (MWD) of the small molecular weight polymers (1000 g/mol 1-tail and 2-tail, 2000 g/mol 1-tail and 2-tail) is very close to 1. But for the large molecular weight polymers, the distribution is far from 1 because it takes a longer time to form the larger molecular weight polymers. Comparing NMR and GPC data, we think that molecular weights calculated from NMR are more reliable. This is because GPC measures

molecular weight relative to polystyrene, which has a different hydrodynamic volume than poly(dimethylsiloxane).

Methylation of leucinol

(S)-leucinol, formic acid and formaldehyde were stirred and heated at 100C for 18 hours. Sodium hydroxide solution (5M) was added to wash the extra acid and the solution was extracted three times with ether. The ether was dried and evaporated to give the product in an 85% yield. The product was tested for purity using thin layer chromatography (TLC).




Scheme 2. Methylation of leucinol

$^{1}$H NMR and $^{13}$C NMR spectra (Figures 11, 12, and 13) and $^{1}$H NMR spectra of leucinol (Figure 14) confirmed the structure of this compound. The IR shows a broad peak in the O-H region (3420 cm$^{-1}$). Seven carbon peaks are consistent with the structure of dimethyl leucinol. There is a big singlet at δ=2.16 (6H, s, N*Me*$_2$) (Figure 12) instead of a broad and short singlet δ=2.58 (N*H*$_2$) (Figure 14). Other peaks of dimethyl leucinol and leucinol are the same in Figure 12 and Figure 14.

