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Intermolecular Interactions of Two Non-Ionic Surfactants with Water Studied Through Nuclear Magnetic Resonance

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Department of Chemistry

This paper was submitted on May 14, 2005 to the Thesis Committee of the Department of Chemistry and t the Director of the Honors Program at the State University of New York, College at Brockport, in completion of the thesis requirement specified in the guidelines for to award of honors in chemistry.

We the undersigned have read this thesis and recommend the award of Honors in Chemistry to Megan E. Bennett upon completion of all requirements for graduation.

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from all of the hydrogen atoms bonded to the methyl groups on the surfactant except the hydrogen atoms bonded to the two-methyl groups within the ethoxy groups. Peak 2 represents the hydrogen atoms bonded to the two-methyl groups within the ethoxy group. The hydrogen atoms bonded to the two terminal methylene groups on the alkyl chain give rise to Peak 3. Peak 4 is a result of the hydrogen atoms bonded to the remaining methylene groups. The shoulder (peak 5, ppm value of approximately 3.3) is derived from the hydrogen atoms bonded to the two terminus methylene groups on the isopropoxy group and the two terminus hydrogen atoms of the methylene groups of the terminal ethoxy group. Peak 6 arises from the hydrogen atoms within the remaining ethoxy group (excludes the two terminus methylene groups and the hydrogen atoms bonded to those two methylene groups). Peak 7 is the hydrogen atom from the hydroxyl group.

Figure 10 b). The spectral assignment based on chemical shift values, for a carbon thirteen spectrum. The color of the peak number corresponds to that of the highlighted structure above the spectrum. The tall peak at zero ppm (ppm) is the internal standard tetramethyl silane (TMS). Peak 1 represents the carbon atoms bonded to the majority of the methyl groups except the carbon atoms bonded to the two methyl groups in the isopropoxy groups. Peak 2 represents the carbon atoms of the two methyl groups within the isopropoxy groups. Peak 3 are the carbon atoms of the two methlyene groups on the alkyl chain. Peak 4 represents all of the carbon atoms of the methine groups and the unmarked carbon atom. Peak 5 represents all of the carbons within the ethoxy chain. Peak 6 represents the carbon atoms bonded to the hydroxyl group. Peak 7 represents the

carbon atoms of all of the methylene groups bonded to the beginning of the ethoxy and the carbon atoms of all of the isopropoxy groups.

Figure 11. ^{1}H-NMR spectra of surfactant CHEM 29 as water content is increased. The exact ratio of the number of surfactant molecules to the number of water molecules is denoted on each spectrum in the form of molecules of surfactant: molecules of water. In this figure very clear spectral changes are observed as water content is increased. First, it is observed that the left most peak, the water peak, grows in intensity, as water is increase, which is expected because the number of hydrogen atoms present in water is increased as water content increases. It is also observed that the water peak migrates to higher chemical shift values as water content is increased. Another observation from this plot is, that the ethoxy peak is growing in intensity. The ethoxy peak is the peak immediately to the right of the water peak.

Figure 12. The ^{13}C-NMR spectra of CHEM 29 with increasing water content from pure surfactant to a ratio of surfactant molecules to water molecules of 1 to 200. These spectra exhibit very little changes. The ethoxy peak, the third peak from the left, undergoes a chemical shift change at a sample concentration of 1 molecule of surfactant to 10 molecules of water. The chemical shift value of the sample containing 1 molecule of surfactant to 9 molecules of water is 70.242ppm whereas the chemical shift vale of the sample containing 1 molecule of surfactant to 10 molecules of water is 70.516. This may be due to the fact that when a peak is set to a certain value in the software used for processing the NMR data, NUTS, does not pick the same exact point every time when setting a ppm value of a peak.

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Abstract

Through the use of various nuclear magnetic resonance (NMR) spectroscopic experiments we have studied the intermolecular interactions of two non-ionic surfactants with water. For the two surfactants used in these studies a proton NMR peak assignment has been completed. From the spectral assignments there are several different structures that the surfactant forms depending on the water content of the samples. First, we investigated the intermolecular interactions between water and a non-ionic surfactant, CHEM 1260, having an average of five ethoxy groups per alkyl chain (C_aE_5, where a is the number of alkyl carbons present in the surfactant and E stands for ethoxy). Proton NMR (^{1}H-NMR) has allowed for the identification of several cross-linking structures formed by the surfactant as water content increases. The second part of this research investigated the intermolecular interactions of a non-ionic surfactant, CHEM 29, consisting of seven ethoxy groups and two isopropoxy groups ($C_aE_7P_2$, where P stands for iospropoxy) and water. Both ^{1}H-NMR and ^{13}C-NMR were employed in this study. In the CHEM 29 study the presence of water in two different chemical environments was not observed as in the CHEM 1260 study, which lead to the idea that CHEM 29 behaves differently than CHEM 1260 in the presence of water.

Chapter 1

Introduction

1.1 Surfactants

Surfactant is an acronym for *surf*ace *act*ivating *a*g*ents* and they are generally thought of as cleaning agents [1]. Surfactants are categorized into four classes, which include non-ionic surfactants, anionic surfactants, cationic surfactants and amphoteric surfactants [1]. The intermolecular interactions of water and two non-ionic surfactants were studied in this research. Recently, research involving surfactants has moved away from surfactant's traditional role as cleansers towards the use of surfactant as green solvents. Surfactants have been recently used as green solvents in the research done by Dr. Markus M. Hoffmann and Anthony J. Marshall over the course of 2003-2005. The research discussed in this paper serves a dual purpose. An understanding of the intermolecular interactions of liquid non-ionic surfactants with water is sought, to improve the quality and uses of surfactants as cleaning agents but also an understanding under what conditions non-ionic surfactants could be used as green solvents to replace traditional organic solvents.

Surfactants are a class of solutes that affect surface tension [1]. Non-ionic surfactants have two components to their structure. The hydrophobic or water fearing component of the structure is usually an alkyl chain. The hydrophilic or water loving component of the structure for the two surfactants studied consists of five ethoxy groups in one case and seven ethoxy and two isopropoxy groups in the other case. The surfactant molecules form layers at the surface of the water in which the hydrophilic portion of the molecule is

in contact with the water and the hydrophobic portion of the surfactant molecule is directed away from the water when water is present in the system. The hydrophobic regions of the surfactant align with one another so that they are tail to tail, as demonstrated in Figure 1.

Surface tension is a force that operates perpendicular to the surface of the solution [2]. In our study, the surface tension of the surfactant is changed as the water is introduced into the system. Surface tension as a force is depicted in Figure 2. Surface tension can be thought of as surface "free" energy [2]. It is known that work is equal to force multiplied by change in distance ($W= Fdx$) and if surface tension is a force that is proportional to the area of the surface then work equals surface tension (γ) multiplied by the change in area of a surface ($W= \gamma dA$). From the relationship $W= \gamma dA$, the units of surface tension are determined to be joules / meter^2, these units convey that surface tension is not only a force but also an energy that is proportional to the area of a surface [2]. Because we know that surface tension is a measure of energy it can now be demonstrated how the addition of a non-ionic surfactant changes the surface tension of the aqueous solution. As the surfactant is added to the water the entropy or disorder of the system is increased, even above the critical micelle concentration, CMC (approximately 0.05 mass percent for the surfactants studied in this work). When the surfactant is added, at levels above the CMC, the surfactant orients itself in a fashion such that the hydrophobic regions are away from water and the hydrophilic regions are surrounded by water, this is the formation of micelles.

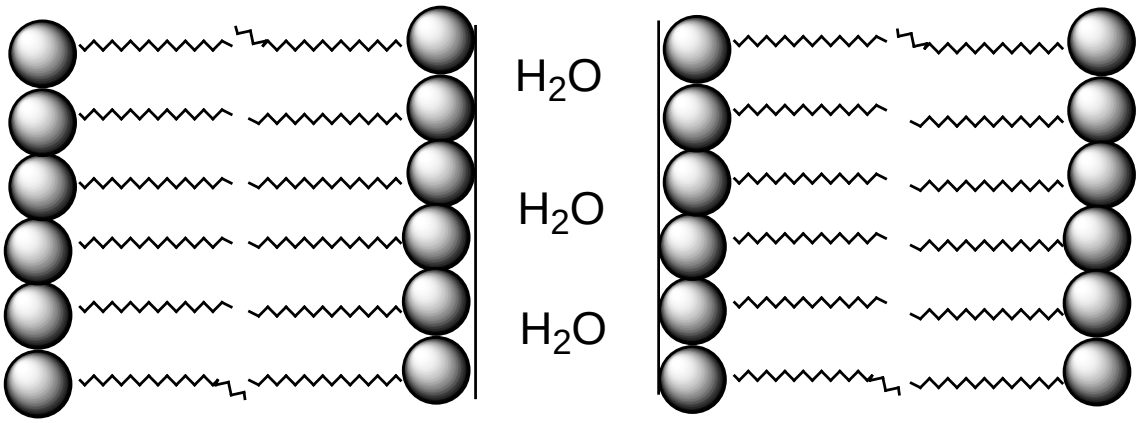

Figure 1. A depiction of the hydrophobic, meaning fear of water, region of the surfactant aligning with one another, as well as the hydrophilic, meaning water-loving, region of the surfactant aligning with water. The hydrophobic region is represented with a line and the hydrophilic region is represented as the circular shapes

