COMPARISON OF CLOUD POINT CHANGES AND SURFACTANT DECOMPOSITION UNDER CONDITIONS OF THE EKOFISK RESERVOIR

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PREFACE

This study was conducted as part of a much larger project at Phillips Petroleum in Bartlesville, OK which focused on the use of wettability reversal to increase oil production from the Ekofisk reservoir in the Norwegian fields. This wettability reversal work in the Ekofisk reservoir involves the use of surfactants that must be stable under it's elevated temperature. This portion of the work was conducted to test the usefulness of cloud point measurement as a proposed surfactant stability indicator by comparing changes in surfactant cloud points after aging to their stability as measured by more traditional methods.

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CHAPTER I

INTRODUCTION

I.A. Objectives and Thesis Overview

This research is both an attempt to ascertain the usefulness of a possible surfactant stability indicator, changing cloud points, and in doing so the correlation of cloud point changes to thermal degradation effects observed for six surfactants. Background information relevant to topics, such as the oil recovery process, cloud point phenomena, and surfactant stability characterization techniques, are given in this text. Chapter 2 will focus on the aging and subsequent cloud point measurements of the surfactants including a discussion of factors that may affect observed cloud points. Chapters 3-8 will consist of the description of complementary analytical techniques which were used to characterize the surfactant aging effects and their relation to cloud point changes. The work presented in Chapter 3 will consist of the surface tension changes in two of the surfactants as they age and estimates of their changing concentrations. Chapter 4 includes chromatographic (headspace GC/MS) and spectroscopic (FTIR, NMR) methods aimed primarily at the identification of specific structural changes that have occurred with aging. The work in Chapter 5 includes measurements of some other consequences of surfactant solution aging known to effect cloud points. Chapter 6 summarizes the work and describes conclusions regarding the stability of the six surfactants, the usefulness of cloud point as a stability indicator, and suggestions for additional work.

I.B. Background

I.B.1. Ekofisk Reservoir

The Ekofisk reservoir, located in the North Sea, is one of Phillips Petroleum's largest oil fields. Ekofisk is a chalk reservoir and, like most oil reservoirs, is under conditions of high pressure (about 4,000 psi), high temperature (268 °F/131 °C), and high salinity (about 3.4% total dissolved solids). The present work deals with a surfactant based enhanced recovery technique which is under consideration for use in this reservoir. Many surfactants are unstable under such conditions, and their stability must be established prior to their use in the field. This work focuses on the question of surfactant stability under conditions approximating the temperature and salinity conditions found in the Ekofisk reservoir. The effects of the chalk substrate and pressure effects on surfactant stability are not accounted for in this work, due to limitations in the available experimental apparatus.

I.B.2. Enhanced Oil Recovery

In the United States, oil recovery methods are usually categorized into primary, secondary, and tertiary recovery phases. The first phase of recovery includes the production that occurs from (1) the field's natural pressure due to the elevated temperature and expansion of volatile components, and (2) any pumping that is done to assist oil extraction. The primary phase usually results in a recovery of less than one third of the available oil. When a well's natural energy is depleted, the secondary recovery phase, water flooding, is initiated. Water injection drives oil recovery by displacing oil from the matrix through drainage or imbibition. Waterflooding usually continues until the oil/water production ratio becomes low enough to make continued production uneconomical. The primary and secondary methods alone usually result in recoveries of less than 40% of the available oil in the reservoir. The large quantity of oil left unrecovered when the two initial extraction phases are employed is the target of tertiary phase recovery. The tertiary phase, often called enhanced oil recovery, focuses on increasing the overall yield through the use of one or more improved recovery methods.

Enhanced oil recovery (or EOR) techniques, which augment the secondary recovery phase, include the following: placement of chemical compounds within the injection water, miscible gas injection alternating with water injection, injection of micellar solutions, injection of steam, and in-situ combustion[1]. Because of the large commercial value of the residual oil in reservoirs, enhanced recovery processes are constantly being sought and existing ones are the subject of optimization studies. EOR techniques are often dependent upon the particular characteristics associated with a selected reservoir, due to differences in parameters such as the temperature and pressure of the reservoir, composition of the crude, and chemical makeup of the reservoir rock itself.

This study was performed to a great extent at Phillips Petroleum Research Laboratories (Bartlesville, OK) as part of an international project being conducted for the enhanced production in the subsea chalk reservoirs of Norway. These chalk reservoirs have an estimated average primary phase recovery rate of 27%. The Ekofisk reservoir represents a portion of the Norwegian fields, and it has been the only Norwegian site employing secondary phase methods. The Ekofisk reservoir has an improved estimated recovery factor of 32%, due at least in part to the decision to begin waterflooding in

1983[2]. There is substantial interest in the possibility of using tertiary recovery methods at Ekofisk, and these surfactants are under consideration for this location.