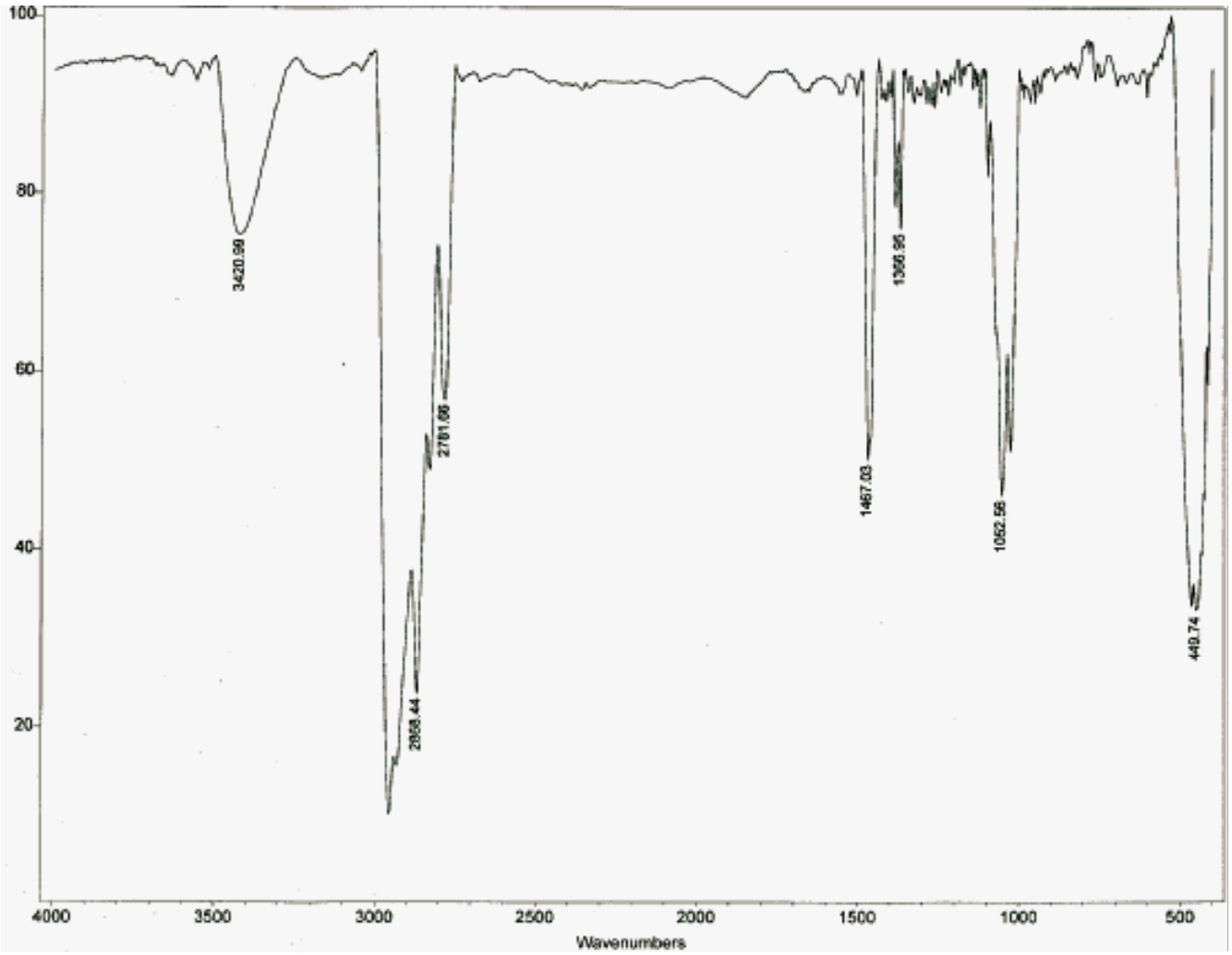



Figure 11. IR spectrum of dimethyl leucinol

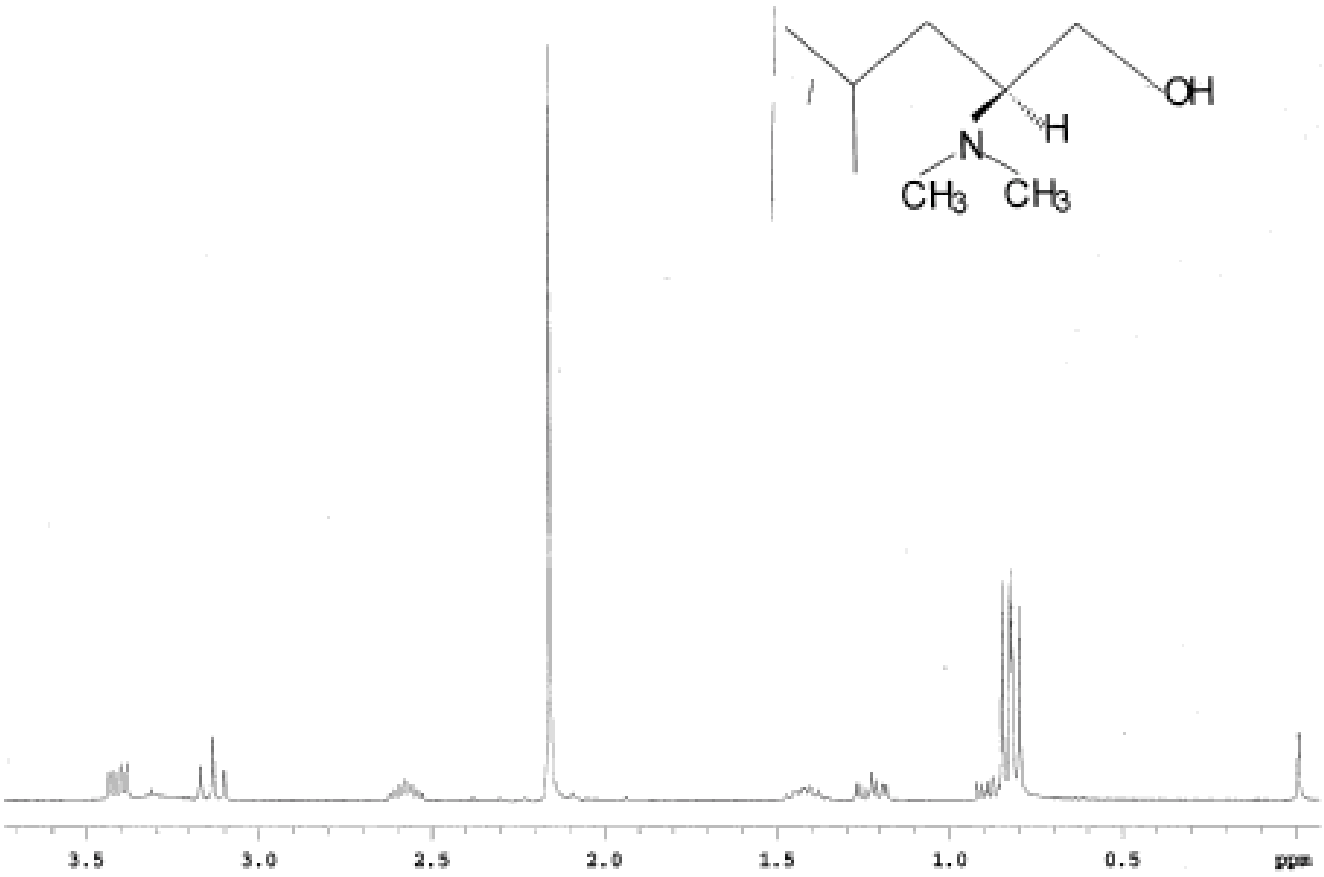