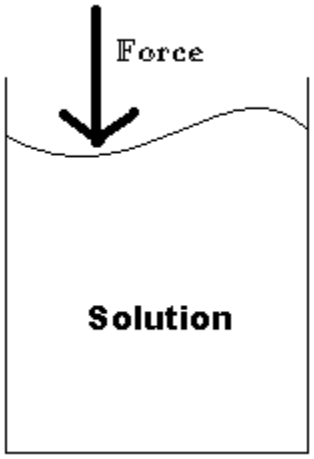

Figure 2. Description of surface tension is seen here. Surface tension is a force that operates perpendicular to the liquid gas interface of a solution or liquid. As the applied force is increased the area of the interface tends to decrease

Intuitively, one would expect that the organization of the surfactant monomers into micelles results in a decrease of the system entropy. However, when micelles are formed there is an overall increase in entropy of the system. The overall system increases in entropy because water molecules can form a more extensive hydrogen-bonding network once micelles are formed [1]. Prior to the surfactant forming micelles the hydrophobic tail of the surfactant is embedded in the water and no hydrogen bonds form because there are no lone pairs of electrons on the carbon atoms of the alkyl chain with which hydrogen can bond. Still prior to micelle formation, the water molecules at the surface of the surfactant chain aggregate and attempt to form a hydrogen-bonding network and the system becomes more ordered around the surfactant, decreasing entropy [1]. Once the surfactant forms micelles the highly ordered water molecules return to the normal hydrogen-bonding structure of pure water, which increases entropy. However, the entropy for the surfactant itself decreases because the surfactant, when in micelles is in a more rigid, more ordered form [1]. Due to the fact that the overall entropy of the system is increased, the amount of force necessary to break the surface of the water decreases and therefore surfactants decrease the surface tension of water. Figure 3 demonstrates the entropy changes of the overall system upon formation of micelles. The formation of micelles is important in understanding the intermolecular interactions between water and the non-ionic surfactants studied in this research because the research deals with the surfactant as a solvent and not water as a solvent. Therefore the surfactant is well above CMC and micellar or other aggregates are the dominant form of the surfactant, not single straight chains.

Figure 3. a) Depicts the solution when micelles are not formed (the solution is below critical micelle concentration, CMC). The water molecules are unable to move over the entire container due to the hydrophobic tails of the surfactant in the solution. However, in b) micelles have formed and the water can move about the container more freely than in a). Water moving more freely demonstrates an increase in entropy of the system.

In order to use surfactants as green solvents one must be able to predict and understand the behavior of water in surfactants, which is present due to the hygroscopic nature of the surfactants. If the intermolecular interactions of non-ionic surfactants and water can be understood, then not only improved and more efficient cleansing products will be produced but also a path towards using surfactants as green solvents may become easier.

Rochester Midland Corporation, based in Rochester, New York, supplied the liquid non-ionic surfactants used in this research. Rochester Midland Corporation produces cleansing agents ranging from surfactant mixtures used to clean food vats to surfactant mixtures used to clean public restrooms. With a greater understanding of the

intermolecular interactions of surfactants and water Rochester Midland Corporation's most widely used surfactant ingredients, CHEM 1260, (C_aE_5), and CHEM 29, ($C_aE_7P_2$) Rochester Midland Corporation will be able to improve their products.

This research also serves as a vehicle to better understand how a green solvent or environmental friendly solvent may be used to replace traditional hazardous organic solvents such as hexane. Traditional organic solvents tend to be widely used but they are heavily regulated, expensive to dispose of, extremely flammable, hazardous to one's health and they maybe corrosive [3]. If surfactants can be used to replace these traditional organic solvents then the problems associated with disposal and use could be virtually eliminated.

Chapter 2

Theory

2.1 Nuclear Magnetic Resonance Theory

In order to study the surfactant's behavior at varying water concentrations nuclear magnetic resonance (NMR) spectroscopy was employed. NMR spectra arise from the energy required for a nuclear spin that is aligned with the applied magnetic field to transition to non-alignment with the applied magnetic field. In order to understand NMR spectra, a basic understanding of NMR theory is useful. NMR is possible because a nucleus posses a magnetic moment as well as the property of angular momentum [4]. The magnetic moment of the nucleus interacts with a static field, which in NMR spectroscopy is the applied magnetic field [4]. Due to the strength of the field the magnetic moment of the nucleus is forced to align with the direction of the static field and due to the angular momentum of the nucleus, the nucleus precesses around the static field [4]. In NMR the direction of the applied field is typically considered to be the *z*-direction in a Cartesian coordinate system. The precession frequency also known as the Larmor frequency, ω, can be derived using a quantum mechanical approach. The nucleus of an atom is not perfectly aligned with the applied magnetic field and therefore the nucleus has spin angular momentum, which causes the nucleus to precess about a different axis then that of the applied magnetic field with a certain frequency, ω [5]. The derivation of the Larmor frequency is shown in the following equations [6]. Equation 1 is the equation for magnetic dipole moment, μ. The magnetic dipole moment is equal to the current multiplied by the area of the loop the current is traveling in.

$$\mu = iA \tag{1}$$

If the precession of the nucleus is considered to be a circular loop about the *z*- axis then Equation 2 is the equation for area and when Equation 2 is substituted into Equation 1 then Equation 3 is obtained. In equation 1 and 3 *q* is the charge and the charge is moving at velocity, ν, and the electron is precessing around the radius of the atom, *r*.

$$A = \pi r^2 \tag{2}$$

$$i = \frac{q * \upsilon}{2\pi r} \tag{3}$$

$$\mu = \frac{q\upsilon}{2\pi r}\left(\pi r^2\right) \tag{4}$$

The dipole moment, μ, can also be expressed in terms of momentum, ρ and angular momentum, *L*, where $\rho = m\nu$ and angular momentum, $L = (\rho \times r)$. The substitution of momentum and angular momentum is shown in Equation 5

$$\mu = \frac{q(\rho x r)}{2m} = \frac{qL}{2m} \tag{5}$$

In reality the nucleus does not precess around the *z*-axis in a circular loop. Therefore, the classical angular momentum, *L* is replaced with the spin angular momentum of the nucleus, *I* to obtain Equation 6:

$$\mu = g_N \frac{q}{2m_N} I \tag{6}$$

In Equation 6, g_N is the gyromagnetic number and accounts for the conversion from classical angular momentum to spin angular momentum. The nuclear magneton, $B_N = \frac{q}{2m_N}$ can be substituted into the magnetic moment, Equation 6, to obtain Equation 7:

$$\mu = g_N B_N I \tag{7}$$

In Equation 8, the gyromagnetic constant,γ is introduced. Where $\gamma = g_N B_N$, can be substituted for $g_N B_N$ to obtain a simplified version of μ.

$$\mu = \gamma I \tag{8}$$

The nucleus aligns with the magnetic field, B_o, and has potential energy, υ, according to Equation 9.

$$\upsilon = -\mu B_o \tag{9}$$

Because the magnetic field is applied along the *z*-axis, which is also the precession axis of the nucleus, only the *z*-component needs to be taken into account for the scalar product leading to Equation 10:

$$\upsilon = -\mu_z B_z \tag{10}$$

When μ_z in Equation 10 is replaced with Equation 8, Equation 11 is obtained, which describes the potential energy of a spin-bearing nucleus in the presence of a magnetic field:

$$\upsilon = -\gamma B_z I_z \tag{11}$$

According to the second postulate of quantum mechanics, for every observable measurement in classical physics there is a corresponding Hermitian operator in quantum mechanics. In this case, the observable measurement is spin angular momentum, which corresponds to the Hermitian operator $\hat{I}_z$. The Hermitian operator $\hat{I}_z$ is defined in Equation 12.

$$\hat{I}_z = \pm \frac{1}{2} \hbar \tag{12}$$

Because the nucleus has potential energy the Hamiltonian operator can be used, seen in Equation 13.

$$\hat{H} = -\gamma B_z \hat{I}_z \tag{13}$$

For the spin of a proton kinetic energy is not considered due to the fact that the physical motion of the nucleus is irrelevant, because in NMR the transition of the spin-state is being examined. In quantum mechanics motion and spin transitions are statistically independent, which is why the wave function can be separated into variables of motion and spin. The Hamiltonian operator, Ĥ, in Equation 13 can be substituted into the Schrödinger equation, Equation 14, to obtain Equation 15.

$$\hat{H}\psi = E\psi \tag{14}$$

$$-\gamma B_z \hat{I}_z \psi = E\psi \tag{15}$$

Equation 15 is the energy eigenvalue equation with $\hat{I}_z\psi = \hbar m\psi$ where *m* is $\pm\frac{1}{2}$.