The residual oil in reservoirs, such as Ekofisk, is mostly the result of oil trapped in the pores of the rock in regions well covered by waterflooding, and oil left in less accessible regions of the reservoir which is passed over by the water because of nonuniform flow[1]. The target of enhanced recovery is the oil left in accessible regions, which typically consist of smaller interconnected pores. Thus, capillary forces and wettability become very important considerations. It has been shown that capillary forces are more important in the displacement of oil trapped in chalk pores than either viscous or gravity forces. It has also been demonstrated that oil recovery increases as a function of the matrix's water wettability[3]. Although chalk is a water-wetting matrix (it has a slight positive charge), oil contains natural surface active species that adsorb onto the mineral surface, rendering it oil wet[4]. One successful enhanced recovery method involves the displacement of this natural surfactant layer through the use of a more strongly adsorbing species. Using this method, the rock becomes water-wetting and promotes oil recovery by allowing the oil to be displaced by the imbibed water[4,5]. An alternate mechanism of wettability reversal will be employed here. The adsorption of the hydrophobic tail of a surfactant onto those areas of the surface that were made oil-wet (or less water-wet) by oil deposits would return it to a water wet state by the formation

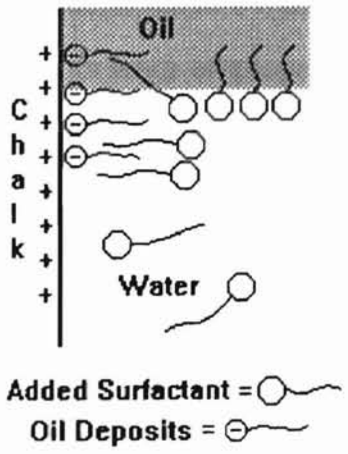

Figure 1.1.

Wettability Reversal

of a bilayer as shown in Figure 1.1. It is evident that for such an enhanced recovery project to be successful, the recovered oil to surfactant used ratio must be high. Therefore an ideal surfactant would have the following properties: a hydrophilic group that is very-weakly or non-adsorbing onto the water-wet areas, a hydrophobic group that is moderately adsorbing onto the oil-wet regions of chalk, and a very high degree of stability under conditions which are prevalent in the reservoir. This work focuses primarily on the issue of thermal stability of surfactants which are feasible for use in EOR operations.

I.B.3. Cloud Point Phenomena/Surfactant Screening

Researchers must choose from a great number of possible surfactants when trying to identify a useful surfactant for EOR or any related applications. Because detailed thermal stability testing and imbibition enhancement effectiveness cannot be feasibly conducted for every surfactant, large numbers of surfactants are culled prior to these tests through fast and simple screening processes. Cloud point measurements are considered to be among the most useful screening methods, since most surfactant applications require that the solutions be uniformly mixed[6]. Cloud point measurements were employed for the Ekofisk wettability reversal EOR studies, and changes in cloud point resulting from aging effects were correlated with fundamental structural modification as determined by chemical analysis. This work represents the first such known effort to correlate changes in the easily observed macroscopic test cloud point, as a function of chemical aging effects in surfactant systems.

All nonionic surfactants and a few ionic surfactants exhibit cloud points[6]. When a surfactant solution exhibiting a cloud point is heated to a specific temperature, it becomes turbid and separates into two distinct phases[7]. The minor (or coacervate) phase is concentrated in surfactant, and the major or dilute phase contains relatively little surfactant[8]. Cloud point depends upon a surfactant's structure, it's concentration, and the concentration of other additives[7,9].

I.C. Surfactant Stability Research

Once an initial screening process is complete, surfactants will typically undergo a stability testing process. There does not seem to be any defined method by which surfactant stability is characterized. Methods depend upon the type of surfactant being tested, and the exact nature of the enhanced recovery method. Because the large majority of recent surfactant stability/enhanced recovery work is focused on the use of sulfate surfactants one common method of quantifying surfactant degradation involves the use of titrations to determine percentage of active surfactant. Many studies sensibly characterize surfactant stability by the property which is important to their recovery method. For recovery methods in which foaming is an important surfactant property (CO_2 mobility control), surfactants are often characterized by emulsion height/emulsion stability. Recovery methods relying on a surfactants surface activity often utilize measurements of surface tension to indicate stability. Other, sometimes surfactant specific, stability measures occasionally used include: liquid chromatography, NMR, headspace GC, UV absorption, and pH.

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CHAPTER II

CLOUD POINTS AND SURFACTANT AGING

II.A. Background

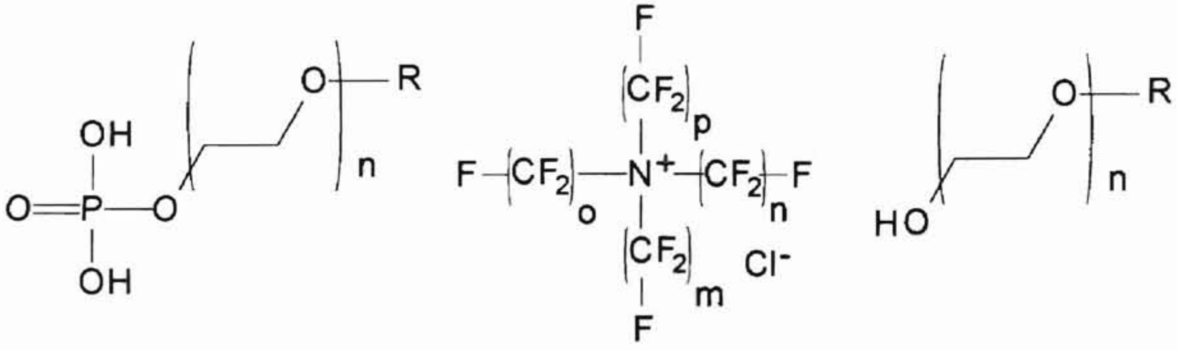
Aqueous solutions of all nonionic surfactants, and a few ionic surfactants, separate into two phases when heated to a well defined temperature called the cloud point[1-5]. Micellar behavior of ionic and nonionic surfactants are generally quite different[1]. In solutions of nonionic surfactants, micellar size usually increases when heated[1,3,6,7],. Solutions of ionic surfactants, in contrast, are reported to have micellar dimensions which are reduced upon heating[1]. For these reasons there is a lack of agreement regarding the mechanism of the cloud point phenomenon. In the case of nonionic systems, it is most commonly suggested that cloud point behavior is caused by: 1)The increased aggregation number of micelles at higher temperatures which leads to particles of such size to become visibly turbid accompanied by phase separation[3,7]. 2) The dehydration of the hydrophilic group with increasing temperature. Dehydration of the hydrophilic group leads to reduction in the intermicellar repulsions/ increased van der Waals attractions of micelles, and therefore clustering of micelles[2,3,8-10]. The phase separation is reversible upon cooling. There is, however, much conjecture and little agreement regarding the mechanism of cloud point origin in solutions of ionic surfactants[1,8,11]. It is generally accepted that the cloud point of surfactant solutions depends upon the concentration and structure of the surfactant[1,11,12]. Changes in the molecular structure of a surfactant that occur during the aging process are expected to be accompanied by a corresponding change in cloud point. The main focus of this work lies in the characterization of changes that occur in a surfactant cloud point after aging, and the use of this information to predict the stability of the surfactant. Changes in the cloud point with aging are identified in this chapter along with supplemental measurements of the effects of other species on the cloud point.