Figure 12. $^{1}H$ NMR spectrum (400MHz $CDCl_3$) of dimethyl leucinol

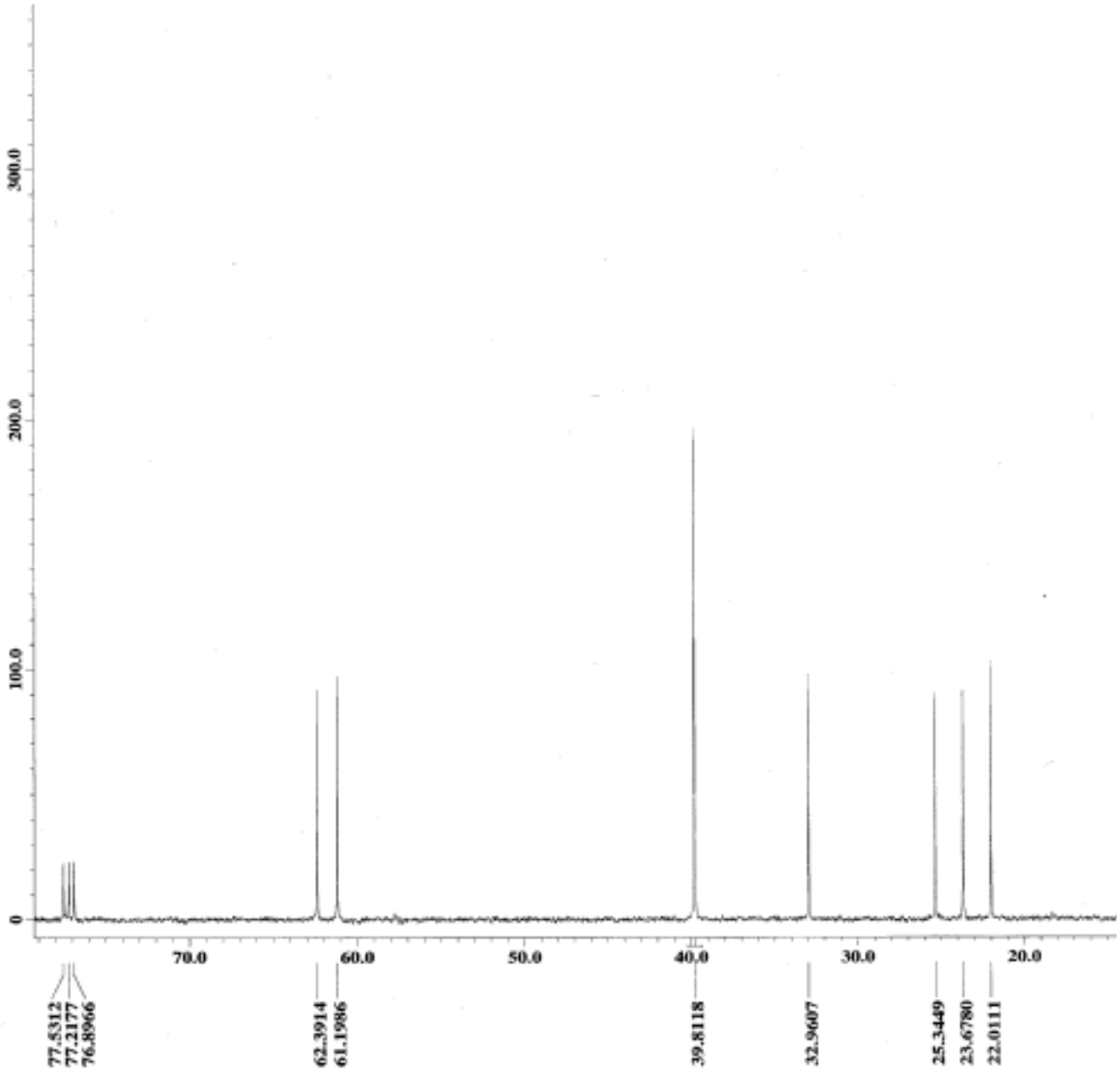



Figure 13. $^{13}C$ NMR spectrum (100MHz $CDCl_3$) of dimethyl leucinol

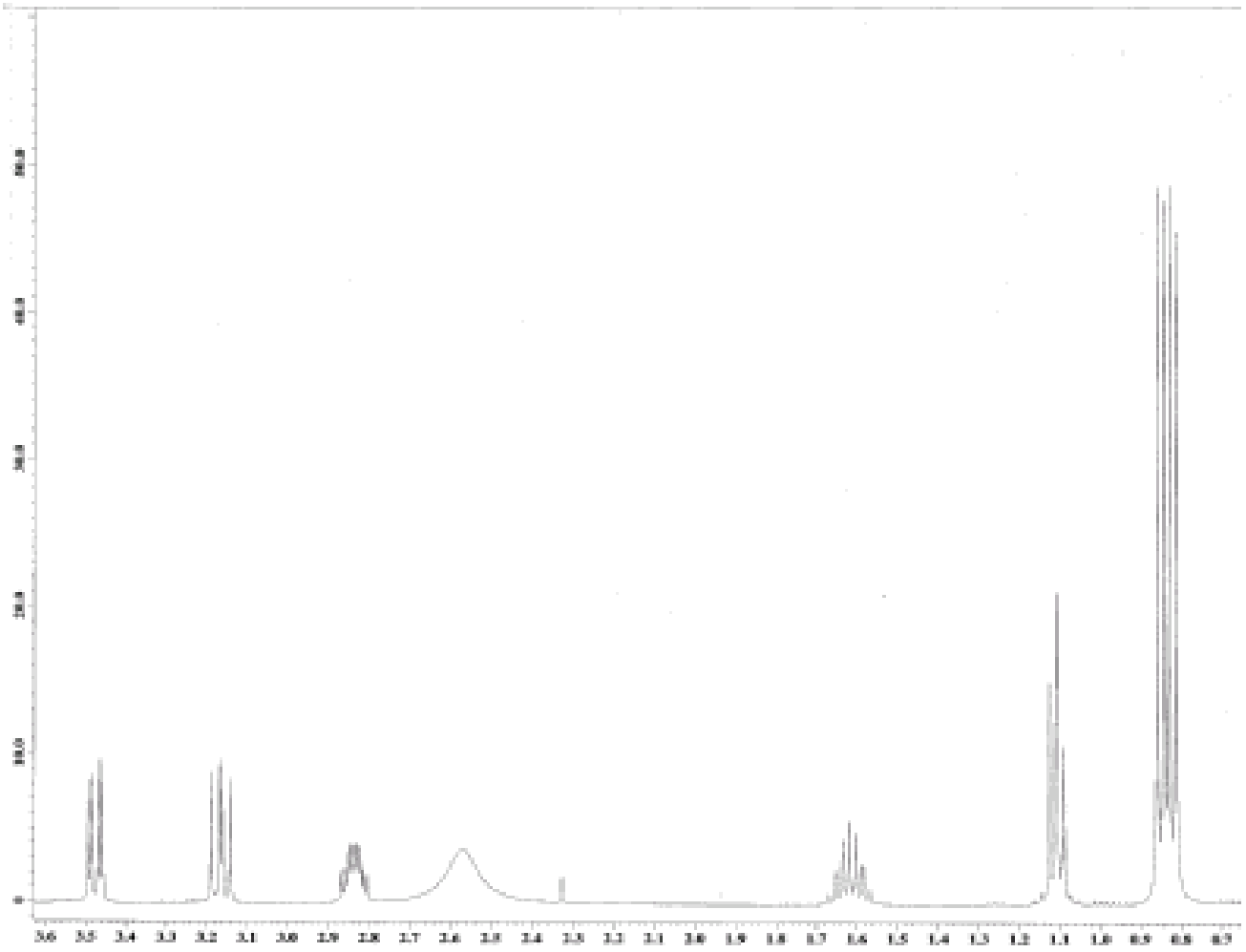
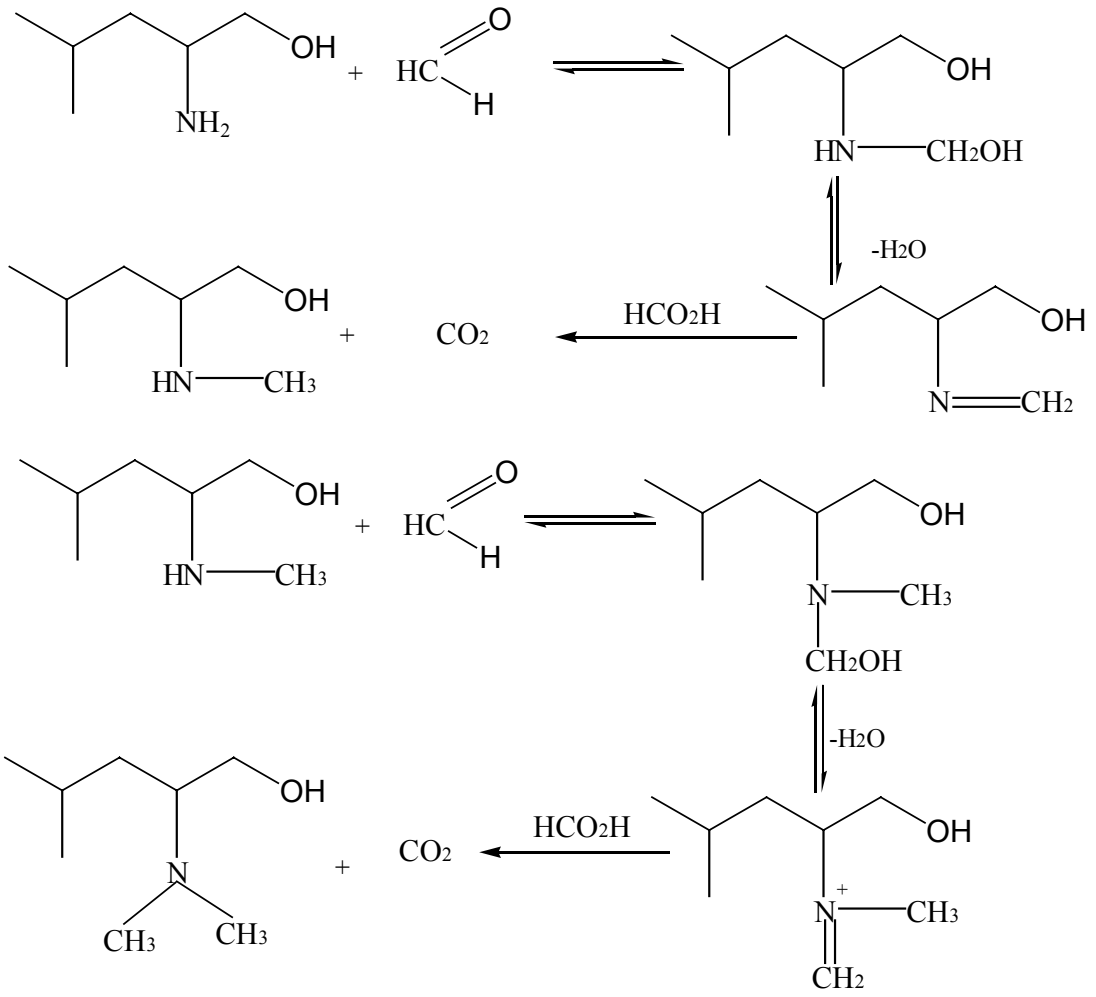