Equation 16 and Equation 17 follow then from Equations 14 and 15.

$$-\gamma B_z \hat{I}_z \psi = \hbar m \psi \tag{16}$$

$$E = -\hbar m \gamma B_z \tag{17}$$

Equation 17 is then evaluated with respect to the change in energy, ΔE, and *m* is set equal to $-\frac{1}{2}$ in the first energy evaluation because the spin, in its final state, is inverted from $+\frac{1}{2}$ to $-\frac{1}{2}$. For the second part of the energy evaluation, *m* equals $+\frac{1}{2}$ because initially the

nucleus is aligned with the field and is therefore a positive value. Thus we obtain for ΔE Equations 18 and 19 where $\hbar = \frac{h}{2\pi}$.

$$\Delta E = (-\hbar\left(-\frac{1}{2}\right)\gamma B_z) - \left(-\hbar\left(\frac{1}{2}\right)\gamma B_z\right) \tag{18}$$

$$\Delta E = \hbar\gamma B_z \tag{19}$$

It is also known that $\Delta E = h\nu$, where $h\nu$ is the frequency of a light photon absorbed in the energy transition, this is shown in Equation 20. Therefore, if $\Delta E = \hbar\gamma B_z$, the solution to Equation 19, is set equal to $\Delta E = h\nu$ then ΔE can be solved for and the Larmor frequency can be found, Equation 22. Equation 21 is Equation 3 only solved for y, ν. The derivation of the Larmor frequency is shown in Equations 20 through 24.

$$\Delta E = h\nu \tag{20}$$

$$\nu = \frac{\gamma B_z}{2\pi} \tag{21}$$

$$\Delta E = \frac{h\gamma B_z}{2\pi} = \frac{h\gamma B_z}{2\pi} = \hbar\omega \tag{22}$$

$$\hbar = \frac{h}{2\pi} \tag{23}$$

If ω is solved for in terms of the magnetic field felt by the nucleus, B_z, or in actuality the magnetic field locally seen by the nucleus (B_{local}), as well as substituting in for the gyromagnetic constant, γ the Larmor frequency, ω is obtained. The Larmor Frequency is shown in this Equation 24.

$$\omega = B_{local}\gamma \tag{24}$$

After deriving the Larmor frequency it is important to consider how NMR spectroscopy functions. In an NMR spectrum different peaks correspond to differing chemical environment. Therefore, in an NMR spectrum the chemical shift value, σ (difference in two chemical environments divided by the strength of the magnetic field), is actually being studied. The chemical shift value can be obtained using the Larmor frequency equation (Equation 24) as seen in Equation 25.

$$B_{local} = B_o(1-\sigma) \tag{25}$$

B_o is the applied magnetic field, which in this study was 300MHz . The term (1-σ) accounts for distortion of the electron orbitals that shield the nucleus from feeling the applied magnetic field in full [7]. Chemical shift actually indicates the difference in chemical environment between two different protons. The symbol σ represents chemical shift, which is equal to the frequency difference between two different chemical environments divided by the frequency of the applied field. This definition of chemical shift allows the chemical shift to be independent of the applied magnetic field. Chemical shift is thus a dimensionless quantity usually given in parts per million (ppm) [7].

In our surfactant study the behavior of the surfactant in differing water environments are of interest. The surfactant has a large number of oxygen atoms in which hydrogen-bonding is possible. Based on the possibility of hydrogen-bonding it becomes useful to discuss the nature of hydrogen-bonding with regards to NMR. In a system where hydrogen-bonding occurs there is a large resonance frequency due to the proton experiencing very little shielding from surrounded electrons because when hydrogen forms a hydrogen bond it tends to lose electron density [7]. Bernstein, *et al* observed a

difference of 4.5 ppm between water in the liquid phase versus water in the gas phase where the higher chemical shift was observed for liquid water [8]. The large difference in chemical shift values observed by Bernstein demonstrates how strong hydrogen-bonding affects chemical shift. A higher value of chemical shift indicates that more energy is required to invert the spin and therefore the particular nucleus has stronger interactions with the surrounding environment.

Chapter 3

Experimental

3.1 Sample Preparation

All surfactants used in the studies were obtained from Rochester Midland Corporation. If needed, water impurities were removed from the hygroscopic surfactant samples by bubbling nitrogen gas through a half-full, 500-mL bottle of surfactant, for a period of approximately eight hours. After the surfactant underwent the drying procedure the stock bottle of dried surfactant was then stored under a nitrogen environment in a glove box. Samples of various water concentrations were then prepared in the glove box.

The water-surfactant samples of varying water concentrations were prepared using clean, dry 20-mL capped vials. For each sample the uncapped vial was massed; then using a new glass pasture pipette the desired amount of surfactant was added to the vial and the vial was massed again. Finally, using a new pasture pipette the desired amount of de-ionized water was added, then the uncapped vial was massed again. After this procedure was completed the sample was capped, labeled and shaken to ensure mixing. The samples were then allowed to sit to ensure the absence of bubbles and foam generated by the surfactant. Two portions of the sample were then removed from the 20-mL vials. One portion was used to fill a clean, dry NMR tube using a new clean pasture pipette, and the other portion of surfactant was used for several Karl- Fischer titrations to determine the final watercontent of the sample. The NMR sample tubes were then capped and labeled. A group of approximately five NMR sample tubes were then removed from the glove box and were frozen using liquid nitrogen. While each sample was frozen, an inert dry gas, either nitrogen or argon, was blowing over the open sample tube to

minimize exposure to ambient air. After the samples were frozen the NMR tubes were re-capped and then taken to another location and sealed with an oxygen torch. The NMR sample tubes were sealed while a vacuum was applied to the NMR tube. These now sealed samples were relabeled and inspected for imperfections in the seal. The purpose of sealing the NMR sample tubes was to ensure that water content would be constant, and the sample would not be able to acquire water from the environment.

Approximately 5-mL of dried surfactant was removed from the 20-mL sample vial and used for three separate water determinations using a Karl-Fischer titrator. The syringe that was used to inject the samples into the titrator was rinsed with the desired sample three times, and was then massed. A sample of approximately 0.5-g was drawn into the syringe; the syringe was then re-massed and the sample was injected into the titrator. After the sample was injected into the Karl-Fischer titrator the syringe was re-massed. From these mass differences the exact amount of surfactant injected into the titrator was then calculated.

The study involving CHEM 29 did not use a dried surfactant and all samples were prepared outside the glove box. All samples involving the CHEM 29 dilution study were prepared in clean, dry 10 mL Erlenmeyer flasks. For every component of the system (CHEM 29, water) a new glass pasture pipette was used. Samples involving CHEM 29 utilized the same massing procedure for sample preparation, as did the CHEM 1260 dilution study. The samples of CHEM 29 were prepared using the following method. The sample was massed and then subjected to freeze-pump-thaw cycles to degas the samples, after which the samples tubes were sealed. The freeze-pump-thaw method ensures that no oxygen is present in the sample. The presence of oxygen accelerates the

relaxation time (T_1-measurements) of the atoms because the oxygen provides the excited atoms a quicker way to relax down to a more stable vibrational state. The procedure for degassing (deoxygenating) a sample is similar to that of freezing a sample. However, in degassing a sample the sample is frozen in liquid nitrogen then a vacuum is applied to the sample in the NMR tube. The NMR tube containing the sample is then placed in a room temperature water bath (vacuum is still being applied) until the sample is nearly thawed, then the sample is re-frozen using liquid nitrogen. Other thawing procedures were attempted, such as allowing the sample to thaw without assistance. The use of a heat gun or warm water resulted in thawing that was too fast and consequently the sample was drawn into the vacuum tubing, therefore compromising the sample. Freeze-pump-thaw cycles were repeated seven to eight times for every sample. One audible indicator that the sample has been freed of all gas is that one can hear a hissing noise from a more sudden evaporation of the liquid nitrogen close to the point when the entire sample is cooled to 77 K, the boiling temperature of liquid nitrogen. After the degassing procedure is complete the sample is then frozen once more and the NMR tube is sealed using an oxygen torch. The sample is degassed for T_1 measurements because the presence of oxygen in the sample offers an additional relaxation path for the surfactant and d-limonene molecules. The relaxation path offered by oxygen is significantly and artificially faster than that of the true relaxation time, which then leads to incorrect relaxation time data. Unfortunately, T_1 measurements were never completed due to the fact the peak intensity of the inverted peak never matched that of the normal peak and the data was deemed unreliable.

3.2 Instrumental Parameters

All NMR data were acquired using a Bruker instrument that operates at 300.13 MHz, i.e., at a magnetic field of about 7 Tesla. All ^{1}H-NMR data for both samples containing CHEM 1260 and CHEM 29 were acquired with a pulse width of only 1-μs to avoid saturating the detector and a relaxation delay of 1s to ensure fully relaxed samples.

All ^{13}C-NMR data for samples with lower water content, above a ratio of 1 molecule of surfactant to 50 molecules of water, were acquired using 128 scans. Otherwise for the more dilute samples 250 and 1024 scans were acquired to obtain an adequate signal-to-noise ratio.

Chapter 4

Results and Discussion

4.1 CHEM 1260 Study

A detailed interpretation of the data acquired for the dilution study of CHEM 1260 will be explored throughout this section. First, a single ^{1}H-NMR and ^{13}C-NMR, for a pure sample of CHEM 1260 a spectral assignment was completed and are shown in Figure 4a) and 4b). After both ^{1}H-NMR and ^{13}C-NMR spectra were acquired for the various water content samples of CHEM 1260 the spectra were then interpreted. Upon close inspection of the ^{13}C-NMR spectra in Figure 4b) and Figure 5 one can see that there are virtually no changes in the chemical shift values of the differing samples. Due to the finding that the ^{13}C-NMR spectra showed no changes over the sample range it was concluded that no useful information could be obtained from ^{13}C-NMR and the use of this instrumental technique was not emphasized during this study. Several samples having higher water (above 1 molecule surfactant to 100 molecules of water) content have been excluded from Figure 5 due to the fact that the sample produced a poor signal to noise ratio.