Factors known to increase cloud points in nonionic surfactants, such as the polyoxyethylenated surfactants (structure $R\text{-}(\text{-}OCH_2CH_2)_n\text{-}OH$) include: elevated oxyethylene percentage, nonpolar solubilizates (inner core of micelle, ex. aliphatic hydrocarbons), ions that are water structure breakers (ex, large polarizable anions, soft bases: SCN^-, I^-), polyvalent cations, H^+, and Li^+. Factors known to decrease these cloud points include: lower molecular weight, broader distributions of polyoxyethylenated chain length, hydrophobic group branching, replacement of the terminal hydroxyl by methoxyl, replacement of an ether head-tail linkage by an ester linkage, polar solubilizates (outer micelle surface, ex. fatty acids, alcohols, phenol, or benzene), ions that are water structure formers (ex. F^-, OH^-, SO_4^{2-}, Cl^-, PO_4^{3-}), NH_4^+, and Alkali metal cations (except lithium)[6,13].

II.B. Experimental Methods and Procedures

Commercial surfactants representing both ionic and nonionic types were chosen from those found to exhibit cloud points from initial screening studies. The majority of these surfactants which are industrial blends, had proprietary compositions and/or structures which remain unreported. Of the six surfactants chosen for study, two (Fluorad FC-754 and Rhodafac PL-620), are of the ionic type. Fluorad FC-754 is described as a mixture of fluorinated alkyl quaternary ammonium chlorides, while Rhodafac PL-620 is described as a mixture of C10-C16 alkyl ethers, phosphates. Four nonionic surfactant mixtures from the

Neodol series (Neodol 45-20, 91-20, 25-12, and 25-7), polyoxyethylenated straight chain alcohols of general structure R-(-OCH_2CH_2)$_n$-OH were also selected. Neodol blends are named such that the first number (i.e., 45 in Neodol 45-20) indicates the average size of the R group (i.e. 14-15 carbons for Neodol 45-20). The second number(i.e., 20 in Neodol 45-20) indicates the average repeat length of the polyoxyethylene chain, or n (i.e., n = 20 for Neodol 45-20). Neodol 91-20 has average R of 9-11 carbons, n of 20, etc.. Representative structures for the three surfactant types are shown in Figure 2.1. To more closely simulate the commercial usage conditions of these specimen mixtures, the commercial surfactants were used as obtained from the manufacturer.



Rhodafac PL-620 Fluorad FC-754 Neodol (General)

Figure 2.1 General structures of surfactants studied

Surfactant/Sea water stock solutions were prepared for the six surfactants in concentrations of 5000 ppm. The synthetic sea water was made as an aqueous solution containing 0.429% Na_2SO_4, 2.38% NaCl, 0.164% $CaCl_2 \cdot 2H_20$, 1.08% $MgCl_2 \cdot 6H_2O$ and, 0.0205% Na_2CO_3 in distilled water. The 5000 ppm stock solutions were directly divided into samples for later use in cloud point aging studies and in structural analysis aging studies (Chapter 4). The remainder of the 5000 ppm stock solutions were diluted into 1000 ppm or

500 ppm samples for cloud point studies as a function of concentration, and into 250 ppm samples for surface tension studies (Chapter 3). Each study group was sub-divided into samples for seven aging categories: 0, 3, 7, 21, 35 , and 77 days of oven aging at 268°F (131 °C), and one for room temperature aging. Solutions were placed in glass ampoules, constructed at Phillips, of the type sealed via melting the glass neck. The vials were evacuated and flushed twice with nitrogen before sealing. The sealed specimens were placed in an oven maintained at 268°F (131 °C). Each sample was removed from the oven upon completion of the specific aging period without disturbing the others in any way.