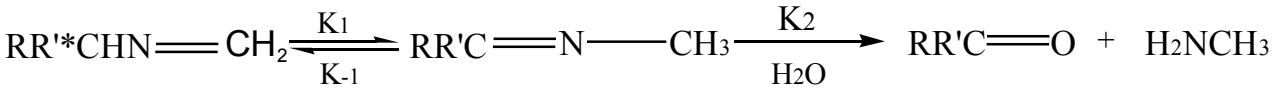
Figure 14. $^{1}H$ NMR (400MHz $CDCl_3$ ) of leucinol

The reaction proceeds through the formation of a Schiff base followed by reduction with the formic acid and subsequent loss of carbon dioxide. Addition of a second mole of formaldehyde readily leads to the tertiary amine as shown in Scheme 3.[28]



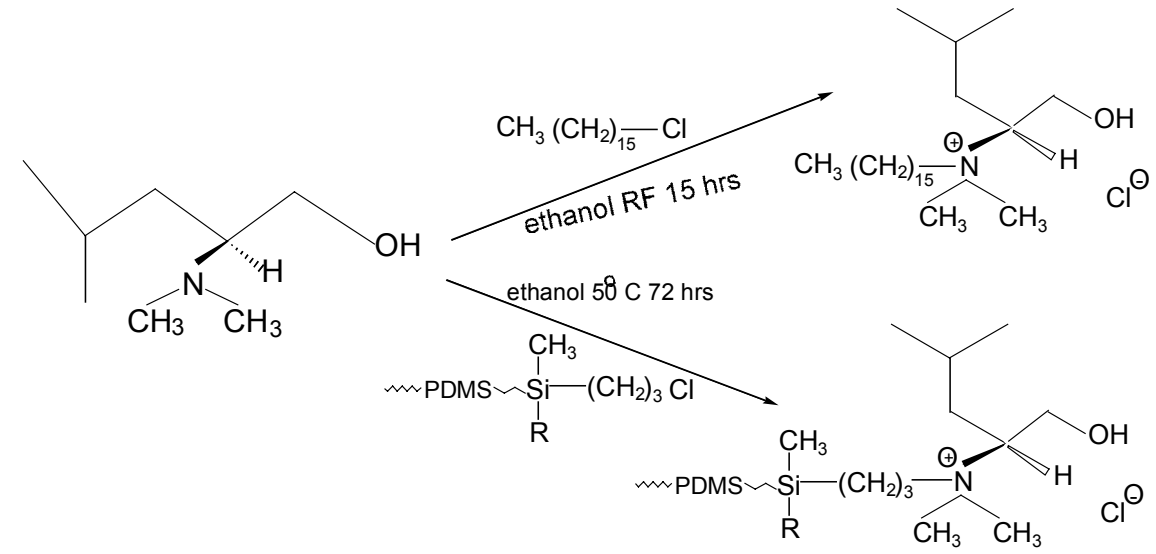

Scheme 3. Mechanism for methylation.

It has been demonstrated[29] that the methylation of an optically active amine in which the nitrogen atom is connected to an asymmetric carbon atom does not lead to loss of optical activity in the resulting tertiary amine because the rate of hydrolysis of the isomerized Schiff base is much faster than isomerization back to the Schiff base; i.e. $K_2 > K_{-1}$.




Formation of surfactants

The tertiary amine was attached to the siloxane polymer to form siloxane-based surfactants and was also attached to the alkyl halide to form leucine-derived surfactants. Both of these




Scheme 4. Formation of surfactants.

reactions take place using simple nucleophilic substitution chemistry, as seen in scheme 4.