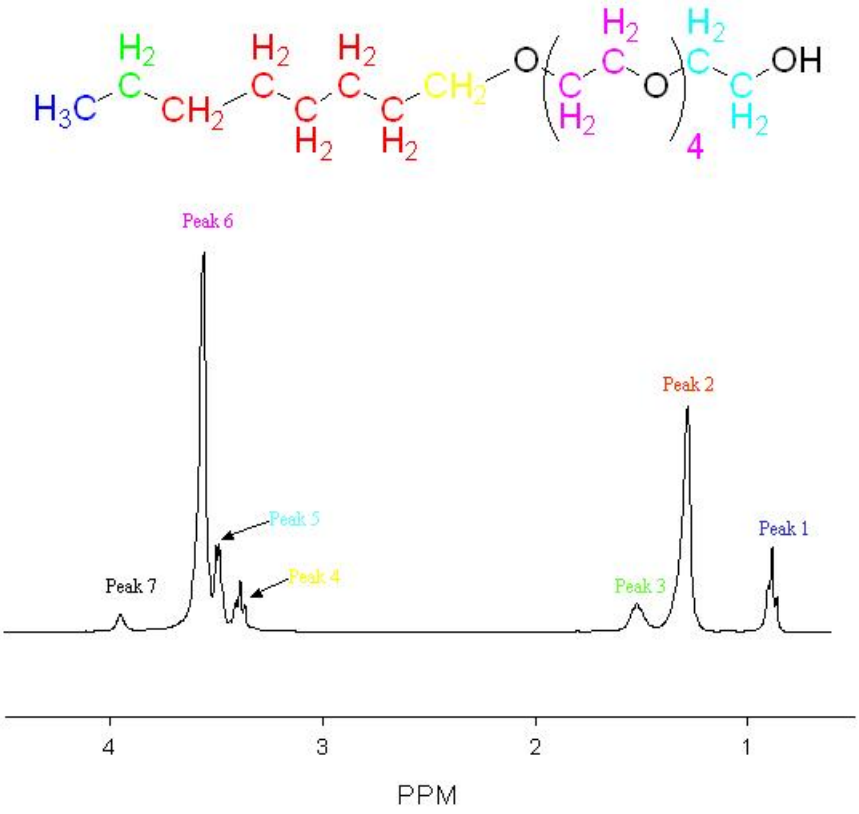

Figure 4a: Spectral assignment for a proton spectrum of surfactant CHEM1260: The color of the peak number corresponds to that of the highlighted structure above. Peak 1 is the methyl peak. Peak 2 is the alkyl chain. Peak 3 is the methylene group bonded to the methyl group. Peak 4 is the methylene group bonded to the oxygen just prior to the start of the ethoxy groups. Peak 5 are the alpha and beta methylene groups bonded to the hydroxyl group. Peak 6 consists of the four-ethoxy groups. Peak 7 is the hydroxyl/water peak.

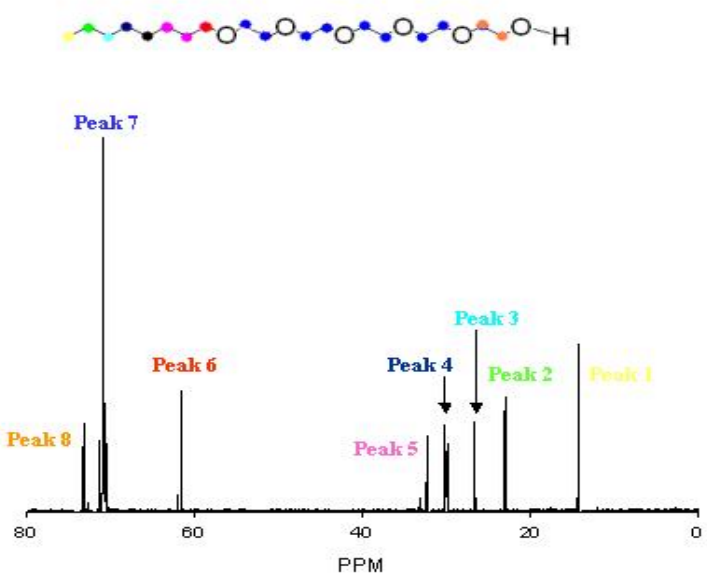

Figure 4 b). The spectral assignment for a ^{13}C NMR spectrum of surfactant CHEM 1260. The color of the peak number corresponds to that of the highlighted structure above. Peak 1 is the methyl carbon. Peak two is the carbon atoms from the methylene group bonded to the methyl group carbon. Peaks 3, 4 and 5 represent the alkyl carbons. Peak 6 is the terminal alkyl carbon (right of the ethoxy oxygen) bonded to first oxygen of the first ethoxy group. Peak 7 represents the carbon atoms in the ethoxy groups. Peak 8 are the carbon atoms from the two-methylene groups (to the left of the hydroxyl) of the terminal ethoxy group.

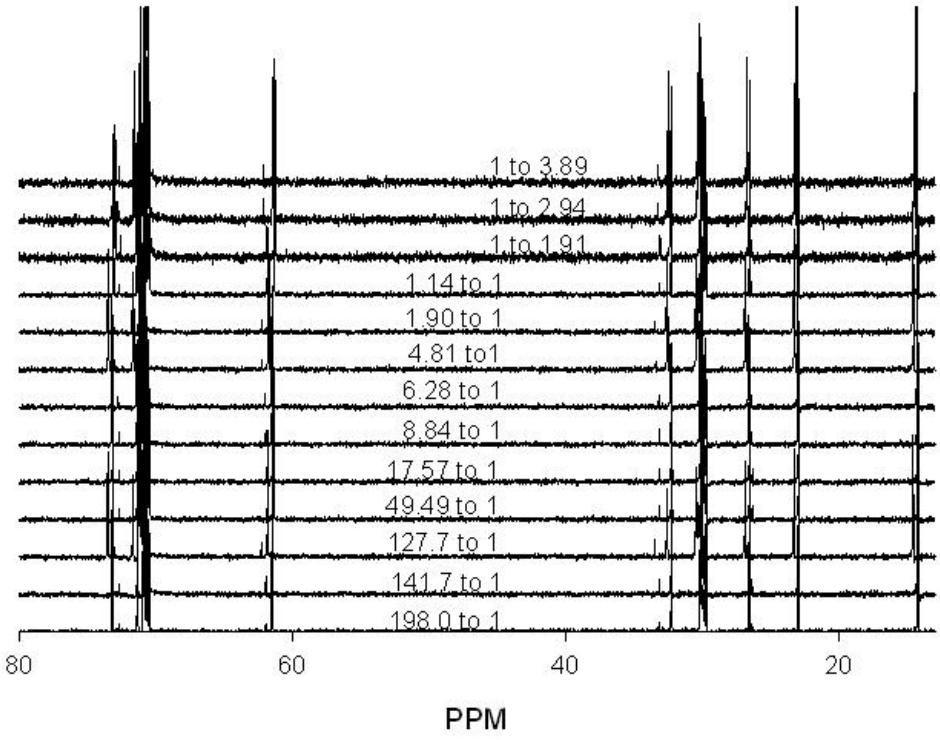

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Figure 5. ^{13}C-NMR spectra of CHEM 1260 with increasing water content from the bottom to the top of the spectra. There are virtually no changes seen in the spectra, which indicate that there is not an observable change in the way carbon atoms of the surfactant are bonded to one another. Due to no changes in the ^{13}C-NMR spectra of CHEM 1260 it was decided that ^{1}H-NMR would be used to investigate the intermolecular interactions of CHEM 1260 with water.

The ^{1}H-NMR experiments were performed on the same set of sealed samples. The results of the ^{1}H-NMR experiments can be seen in Figure 6. In this figure it is observed that there are definite changes in the spectra as water content is increased. Specifically, these changes are located in the water and hydroxyl proton peak region of the spectra. A close-up of the water and hydroxyl proton peak region of the spectra, Figure 7 shows there are indeed vast changes occurring within the samples as water content is increased. In Figure 7 one can more clearly see significant changes in the spectra. At a surfactant to water ratio of 1.90 molecules of surfactant to 1 molecule of water the hydroxyl peak appears to begin to split into two different peaks. At a ratio of 1 molecule of surfactant to 1.90 molecules of water the hydroxyl peak has completely split into two separate peaks. At a ratio of 1 molecule of surfactant to 8.2 molecules of water the farthest left peak of the split water/hydroxyl peak has virtually disappeared and the right peak of the split water/hydroxyl peak is increasing in magnitude. Finally, at a ratio of 1 molecule of surfactant to 41.3 molecules of water there is no indication of the left peak from the split water/hydroxyl peak existed, while the former right peak of the split water/hydroxyl peak continues to increase in magnitude. Also, as we look at the spectra of increasing water content it is observed that the hydroxyl peak moves from just below 4.0 ppm in the 127.8 molecules of surfactant to 1 molecule of water sample up-field to slightly below 4.25 ppm in the 1.90 molecules of surfactant to 1 molecule of water spectrum.