The cloud point determination instrument (Figure 2.2) was constructed at Phillips and is detailed more thoroughly in Review of Scientific Instruments^{14}, but has since been modified in several respects. It originally consisted of a high pressure stainless steel cell, a Sybron/Brinkmann PC801 Colorimeter, and a Soltec X-Y recorder. Typical methods of cloud point determination cannot be performed at elevated temperatures due to solvent loss. Thus, the Phillips instrument was designed to

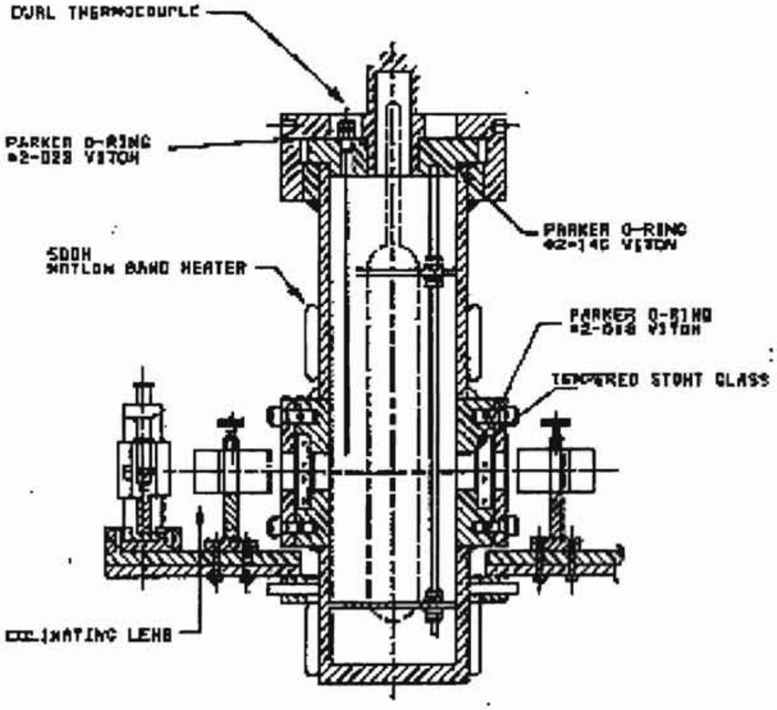


Figure 2.2. Cloud point apparatus

facilitate cloud point measurements at elevated temperatures using specimens in sealed glass ampoules. The steel cell was designed to operate at pressures up to 200 psig and temperatures up to 200 °C. The cell has a light path through it's lower center fitted with tempered sight glasses through which the colorimeter's light source and detector are connected via fiber optic cables. The light source is focused through a collimating lens and through the observation window onto the ampoule which is centered vertically in the cell. The transmitted light is focused by another lens onto the detector fiber optic. Presently, the temperature is controlled by a Eurotherm model 808 temperature controller connected to two 500W Watlow band heaters, which are clamped around the cell immediately above and below the observation window. The cell contains approximately 500 ml of Dow Corning Fluid 200, a silicone oil which is suitable for high temperature use. A thermally uniform bath is achieved through the use of a magnetic stirrer. Temperature is monitored via thermocouples fitted through the top of the cell. The cell is pressurized with nitrogen to stabilize the glass ampoules at higher temperatures, and is fitted with relief valves for safety. Data acquisition of specimen absorbance as a function of bath temperature is achieved using an IBM PC in conjunction with a Hewlitt Packard 3497A Data Acquisition/Control Unit and Labtech Control software.

Some errors in cloud point measurement occur because a lag between the temperature at the thermocouple and the temperature within the ampoule always exists. Researchers typically obtain accurate cloud points by either using very slow heating rates, such as .1 °C per minute(to minimize any temperature differences), or by averaging the cloud points from both the heating and cooling cycles. Due to the higher cloud point temperatures of our surfactants, faster heating rates of 1.5 °F per minute were used to keep measurement times to reasonable periods (.1 °C per minute would result in ~ 45 hours per measurement) , and to minimize thermal drift in the instrument. Averaging of heating and cooling cloud points was not performed as cooling rates were not controlled and were therefore non uniform (this would also double measurement time). The standard measurement procedures were developed for very accurate determination of cloud points. This study was concerned with significant changes in cloud points, not the exact value of the cloud points themselves. The small errors (2-3°F) obtained in our measurements are inconsequential for our purposes, and should be systematic in nature, not affecting the directional change of cloud point with surfactant aging. Measurement run times of 3 hours per sample were typical.

II.C. Results and Discussion

II.C.1. Surfactant Concentration and Cloud Point

Cloud points were obtained for each of the surfactants at two concentrations to probe the effect of concentration on the cloud point. Cloud point behavior results, in effect, from a lowering of micellar solubility at higher temperatures. Therefore cloud points are typically inversely related to concentration. The magnitude and direction of the concentration effect on a given surfactant's cloud point can be seen by comparing the observed cloud points of the two tested concentrations (see Table 2.1).

The lower concentration of Fluorad chosen had no observed cloud point in our range. This was probably a result of being below the critical micelle concentration of Fluorad at the elevated temperature. Because no two definite cloud point/concentration points were available the effect of concentration on Fluorad cloud point cannot be gauged.

Surfactants					Days Aged			7-8 wks
Ionic	Conc.	0	3	7	21	35	77	@ RT
Fluorad	1000 ppm	†	†	†	†	†	†	†
(cationic)	5000 ppm	270	245	236	230	218	242	240
Rhodafac	1000 ppm	222	162	144	137	141	148	198
(anionic)	5000 ppm	239	148	144	140	*	152	213
Nonionic								
Neodol 45-20	500 ppm	235	211	214	210	199	220	209
	5000 ppm	230	215	215	202	200	218	201
Neodol 91-20	500 ppm	234	226	*	222	210	*	212
	5000 ppm	223	218	215	215	199	219	203
Neodol 25-12	500 ppm	202	156/200	140/190	134/185	137/177	144/190	182
	5000 ppm	185	183	178	164	169	182	172
Neodol 25-7	500 ppm	130/190	169	165	153/175	160	168	126/180
	5000 ppm	114/185	108/180	104/180	107/165	107/167	*	110/167

† Cloud points either nonexistent or out of range

* These cloud points were unattainable

Table 2.1. Cloud point (°F) of surfactants at various age groups

The Neodol concentrations all had the expected inverse relation to the cloud point. The higher the concentration of Neodol surfactant, the lower the cloud point. The magnitude of the effect in the Neodols ranged from an insignificant difference for Neodol 45-20 to a 17 °F difference in Neodol 25-12. Rhodafac cloud point seemed to be directly related to concentration initially, contrary to what is normally expected, with the significant difference of 17 °F between the cloud points of 1000 and 5000 ppm samples. Immediately after aging (3 day) this effect reversed itself to a notable inverse concentration/cloud point relationship with a difference of 14 °F. The cloud points of the subsequent age groups were not significantly different. This puzzling relationship could not be explained at this point but became clear later in the work.