The structure characterization of the alkyl leucine derived surfactants was done by IR and $^1$H NMR (Figure 15 and Figure 16). The IR shows a broad peak in the O-H region (3295 cm$^{-1}$). Compared with dimethyl leucinol, $^1$H NMR shows the singlet δ=2.16 (6H, s, $NMe_2$) shifted to

lower field δ=2.32 (6H, s, $NMe_2$). Additionally, other peaks of dimethyl leucinol have shifted to low field. This indicated that the dimethyl leucinol is attached on the alkyl halide.

The tertiary amine and the siloxane polymer were heated at $50^{O}C$ because the –O-Si-O- bonds are weaker than regular organic compounds. At a high temperature, these bonds are easily broken. $^{1}H$ NMR (Figure 17) spectrum also shows that the peaks of dimethyl leucinol shifted to lower field and confirms that the tertiary amine is attached on the siloxane polymers.

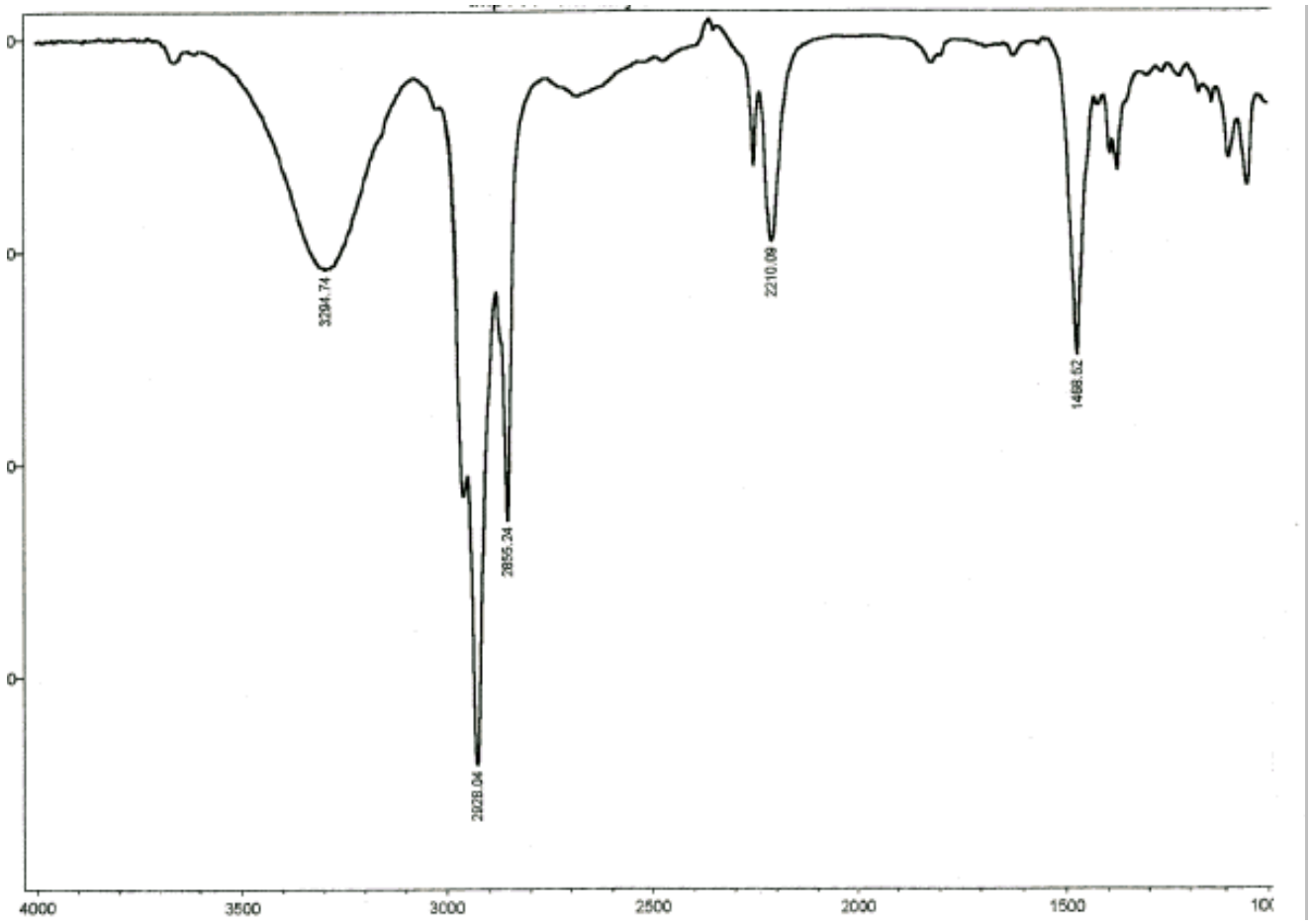



Figure 15. IR Spectrum of alkyl leucine derived surfactants

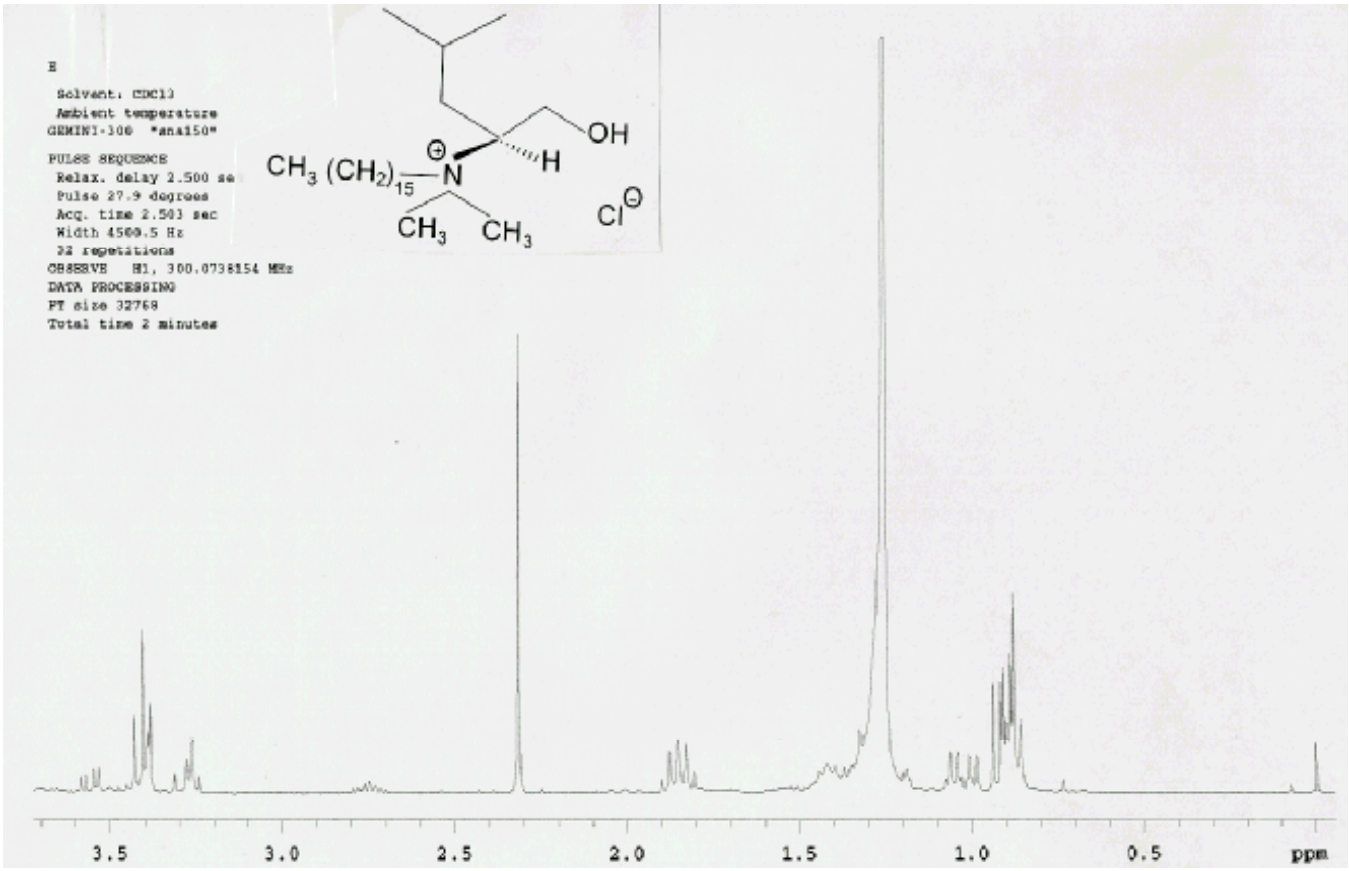



Figure 16. $^{1}H$ NMR spectrum (400MHz, $CDCl_3$) of alkyl leucine derived surfactants