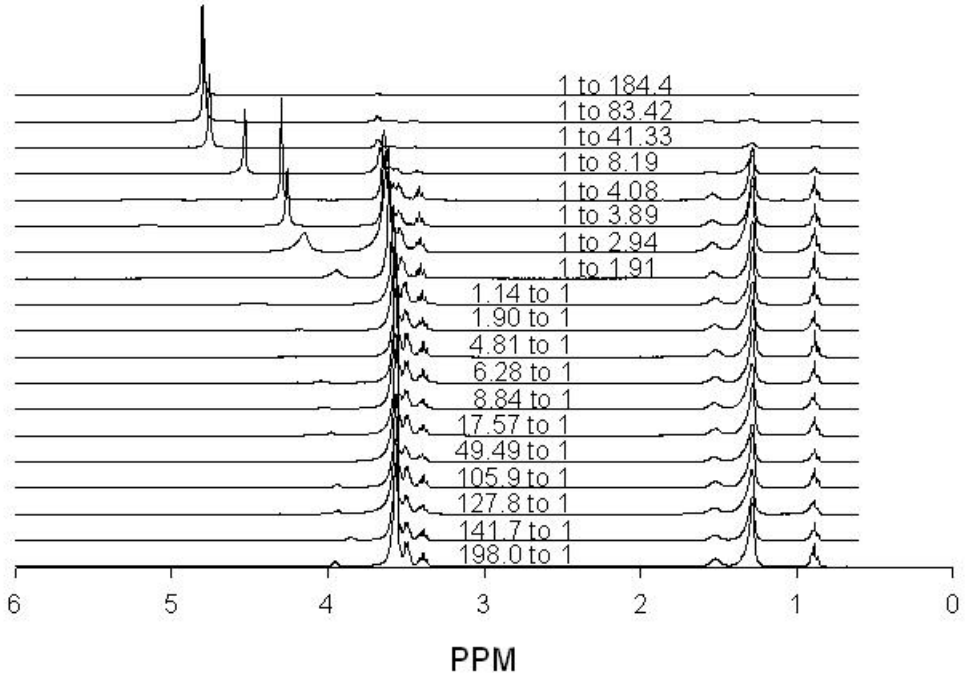

Figure 6. ^{1}H-NMR spectra of CHEM 1260 with increasing water content from the bottom to the top of the spectrum. Upon close inspection, several significant changes are observed in the spectra as water content is increased. These changes can be better seen in Figure 7.

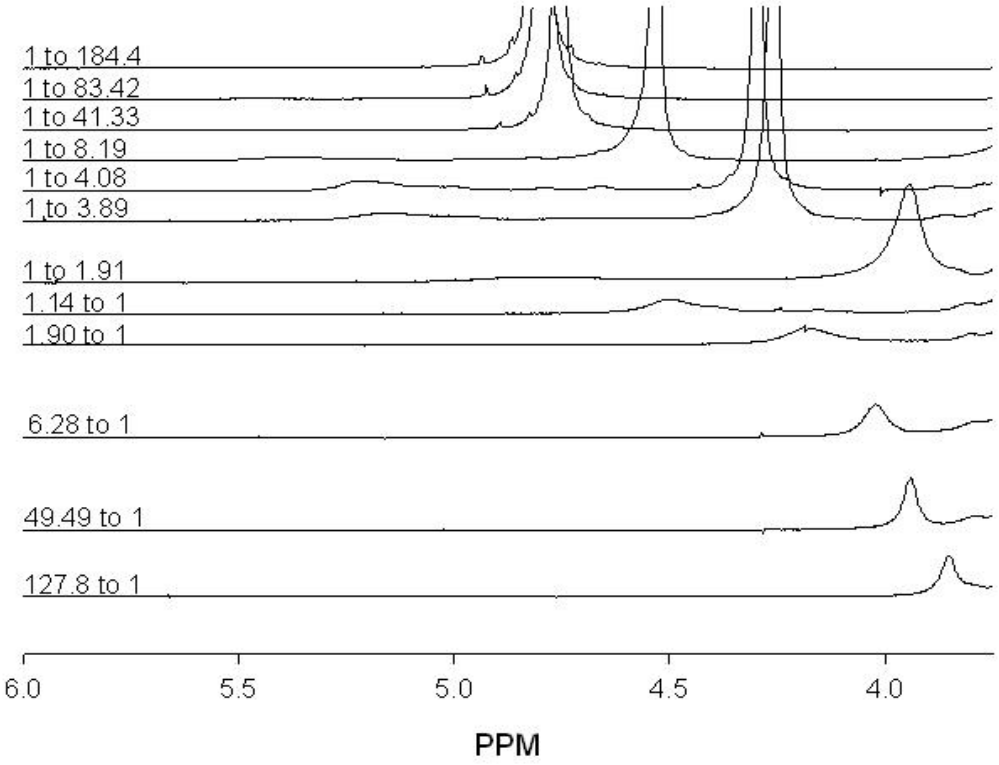

Figure 7. A close up of water/hydroxyl region of Figure 6. At surfactant to water ratios of 1.90 molecules of surfactant to 1 molecule of water the far left peak, consisting of the water and hydroxyl protons, the peak begins to split into two different peaks. At a ratio of 1 molecule of surfactant to 1.90 molecules of water the far left peak has completely split into two separate peaks. At a ratio of 1 molecule of surfactant to 8.2 molecules of water the farthest left peak of the split water/hydroxyl peak has virtually disappeared and the right peak of the split water/hydroxyl peak is increasing in magnitude. Finally, at a ratio of 1 molecule of surfactant to 41.3 molecules of water the left peak of the split water/hydroxyl peak is non-existent, while the former right peak of the split water/hydroxyl peak continues to increase in magnitude.

As the water/hydroxyl peak splits into two separate peaks the left peak shifts up-field to approximately 4.75 ppm; this occurs at the 1 molecule of surfactant to 8.19 molecules to water sample, the sample of highest water content before the complete disappearance of the left most peak occurs. The right peak of the split hydroxyl peak shifts up-field just prior to 4.0 ppm in the 1 molecule surfactant to 1.90 molecules of water sample and shifts up-field to approximately 4.5 ppmat a ratio of 1 molecule of surfactant to 8.19 molecules of water, just prior to the disappearance of the left most peak.

To explain the splitting of the water/hydroxyl peak at a ratio of 1.90 molecules of surfactant to 1 molecule of water and the disappearance of the left part of the split peak in the 1 molecule of surfactant to 8.19 molecules of water sample an explanation involving hydrogen cross-linking was employed as schematically depicted in Figure 8.

Figure 8 shows how the hydrogen atoms from the water are hydrogen cross-linked to the ethoxy groups of the surfactant. The left most peak is actually representative of the surfactant and water system once the hydrogen cross-linking structure has commenced. The resonance of a hydroxyl group is well known to exist at 3.9ppm. In Figure 8 a) it is shown how a fast equilibrium is established once a cross-linking structure has been established. The two hydrogen atoms from the water molecule associate or cross-link with two ethoxy groups and one hydrogen bond to just one ethoxy group. In Figure 8 b) it is shown how the water "walks" or migrates from ethoxy group to ethoxy group, which is a slow equilibrium.

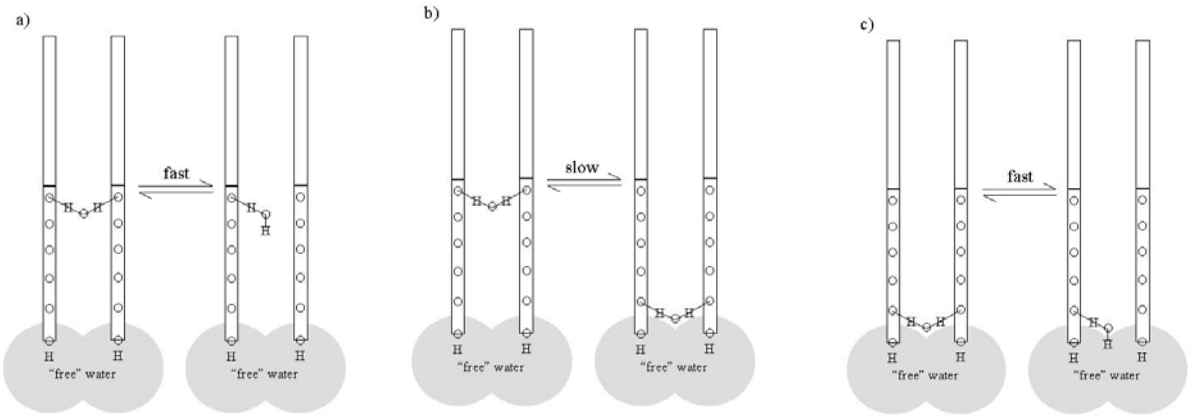

Figure 8. Demonstrates the hydrogen cross-linking explanation. Shown here is how the hydrogen atoms from the water is cross-linked to the ethoxy groups of the surfactant. In Figure 8 a) a fast equilibrium between the two hydrogen atoms from the water that associate or cross-link with two ethoxy groups and one hydrogen-bonding to just one ethoxy group. Figure 8 b) shows the water migration from ethoxy group to ethoxy group, is a slow equilibrium is shown. Figure 8 c) shows a fast equilibrium. There is a fast equilibrium because protons that are still entangled within the surfactant are freely exchanging with the "free" water, that is pooled at the bottom of the two surfactant chains.