II.C.2. Cloud Point and Molecular Structure

The four different Neodol specimens were chosen so that molecular structural effects on cloud point could be assessed for the nonionic specimens. Structural effects on cloud point can be seen by inspection of Table 2.1. The effect of hydrophobic chain length is noted, by comparing cloud points of Neodol 45-20 with Neodol 91-20. Neodol 45-20 has an average chain length of 14-15 carbons, and Neodol 91-20 has an average chain length around 9-11 carbons. The effect size of the hydrophobic chain length seems to be rather small, probably within experimental error, but the chain lengths tested here (14-15C and 9-11C) was likewise not so very large. Therefore any chain cleavage occurring during aging on this scale (loss of 4-5 carbons) would not result in significant cloud point changes. A more extreme loss in the hydrophobic group should produce a noticeable change in cloud point.

Comparison of cloud points in Table 2.1 also illustrates the effect of the number of oxyethylene units on the cloud point. Neodol 25-7 contains an average of seven oxyethylene units, and Neodol 25-12 an average of 12 oxyethylene units. Although Neodol 25-7 showed a "dual" cloud point (this feature is discussed more thoroughly in section II.C.5.c.) which makes exact interpretation difficult, the cloud point values for the Neodol 25-7 are clearly lower than those of Neodol 25-12. Comparisons can also be made between Neodol 25-12 and Neodol 91-20 or 45-20 due to the small effect on cloud point of the other differing factors between these surfactants. The larger the number of oxyethylene units, the higher the cloud point. Therefore any thermal degradation to the surfactant molecule that results in lowering of oxyethylene number should result in a lowering of cloud point.

II.C.3. Alcohol Effect on Cloud Point

One possible aging effect in surfactants of the polyoxyethylene type includes the formation of alcohols. The effect of loss of hydrocarbon chain on cloud point was determined above, but the effect of the corresponding production of alcohol was not quantified for our solutions. Therefore it was necessary for us to gauge the magnitude of the effect of alcohol on the cloud point of our particular surfactants/solutions. Because there was some concern about instrument drift in the other aging studies, a smaller 1 week aging study was included on the ordinary samples for direct comparison. The results of these tests can be found in Table 2.2. As discussed in section II.A other researchers have shown that polar solubilizates decrease the cloud point of surfactants.

The results of this study indicate that added ethanol up to 1000 ppm concentration has no significant effect on any of the cloud points of the three types of surfactants.

		Standard Solutions	Added Ethanol	
			500 ppm	1000 ppm
Neodol 25-7	0 days	108/170	108/170	107/167
	3 days	109/175		112/?
	1 week	109/180		
Fluorad FC-754	0 days	244	244	243
	3 days			245
	1 week	244		
Rhodafac PL-620	0 days	215	215	215
	3 days	150		136
	1 week	150		

Table 2.2. Effect of Alcohol on Cloud Points (°F)

II.C.4. Sea Salts and Cloud Point

The effect of ions on surfactant cloud point depends upon the particular ionic species added (some raise and some lower cloud points). The magnitude of each ion's effect is also different. In order to find what effect our sea salt mixtures had on the cloud points, and to help predict the effect of the higher salinity waters in the reservoir on cloud point, cloud points of the three surfactant types were measured at different salt concentrations. It was also noted that some of the samples formed precipitates upon aging. These precipitates are thought to be mostly composed of silicates, but do contain some sea salts. The effect of this lowering of the salt concentration can also be predicted from these studies. The specimens used were made from regular sea salt solutions, at one-half of normal salt concentration, and in distilled water.

		Standard	1/2 Conc. SNSW	Distilled Water
Neodol 25-7	0 days	108/170	115/175	124/184
	3 days	109/175	112/183	119/192
	1 week	109/180	111/184	118/189
Fluorad FC-754	0 days	244	154	>360
	3 days		144	>360
	1 week	244	146	>360
Rhodafac PL-620	0 days	215	224	220
	3 days	150	160	177
	1 week	150	159	170

Table 2.3. Effect of Sea Salts on Cloud Points (°F)

The results of this study are contained in Table 2.3. The effect of salts on the cloud point of surfactant was dramatic. It can be seen that the combined effect of the sea salts is to lower the Neodol and Rhodafac cloud points. Therefore upon contact with the higher salinity formation waters these cloud points would be lower than those measured in this study. The effect of salt precipitation during the aging study would be to raise the cloud points of these surfactants. The Fluorad cloud point was raised by the presence of the sea salts, but did not exist without them. The Fluorad surfactant would therefore have a higher cloud point upon mixing with formation water. The effect of salt precipitation during the aging study would be a lowering of Flourad cloud point. The different salt concentrations seemed to have little effect on the rate of change of the cloud point with aging. This would imply the salts are not involved in any of the cloud point changing decay mechanisms of the surfactants.