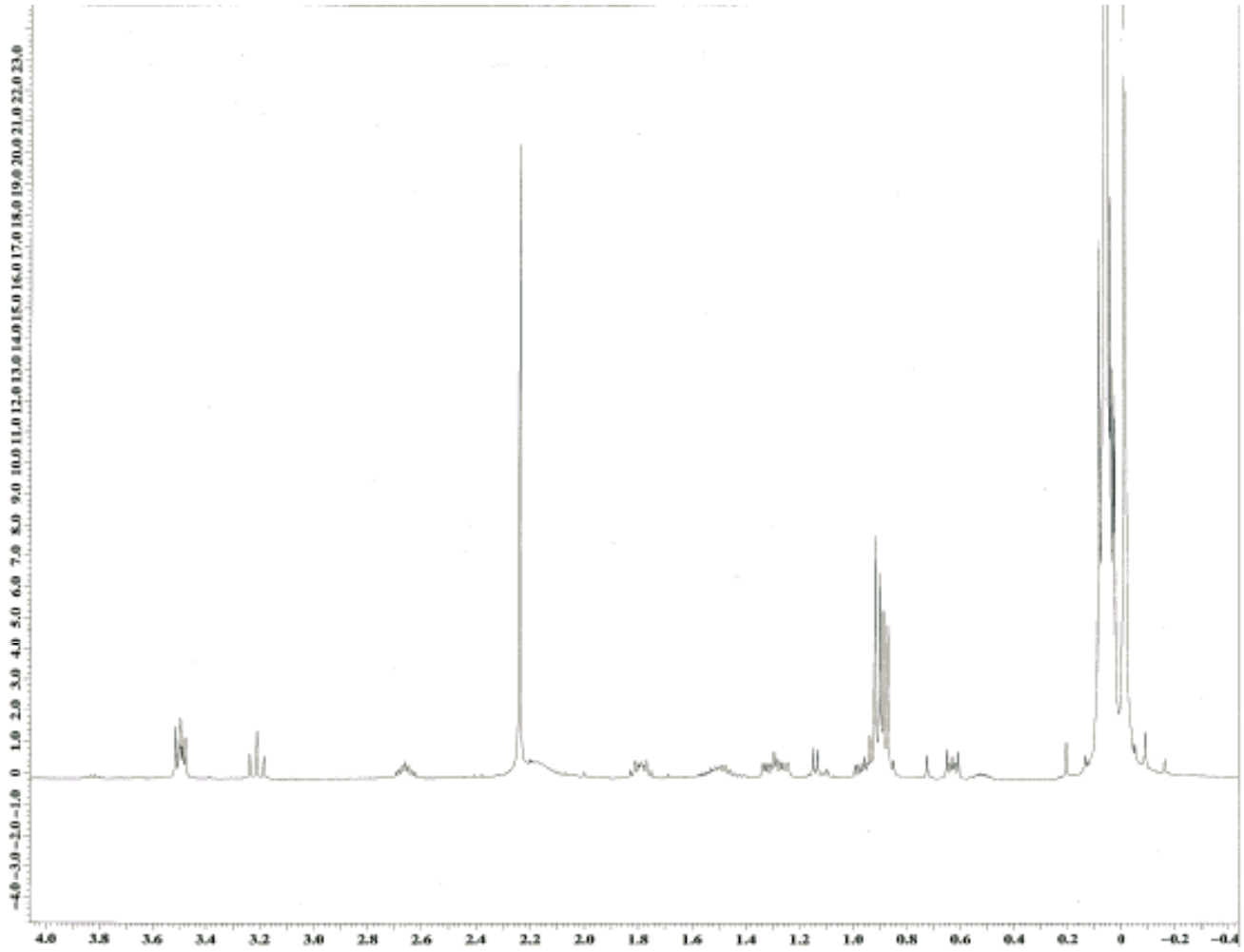


Figure 17. $^{1}H$ NMR spectrum (400MHz, $CDCl_3$) of siloxane-based surfactant

Tests of surfactant activity

Solubility of siloxane-based surfactants in carbon dioxide was carried out at the University of North Carolina. Initial solubility was determined by a simple constant volume cell instrument (Figure 18) a high-pressure stainless steel cell equipped with sapphire windows. The cell had a volume of 2.5 mL and an observation path length of approximately 1.30 cm. About 0.025 g of surfactant was added to the cell at room temperature. The cell was flushed and pressurized with carbon dioxide to a particular density, and the contents were then thoroughly mixed using a magnetic stirrer. Observations regarding solubility were then made, after which additional carbon dioxide was added to allow observations regarding solubility at higher fluid densities. Observations regarding solubility were usually made 10 minutes after mixing, and the cloud points were read as well.

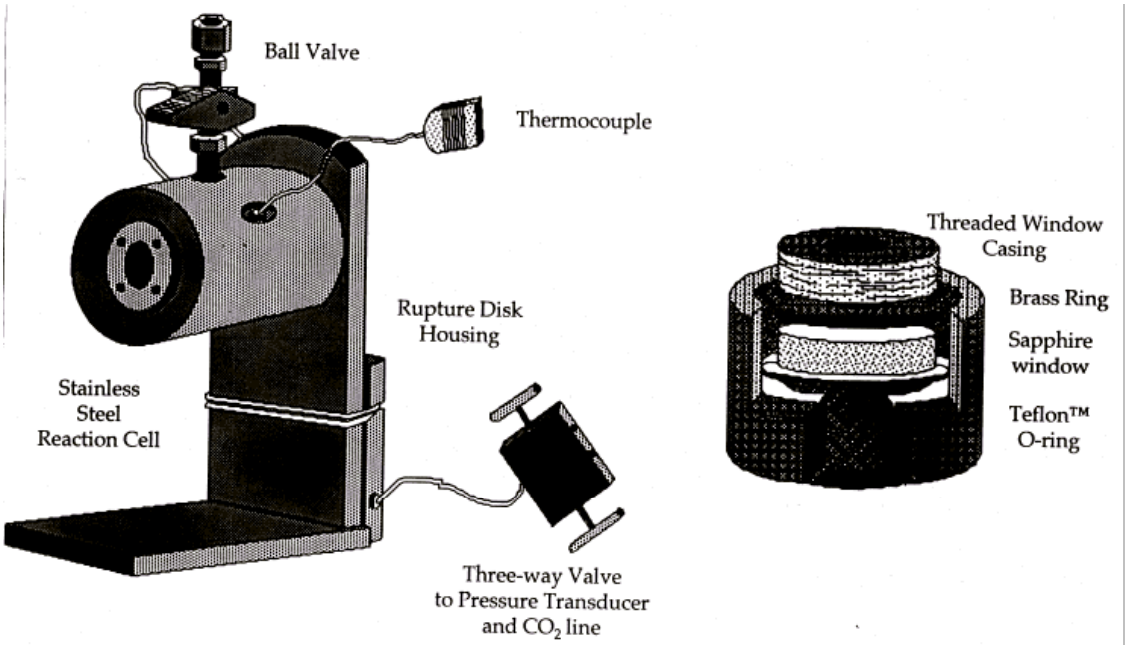



Figure 18. Structure of the constant volume cell

Initial investigation of the solubility of siloxane-based surfactant indicates the average 1.0% (w/v) of surfactants is quite soluble, as shown in Table 5.

Table 5. Solubility of siloxane-based surfactant at room temperature

| Chemical identification | Observation |
|---|---|
| 2000MW 1-tail siloxane-based polymer (1.22%w/v) | Soluble (1800 psig) |
| 2000MW 2-tail siloxane-based polymer (1.14%w/v) | Soluble (1900 psig) |
| 25000MW 1-tail siloxane-based polymer (1.06% w/v) | Soluble (2310 psig) |
| 25000MW 2-tail siloxane-based polymer (1.22%w/v) | Soluble (2520 psig) |

More sophisticated investigations of the solubility of surfactants were done by using a variable volume cell instrument. One percent (w/v) of surfactant was added to the cell, and the initial volume is 6 mL. After a certain amount of carbon dioxide was added, the valve was closed so the initial pressure was fixed. Increasing or decreasing the volume of cell or temperature can change the pressure of the cell. Investigations of solubility of the siloxane-based surfactant in $CO_2$ show that the different molecular weights of surfactant are quite soluble, as described in Figure 19.

The tests of solubility in $CO_2$ are done because of the beneficial properties of carbon dioxide: it presents a benign alternative to volatile organics and aqueous solvent; it is very easily recyclable; specifically, it is a processing fluid having a low cost and it has tunable density and dielectric constant. The siloxane-based surfactant can be soluble in $CO_2$, so we can combine the advantages of both in future applications, including extractions, stabilizers for emulsions, and a host of chiral organic and industrial application.