The chemical equilibrium in Figure 8 b) is slow due due to hydrogen bond strength. Because hydrogen bonds are fairly strong it is difficult to break both of the hydrogen bonds, which is needed in order for the water molecule to "walk" down the ethoxy chain. Therefore, a slow equilibrium is observed. This is represented in the ^{1}H-NMR spectra by the splitting of the water/hydroxyl peak beginning at a ratio of 1.90 molecules of surfactant to 1 molecule of water where the a slow exchange of protons between the "bound"""bound"" water and the "free" water is coming into place. In Figure 8 c) it is shown that when the water, entangled within the surfactant, approaches the group of "free" water it can freely exchange a proton with the "free" water. This is a fast equilibrium, which is a result of the larger "free" water domain. "Free" water is water that can readily move and exchange protons with other water molecules. This second fast equilibrium, seen in Figure 8 c) accounts for the disappearance of the left part of the split peak in Figure 7 at the ratio of 1 molecule of surfactant to 8.19 molecules of water sample. This fast equilibrium is due to the overwhelming amount of "free" water, indicating by the progression of Figure 9. As the "free" water domain increases it allows for faster proton exchange between the cross-linked water protons and the "free" water protons because the "free" water domain is expanding farther and farther up into the ethoxy chain. One would expect this to actually occur at a stoichiometric ratio of 1 molecule of surfactant to 5 molecules of water but the ratio obtained in this study was 1 molecule of surfactant to 8 molecules of water. The larger value of 8 molecules of water is acceptable due to the concurrent growth of the "free" water domain. Faster proton exchange between the hydroxyl and the water protons should start to occur at a ratio of 1 molecule of surfactant to 5 molecules of water because of stoichiometric reasoning. For

every two ethoxy groups there can be a maximum of one water molecule connecting the two ethoxy groups. Hence, a ratio of 1 molecule of surfactant to 5 molecules of water would be obtained. The fact that the faster equilibrium is seen at a ratio of 1 molecule of surfactant to 8 molecules of water and not 1 molecule of surfactant to 5 molecules of water is further explained in Figure 9 c). If all sites on the ethoxy chain are cross-linked with water and the "free" water domain encroaches upon them, the water molecule hydrogen-bonding to the ethoxy groups are more likely to detach from the ethoxy groups and exchange protons with the "free" water domain. The observed ratio of 1 molecule of surfactant to 8 molecules of water would in turn indicate that there must be at least 3 "free" water molecules present for every 5 cross-linked water molecules in order for fast proton exchange to occur. Finally, these results apply only to the range of surfactant to water concentrations used in this study. No study has been conducted above a ratio of 1 molecule of surfactant to 184 molecules of water. However, at a ratio of 1 molecule of surfactant to 184 molecules of water the farthest left to the left, the water peak, has a chemical shift value that agrees with the chemical shift value of "free" water. Thus no further or additional principle changes in the ^{1}H-NMR spectrum would be expected upon further water content increase.

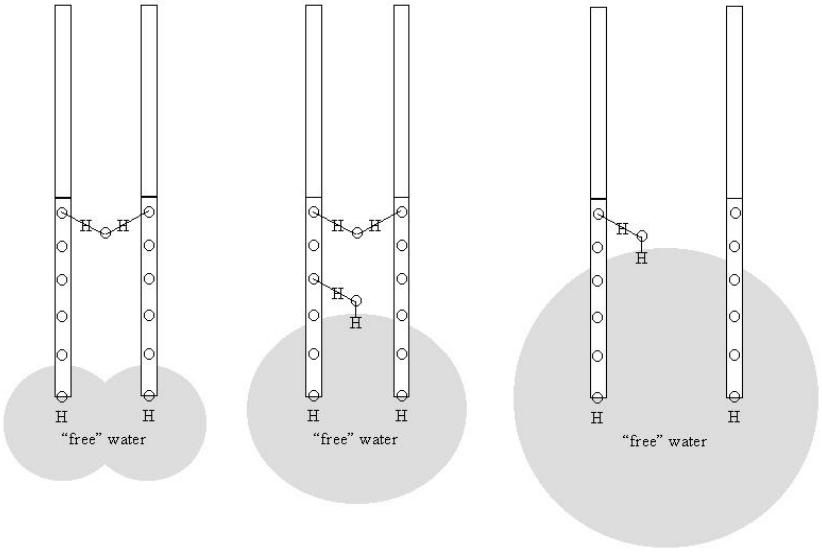

Figure 9. A demonstration of how the equilibrium of the differing cross-linking structures are affected as water is added to the system. As more water migrates to the "free" water area the "free" water increases. As the "free" water area increases faster proton exchange becomes possible because there is a greater amount of "free" water accessible to the ethoxy groups for proton exchange. As a result of faster "free" water exchange the split peak, seen in the ^{1}H-NMR spectra of CHEM 1260 between surfactant molecules to water molecules ratios of 1.90 to1 extending to a ratio of 1 to 8.19 coalesces into one peak at surfactant to water ratios above 1 to 8.19.

4.2 CHEM 29 Study

A detailed interpretation of the data acquired for the dilution study of CHEM 29 will be explored throughout this section. First a single ^{1}H-NMR and ^{13}C-NMR from a pure sample of CHEM 29 was acquired and a spectral assignment was completed. The results can be seen in Figure 10 a) and 10 b). Figure 10 a) shows the proton NMR spectral assignment. Peak 1 arises from all of the hydrogen atoms bonded to the methyl groups on the surfactant except for the hydrogen atoms that are bonded to the two methyl groups within the ethoxy groups. Peak 2 represents the hydrogen atoms of the two methyl groups within the ethoxy group. The hydrogen atoms of the two terminal methylene groups on the alkyl chain give rise to Peak 3. Peak 4 are a result of hydrogen atoms on all of the methine groups. The shoulder (peak 5), are derived from the hydrogen atoms on the two terminus methylene groups on the propoxy group and the two terminus hydrogen atoms on the methylene groups on the ethoxy group. Peak 6 arises from all of the hydrogen atoms within the ethoxy group. Peak 7 is the hydrogen atom from the hydroxyl group. Figure 10 b) shows the ^{13}C-NMR of CHEM 29. Figure 10 b) does not fully match theoretical calculations of chemical shift values based on the structure of CHEM 29, but does not change the research. Despite the mismatch of theoretical values and experimental data the spectra still shows very little change and still would not have been used as the main vehicle to investigate the intermolecular interactions of CHEM 29 and water as shown in Figure 12. The tall peak at 0 ppm is the tetra-methyl silane (TMS). The TMS was used as a reference peak in order to have our spectral peaks at their standard chemical shift values. Tentatively, the peak assignment is as follows peak 1 are the carbon atoms from all of the methyl groups except the two-methyl groups in the

isopropoxy groups. Peak 2 are the carbon atoms from the two-methyl groups within the isopropoxy groups. Peak 3 are the carbon atoms from the two-methine groups on the alkyl chain. Peak 4 are the carbon atoms from all of the methine groups and the unmarked carbon. Peak 5 are all of the carbon atoms within the ethoxy chain. Peak 6 is the carbon atom bonded to the hydroxyl group. Peak 7 are all of carbon atoms from the methylene groups bonded to the beginning of the ethoxy and isopropoxy groups. After both ^{1}H-NMR and ^{13}C-NMR were acquired for the various water content samples of CHEM 29 the observed spectral changes were then interpreted. Figure 11 shows the ^{1}H-NMR spectra for the dilution study of CHEM 29. In this figure an increase in intensity of the water peak, the far left peak as water is increased. In Figure 11 the chemical shift of the water peak begins at a value of 3.785 ppm in the pure sample of CHEM 29 and migrates up to 4.797 ppm in the 1 molecule of surfactant to 200 molecules of water sample. Water, like other molecules, is susceptible to the chemical environment in which it is in and this is why the water exhibits an array of chemical shift values. In Table 1, the expected ratio of molecules of surfactant to molecules of water, based on the mass determination of water content of CHEM 29 and water samples, is compared against the actual ratio of molecules of surfactant to molecules of water, determined using a Karl Fischer titrator, is shown.

Figure 11 reveals an increase in the intensity of the ethoxy peak, peak 6, which is demonstrated in Table 2. In Table 2 the ratio of integration values for the ethoxy peak relative to the aliphatic peaks is shown for every sample. This value was obtained by assuming that the aliphatic chain has constant composition for every sample and therefore a constant intensity. A constant intensity value would result in a constant integration

value. In Table 2 there is an increase in the ratio of ethoxy peaks to aliphatic peaks, this indicates that as water content is increased there is a peak underneath the ethoxy peak. Consistent with the CHEM 1260 study, we believe that the intensity increase is a result of water "bound""""bound"" or cross-linked within the ethoxy chain. Figure 11 and Table 2 both indicate that as the water content of the sample increases water is present in two different environments. One of the water environments is a “"free"” water environment in which the water molecules have the ability to quickly exchange protons within its chemical environment. The chemical shift value and intensity of "free" water corresponds to the far left peak seen in Figure 11. In a ^{1}H-NMR spectrum of pure water the signal resonance for water will be very large and occur around approximately 4.5 ppm. As more water is placed in the surfactant sample the surfactant will become saturated, containing the maximum amount of water possible. When this occurs the majority of the water exists as “"free"” water because the water molecule will move unhindered or "free" of interactions with the surfactant. The data in Table 2 suggest that there is a second form of water. This second form of water is cross-linked by hydrogen-bonding to the ethoxy region of CHEM 29. As more water is placed in the surfactant sample the ethoxy peak grows, indicating that water is "bound""""bound"" within the ethoxy groups. This water that is "bound""""bound"" to the ethoxy portion of the surfactant is referred to as “"bound""""bound"""” water.