II.C.5. Cloud Point and Surfactant Aging

In most cases the effect of aging on the cloud point (see Table 2.1) was a rapid decrease of cloud point during the first three day aging period, followed by a gradual lowering over the next 3-5 weeks. Finally there was a uniform increase in cloud point after 77 days.

In evaluating the changes in the surfactant cloud points, one must also consider the changes in the cloud points of samples that were aged at room temperature. If observed changes in the cloud point are attributed to surfactant decomposition, samples aged at room temperature would only have changes in their cloud points similar to the aged specimens if: a) surfactants were very stable, therefore no decomposition occurred at room temperature or oven temperature, or b) Surfactants were very unstable, therefore decomposition occurred at a similar rate for both room temperature and oven aged samples. Assuming that none of the surfactants are that unstable at room temperature, evaluation of cloud point changes should include a comparison of the room temperature aged samples to the oven aged samples. If cloud point changes are significant, i.e. due to surfactant decomposition, the cloud points of the room temperature aged samples will not fit into the pattern of observed cloud point changes. If cloud point changes are due to instrument drift or some change in solution equilibrium, the room temperature aged sample cloud points will fit into the graph of aging versus time at their respective time of measurement even though no decomposition has occurred.

Evaluation of the effects of surfactant aging on cloud point are categorized in Sections II.C.5.a - II.C.5.d based on the changes observed.

II.C.5.a. Rhodafac

It can be seen by examination of Figure 2.3 (data taken from Table 2.1), that both concentrations of Rhodafac surfactant yielded very large decreases in

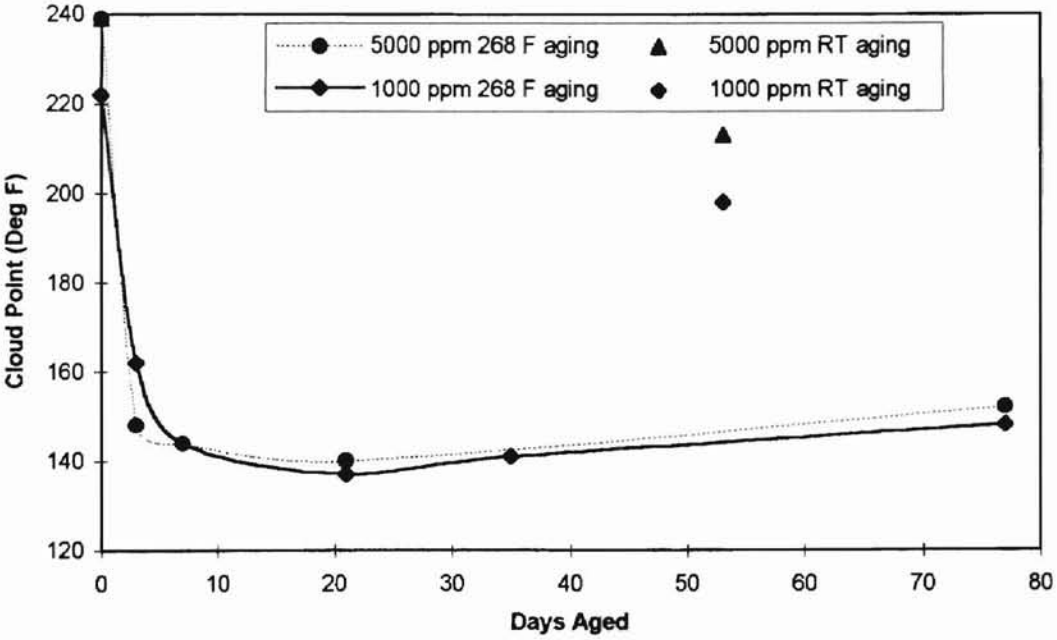


Figure 2.3. Cloud point/Aging changes for Rhodafac PL-620.

cloud point after the first three day aging period. This was followed by a more gradual decrease over the next 3 weeks followed by a slow increase through the 11th week. The cloud point of the room temperature aged specimens stayed much higher than those of the aged samples. Thus, the major cause of the cloud point changes in Rhodafac is surfactant aging. The cloud point method suggests that aging is greatly accelerated for specimens maintained at 131°C (268°F) with respect to comparable specimens maintained at room temperature, and therefore would predict this surfactant to be unstable under reservoir conditions.

Possible explanations for the lowering of Rhodafac cloud point include such things discussed previously in the introduction section, but in general include those structural modifications that would hinder the hydration of the polar or hydrophilic portion of the surfactant, or the formation of degradation products that have a lower cloud point themselves. This type of surfactant is a likely candidate for acid catalyzed hydrolysis of the phosphate group to form a Neodol type (polyoxyethylene) surfactant, which has a much lower cloud point than the parent Rhodafac surfactant.

II.C.5.b. Fluorad

Examination of Figure 2.4 (data taken from Table 2.1) reveals a similar aging pattern for the Fluorad surfactant as observed in section II.C.5.a. Upon comparison of the room temperature aged specimen to the oven aged specimens, one finds that the RT specimen falls close to but not exactly within the pattern of the oven aged specimens. Because there is known to be some fluctuation in these cloud point measurements, no difference between the RT and aged samples can be confirmed. Therefore the cloud point method would give an uncertain prediction as to the stability of this surfactant.