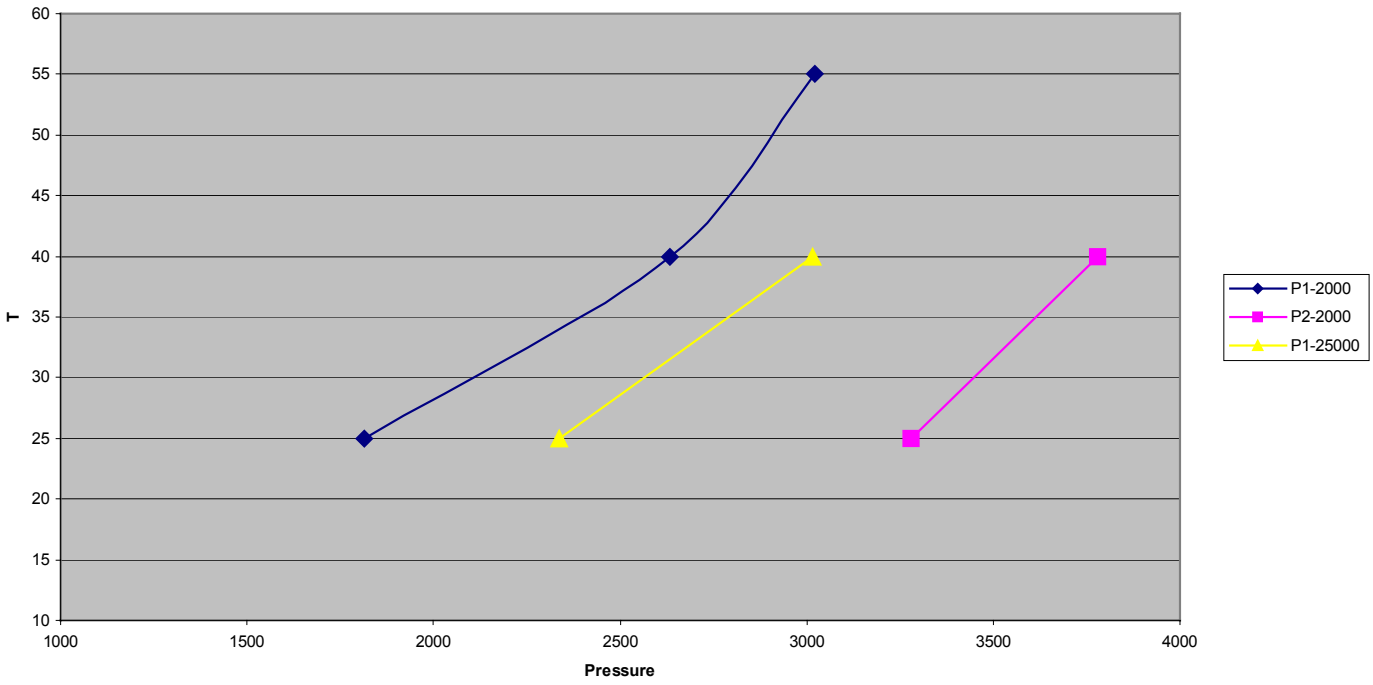


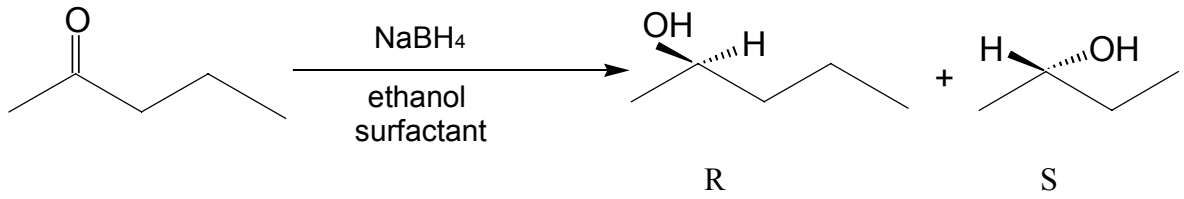

Figure 19. The cloudy points of siloxane-based surfactants in $CO_2$

Solubility of the alkyl leucine-derived surfactants in $CO_2$ was determined by simple visual inspection. The procedure was the same as siloxane-based surfactants. The pressure of the cell was increased from 0 psig to 6000 psig. Observations indicate that alkyl leucine-derived surfactants are not soluble in $CO_2$.

We attempted to ascertain the concentration at which micelles or micellar-like aggregates will be present using a dye method. A dye method can give an appropriate starting point because, in a micellar reaction system, mixed micellar aggregates will be generated. This is also likely to happen when the indicator dye is present. Methyl orange (0.818 g) was dissolved in 100 mL water and a different amount of leucine-derived surfactants was dissolved in hexane (100 mL) to make a series of different concentration solutions. The hexane solution (3 mL) was added to a UV cell, and a small amount of methyl orange solution was added, too. The cell was put into the

UV spectrometer after vigorous shaking. Because water and hexane are not miscible with each other, if the surfactant solution forms the micelle, the water will be carried into the hexane layer, and methyl orange as indicator will be detected by the UV spectrometer. Unfortunately, this test did not succeed in our research. It might be that the hexane is not the proper organic solvent for our surfactant, or the correct concentration was not found. However, the CMC can be determined by further testing such as surface tension.

The enantioselctivity of alkyl leucine-derived surfactants was tested by conducting a reduction of 2-pentanone. Ethanol (95%), 2-pentanone, and alkyl leucine-derived surfactant were added in a round bottom flask in an ice-bath, and then sodium borohydride was added to reduce the 2-pentanone as in scheme 5.




Scheme 5. Reduction of 2-pentanone

Under normal reduction conditions, a racemic mixture is produced. If the chiral surfactant has any influence on the reaction, we would hope to see an excess of one enantiomer. Enantioselectivity was observed when the alkyl leucine-derived surfactant was used. The concentration of alkyl leucine-derived surfactant was varied (1.3%w/v-4%w/v) and the effect on enantioselectives increased (enatiomeric excess ee. 5.4%-6.6%). These studies demonstrate that the nature of the head group can influence the enantioselectivity observed, and they suggest that ultimately it may be possible to tailor the surfactant type to the required product outcome.

# CHAPTER **4**

# CONCLUSION

We have been able to methylate leucinol successfully, and we have also synthesized leucine-derived surfactants and siloxane-based surfactants with chiral head groups. Initial tests of the solubility of leucine-derived surfactants and part of siloxane-based surfactants have been conducted. Also we have tested the change in solubility of surfactants with temperature and pressure in $CO_2$. Initial enantioselectivity was determined by reduction of a ketone (ee. up to 6.6%)

In order to fully evaluate the efficiency of siloxane-based surfactants and alkyl leucine-dervied surfactants for enantioselectivites, total intensity light scattering studies and surface tension measurements should be employed. This kind of work is limited by instrumentation and time. The solubility of siloxane-based surfactants in $CO_2$ should also be explored further.

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