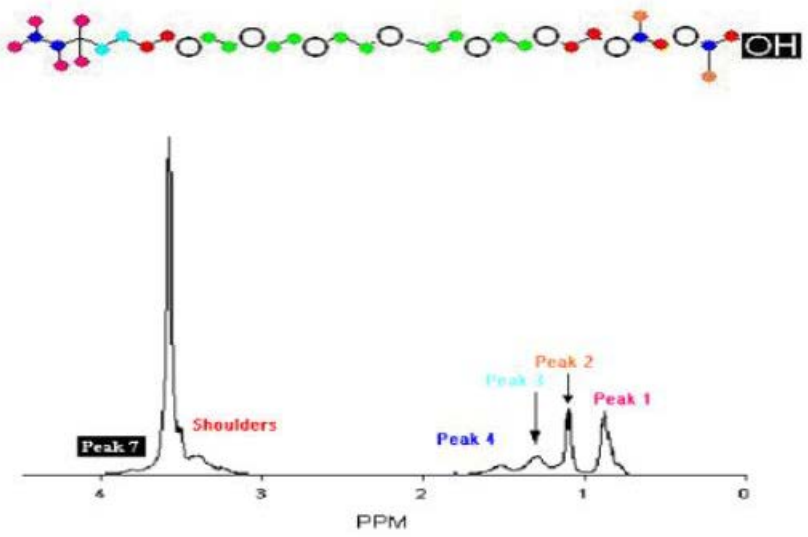

Figure 10 a). ^{1}H-NMR spectral assignment of CHEM 29. The color of the peak number corresponds to that of the highlighted structure above the spectrum. Peak 1 arises from all of the hydrogen atoms bonded to the methyl groups on the surfactant except the hydrogen atoms bonded to the two-methyl groups within the ethoxy groups. Peak 2 represents the hydrogen atoms bonded to the two-methyl groups within the ethoxy group. The hydrogen atoms bonded to the two terminal methylene groups on the alkyl chain give rise to Peak 3. Peak 4 is a result of the hydrogen atoms bonded to the remaining methylene groups. The shoulder (peak 5, ppm value of approximately 3.3), is derived from the hydrogen atoms bonded to the two terminus methylene groups on the isopropoxy group and the two terminus hydrogen atoms of the methylene groups of the terminal ethoxy group. Peak 6 arises from the hydrogen atoms within the remaining ethoxy group (excludes the two terminus methylene groups and the hydrogen atoms bonded to those two methylene groups). Peak 7 is the hydrogen atom from the hydroxyl group.

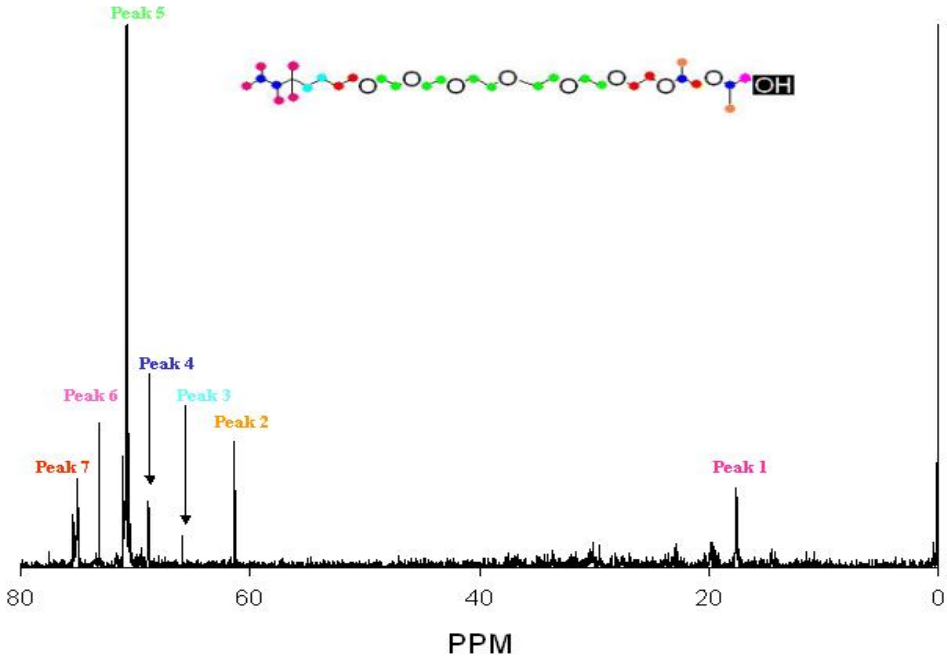

Figure 10 b). The spectral assignment based on chemical shift values, for a carbon thirteen spectrum. The color of the peak number corresponds to that of the highlighted structure above the spectrum. The tall peak at zero ppm () is the internal standard tetramethyl silane (TMS). Peak 1 represents the carbon atoms bonded to the majority of the methyl groups except the carbon atoms bonded to the two methyl groups in the isopropoxy groups. Peak 2 represents the carbon atoms of the two methyl groups within the isopropoxy groups. Peak 3 are the carbon atoms of the two methlyene groups on the alkyl chain. Peak 4 represents all of the carbon atoms of the methine groups and the unmarked carbon atom. Peak 5 represents all of the carbons within the ethoxy chain. Peak 6 represents the carbon atoms bonded to the hydroxyl group. Peak 7 represents the carbon atoms of all of the methylene groups bonded to the beginning of the ethoxy and the carbon atoms of all of the isopropoxy groups.

Table 1. Actual ratio of surfactant molecule to water molecule of each sample as determined by Karl Fischer Titration.

Expected Sample (molecules of surfactant : molecules of water	Actual Sample Water Content (water content)
1:1	0.806
1:2	2.02
1:3	3.13
1:4	4.03
1:5	4.99
1:6	6.01
1:7	7.012
1:8	8.033
1:9	9.003
1:50	50.24
1:100	100.18
1:200	199.80

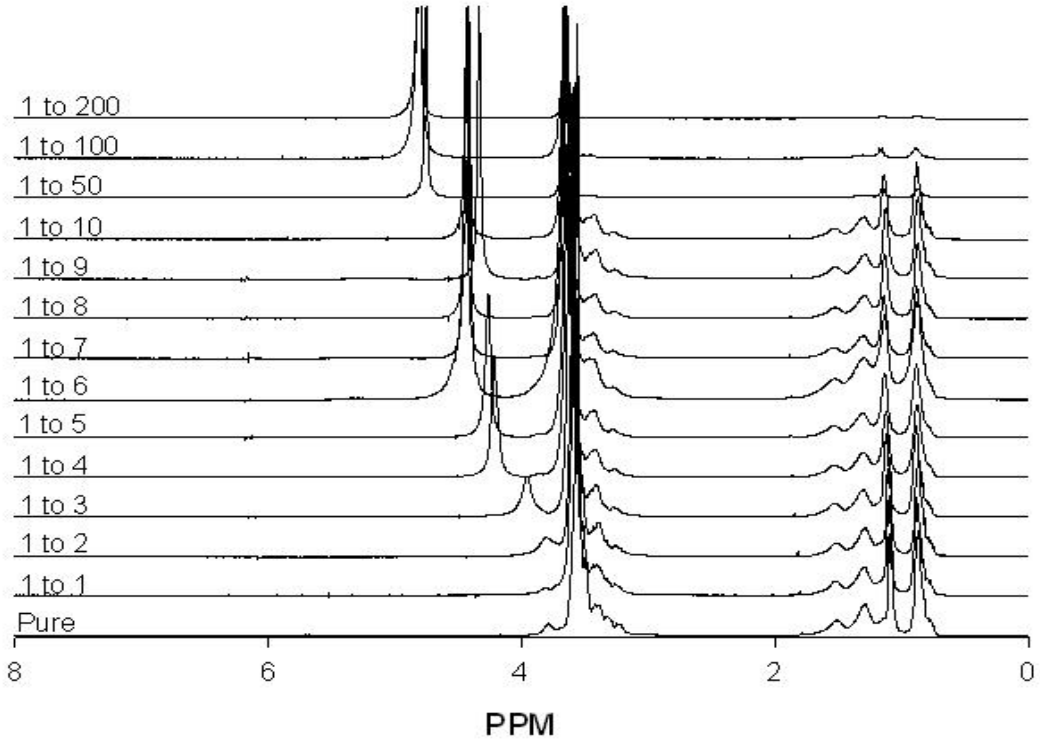

Figure 11. ^{1}H-NMR spectra of surfactant CHEM 29 as water content is increased. The exact ratio of the number of surfactant molecules to the number of water molecules is denoted on each spectrum in the form of molecules of surfactant : molecules of water, In this figure very clear spectral changes are observed as water content is increased. First, it is observed that the left most peak, the water peak, grows in intensity, as water is increase, which is expected because the number of hydrogen atoms present in water is increased as water content increases. It is also observed that the water peak migrates to higher chemical shift values as water content is increased. Another observation from this plot is, that the ethoxy peak is growing in intensity. The ethoxy peak is the peak immediately to the right of the water peak.