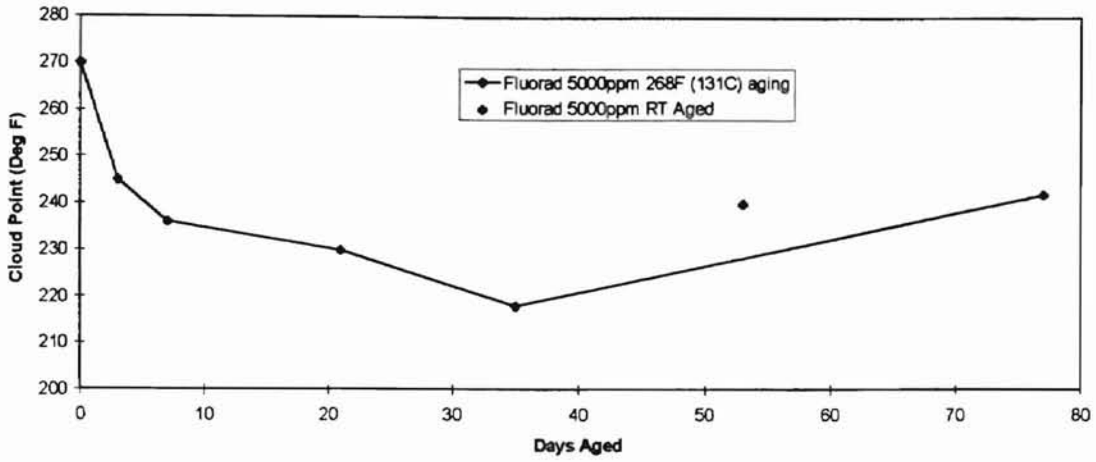


Figure 2.4. Cloud Point with Aging for Fluorad FC-754.

II.C.5.c. Neodol 45-20 and 91-20

After examining the data from Table 2.1 for Neodol 45-20 and 91-20 it was found that these two surfactants followed the trend mentioned in section II.C.5.a, with the exception that the initial downward changes in cloud points were smaller. Comparing the changes in the cloud point of aged samples to those of the room temperature aged samples, it was seen that some variation apart from those associated with decomposition is primarily responsible for the cloud point changes. Possible sources of these changes will be discussed in section II.C.7. The cloud point data would then predict that these two surfactants were very stable under our approximated reservoir conditions.

II.C.5.d. Neodol 25-12 and 25-7

An interesting, but complicating effect that was observed in our cloud point/aging study was the occurrence of double cloud points in Neodol 25-12 and 25-7 (as indicated in Table 2.1). These samples sometimes

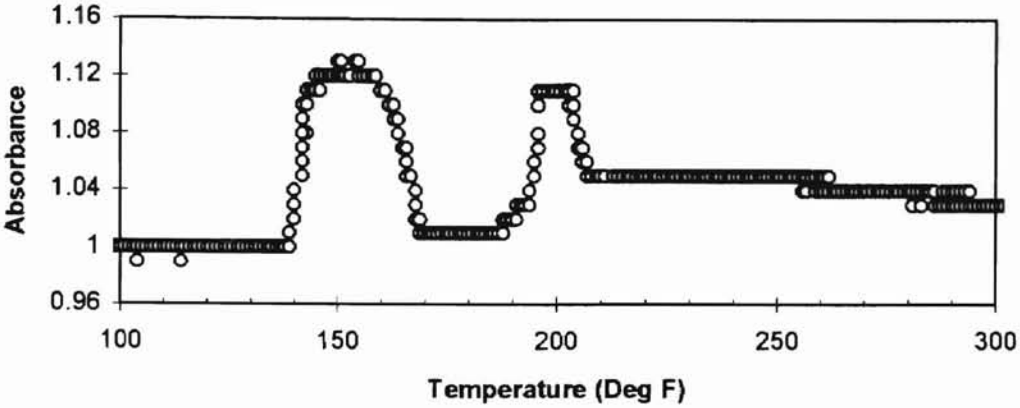


Figure 2.5. "Dual" Cloud Behavior of Neodol 25-12 500 ppm at 1 week aging.

exhibited the onset of a low temperature cloud point, followed by solution clearing, with the onset of a second cloud point at a higher temperature. This behavior is demonstrated in Figure 2.5, which shows the cloud point apparatus output for a 500 ppm Neodol 25-12 specimen after 1 week of aging at 131 °C. Other dual cloud point traces were similar. The phenomenon of double cloud points in nonionic surfactants has been reported previously to be the result of the impurities in commercial blends.

In the case of Neodol 25-12 at 500ppm, one notes that the effect occurs consistently on all oven aged samples, but not on the 0 aged or RT aged samples. One might propose a cause based on aging effects except that the occurrence was absent in the 5000 ppm sample of Neodol 25-12, which was prepared from the same bulk surfactant sample.

The phenomena was even more perplexing in the case of the 500 ppm Neodol 25-7. In these samples the event occurred sporadically, and it can be seen that the average of the double cloud points would be at the expected temperature of the single cloud point. In the case of the 5000 ppm sample of Neodol 25-7 the event occurred in every case, oven aged or not.

This dual cloud point is possibly the result of an ordering in these surfactant mixtures of the different structural types into micelles of different types (ex. micelles of the larger n surfactants and micelles of the smaller n surfactants), and therefore different cloud points. However, this explanation could not explain the random occurrences of the dual cloud point. A better explanation of these events will not be attempted in this work, however their existence must be noted as they serve to complicate the interpretation of these data.

Comparison of the room temperature aged data to the trends from the oven aged data once again shows that the observed cloud point changes in these two surfactants are not due primarily to thermal decomposition. Possible sources of the changes will be discussed in section II.C.7.