Table 2. Intensity of the ethoxy peak (E) divided by the intensity of the aliphatic peaks (A) for CHEM 29 and water samples

Sample Concentration (Surfactant to Water)	**E/A**
Pure	1.65
1 to 1	1.70
1 to 2	1.74
1 to 3	1.71
1 to 4	1.72
1 to 5	1.72
1 to 6	1.73
1 to 7	1.75
1 to 8	1.74
1 to 9	1.73
1 to 10	1.76
1 to 50	1.82
1 to 100	2.01
1 to 200	2.61
Stdev	0.244
AVG	1.81

As discussed in the results section of the CHEM 1260 study (Chapter 4) the two hydrogen atoms of a water molecule hydrogen bond or cross-link to one or two oxygen atoms within the ethoxy chain (Figures 8 and 9). The results of the CHEM 29 study can be explained by the hydrogen cross-linked structures that were observed in CHEM 1260 data. In both surfactant studies, CHEM1260 and CHEM 29, two types of water are present. However, in contrast to the CHEM 1260 study the two types of water never converge into a single type of water in CHEM 29, even at high water content. This observation may be due to the presence of the two-isopropoxy groups in CHEM 29. While the isopropoxy groups in CHEM 29 would provide more sites where a water molecule could hydrogen bond to oxygen atom, the methyl groups on the isopropoxy groups may block the path of the ethoxy "bound" water from reaching the end of the polyether chain where the "free" water resides. If the methyl groups from the isopropxylate groups block the path of the ethoxy "bound" water then the motion for the water is even more restricted than that in CHEM 1260 and this would result in a larger water concentration range where the water resonance is observed compared to where the water resonance is observed in the CHEM 1260 study. An increased number of sites where a water molecule could hydrogen bond to an oxygen atom would change the point at which the surfactant becomes saturated with water. The ratio at which the initial cross-linking structure occurs would not change because for every 2 ethoxy or isopropoxy oxygen present there would be 1 water molecule hydrogen-bonding two CHEM 29 chains together. The surfactant molecule to water molecule ratio at which the surfactant becomes totally saturated with water would change to a much higher surfactant to water ratio than that of CHEM 1260 where there are only 5 possible sites for water to

hydrogen bond with the surfactant. In order to confirm the behavior of CHEM 29 with water further experiments need to be completed on the CHEM 29 and water sample before any conclusions can be drawn from the data.

^{13}C-NMR spectra were also obtained for all of the CHEM 29 samples. However, the 1 molecule of surfactant to 100 molecules of water and the 1 molecule of surfactant to 200 molecules of water samples have been excluded from the plot in Figure 12 due to signal to noise problems. The ^{13}C-NMR did not yield a significant amount of information and the use of ^{13}C-NMR was discontinued as was done in the CHEM 1260 study.

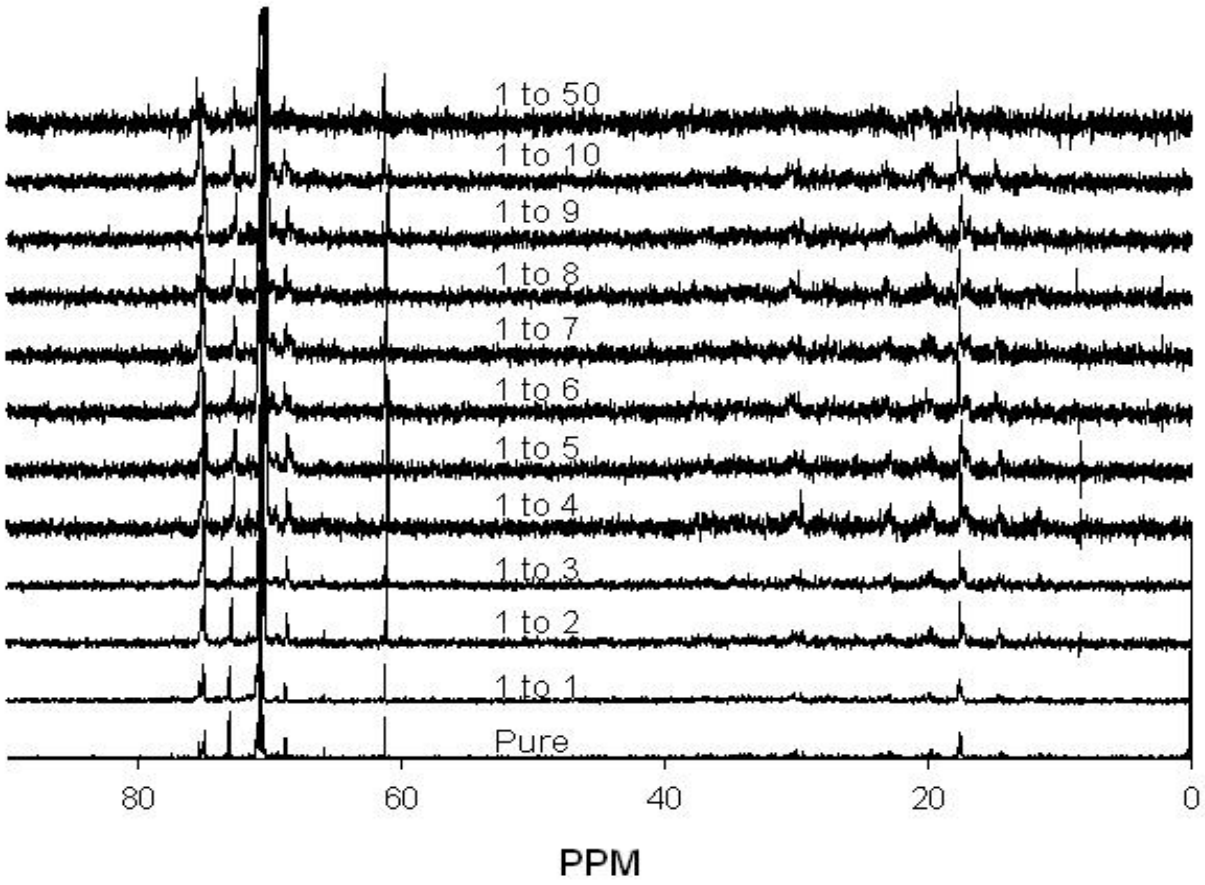

Figure 12. The ^{13}C-NMR spectra of CHEM 29 with increasing water content from pure surfactant to a ratio of surfactant molecules to water molecules of 1 to 200. These spectra exhibit very little changes. The ethoxy peak, the third peak from the left, undergoes a chemical shift change at a sample concentration of 1 molecule of surfactant to 10 molecules of water. The chemical shift value of the sample containing 1 molecule of surfactant to 9 molecules of water is 70.242ppm whereas the chemical shift vale of the sample containing 1 molecule of surfactant to 10 molecules of water is 70.516. This may be due to the fact that when a peak is set to a certain value in the software used for processing the NMR data, NUTS, does not pick the same exact point every time when setting a ppm value of a peak.

Chapter 5

Conclusions

In our dilution study of CHEM 1260 ^{1}H-NMR and ^{13}C-NMR were utilized to investigate the intermolecular interactions of CHEM 1260 and water. The interpretation of the obtained NMR data has led to the idea that several hydrogen cross-linking structures could explain the spectral changes in the ^{1}H-NMR spectra.

A fast equilibrium of proton exchange between ethoxy protons and water protons occurs and is demonstrated by Figure 9. Figure 9 a) gives a reasonable representation of surfactant and water intermolecular interactions until the surfactant to water ratio reaches 1.90 molecules of surfactant to 1 molecule of water value. At the surfactant to water ratio of 1.90 molecules of surfactant to 1molecule of water Figure 8 b) begins to explain the intermolecular interactions of the surfactant and water. Figure 8 b) continues to be accurate until a ratio of 1 to 8.19 is reached. At the surfactant to water ratio of 1 to 8.19 Figure 8 c) begins and continues to explain the intermolecular dynamics of surfactant and water until a ratio of 1 molecule of surfactant to 184 molecules of water is reached. It is believed that Figure 8 c) will explain the spectral changes observed at certain ratios.

In the dilution study of CHEM 29 and water no definite conclusions have been drawn yet but it is suspected that CHEM 29 behaves similar to CHEM 1260 in water. Both CHEM 29 and CHEM 1260 are suspected to for hydrogen cross-linking structures. The difference between the two surfactants is that CHEM 29 has two additional sites where water can hydrogen bond and four methyl groups that may retard the movement of "bound" water throughout the molecule. The two additional hydrogen-bonding sites change the concentrations at which the water/hydroxyl site is expected to disappear. In

CHEM 1260 the water/hydroxyl peak is expected to disappear at the concentration was 1 surfactant molecule to 5 water molecules, where as in CHEM 29 the expected disappearance concentration of the water/hydroxyl peak is at an unknown surfactant molecule to water molecule ratio due to the methyl groups that are "bound" to the isopropoxy group. Both surfactants should have the same concentration at which the water/hydroxyl peak becomes two peaks and that concentration is 2 molecules of surfactant to 1 molecule of water. However, in the CHEM 29 dilution study the water/hydroxyl peak is never observed splitting into two separate peaks and the left most peak is never seen disappearing into the baseline. This observation may be due to the presence of the isopropoxy groups.

In the CHEM 29 study data for extremely low concentrations of water were never collected. In order to directly compare and say with certainty that CHEM 29 behaves similar to CHEM 1260 a study of CHEM 29 with very low water content needs to be completed and additional NMR studies, such as NOESY and COSY experiments need to be completed in order to be certain that water is "bound" to the ethoxy and/or isopropoxy region of CHEM 29. Upon completion of this low water content study, NOESY and COSY NMR experiments definite conclusions may be drawn as to the similarity in behavior of CHEM 29 in water compared to CHEM 1260 in water.

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