II.C.6. Three Day Cloud Point Study

A short term aging study was performed on the three surfactants that showed the greatest initial change in cloud point, to better characterize the change during that period. Cloud point measurements were taken at 0,1,2, and 3 days of oven aging to verify and better characterize the initial change in those three surfactants. The results of this study are shown in Table 2.4.

	0 days	1 day	2 days	3 days
Fluorad FC-754	250	242	244	235
Neodol 45-20 500 ppm	220	202	201	214
Neodol 45-20 5000ppm	219	214	217	213
Rhodafac 1000ppm	214	160	167	
Rhodafac 5000 ppm	226	166	166	166

Table 2.4. Three Day Oven Aging, Cloud Points (°F)

Again the surfactants show an initial decline in cloud points with aging. The change is small and gradual in the Fluorad and Neodol samples, but is both large and rapid in the Rhodafac samples. The large change in the Rhodafac surfactant cloud point signifies either a very unstable species in the surfactant blend or a very unstable portion of the typical Rhodafac molecule.

II.C.7. Cloud Point Inconsistencies

Comparisons of cloud points of identical solutions from Tables 2.1, 2.2, 2.3, and 2.4. shows that the initial cloud points of unaged solutions do not agree well. Also consider the large changes in cloud points of room temperature aged samples, the strange pattern followed by all of the samples (drop, then rise in cloud point), and the occasional random fluctuations in the data (ex. Table 2.4 Rhodafac 1000ppm). Some concern about the reliability of cloud point measure seems to be justified. Possible explanations for these phenomena are discussed in sections II.C.7.a-d.

II.C.7.a. Surfactant Equilibrium

The literature indicates that some surfactant researchers age solutions at room temperature for at least 24 - 48 hours prior to determination of surfactant solution properties (surface tension, cloud point, etc.). The purpose of such aging is to allow solutions to reach equilibrium dissociation of micelles, and full micellar hydration[15,16]. Many of our solutions were aged less before cloud point measurement occurred. This could explain the differing initial cloud points of various experiments (solutions at various degrees of dissociation and hydration), and the change in cloud points in certain surfactants such that the change in oven aged samples agreed with the room temperature aged samples.

II.C.7.b. Unstable Species

It is often noted by researchers that different species in the surfactant blends age at different rates. The existence of a very unstable species or impurity in these industrial surfactant blends can also account for large initial cloud point changes, and changes in the room temperature aged samples over time.

II.C.7.c. Multiple Effects

A very logical explanation exist for the unusual pattern of the cloud point changes. If more than one change is occurring in the solution with aging, and there is at least one factor shifting cloud point in both the upward and downward direction. Differing rates of these changes could have the observed trend in the cloud point changes. A very unstable component of the surfactant blends would decay rapidly causing a rapid downward trend, but as the concentration of the species lessened, an upward trend caused by some other general structural degradation with a slower rate in the main constituents of the blends would eventually shift the direction of cloud point change.

II.C.7.d. Measurement Instability

Of course the simplest explanation of all of these concerns would be error in the cloud point determination: drift in the instrument, differences in sample preparation, etc. The fact that there seems to be an underlying pattern in the changes (see especially Figure 2.3 and 2.4) for all the different types of surfactants, suggests some drift could be occurring in measurement. Concern of instrument drift is lessened due to the differences in magnitude of the initial changes from Table 2.1, the short time in which they take place, and the lack of any large random fluctuations in Table 2.5 which could explain those large size differences.

II.C.8. Precision of Cloud Point Measure

This experiment was intended to test the precision of the cloud point measurements because of the occasional fluctuations in data points apparent from the earlier aging studies. To control for sample preparation differences, a stock solution was created and divided into samples for cloud point measurement. Because room temperature aging effects cannot be halted, this experiment also served to identify possible effects associated with room temperature equilibrium changes as seen by a drift in cloud point values. These goals were accomplished by ascertaining the change in the cloud point of several samples over the course of three days, with most measurements taken consecutively to verify precision. The Fluorad surfactant was chosen here because it has the most readily distinguished cloud point, due to it's sharp transition.

Aging Hrs.	Cloud Pt. (°F)
0	264
24	265
28	263
42	259
45	261
48	258
51	259

Table 2.5. Short term RT Cloud Point Stability in Fluorad FC-754.

The results shown in table 2.5 demonstrate that the consecutive measurements are very precise, within 2-3 °F. Therefore, no evidence was found to indicate significant (i.e. >5 °F) random fluctuations in the cloud point measurements.

There was only a small change, about 5 °F, in the cloud point over the study period at room temperature. This could be the result of error in measurement (i.e. 261±3 °F). It could also be interpreted as instrument drift or equilibrium changes. However, it can be seen that if any equilibrium changes have occurred in the two days, they certainly cannot account for the large changes observed early in the aging studies of sections II.C.5-6. This would suggest that those changes were associated with one of the other possibilities (sections II.C.7.a-d)

II.D. Conclusions

It was noted that concentration changes do not greatly effect the cloud point of our surfactants, but that certain structural changes, such as higher oxyethylene percentage, should produce noticeable changes in our aging studies. While ethanol was found to not have a noticeable effect on the cloud points, the salt concentration had a significant effect, but the directional change seemed to be surfactant dependent.

Unfortunately, there was some question about the certainty of the cloud point measurements, the only indisputable change in the surfactant's cloud points were in the Rhodafac samples. The Rhodafac surfactant showed a definite and extreme initial downward trend in it's cloud point. The cloud point changes in the other surfactants did not appear to be as reliable as the Rhodafac samples. It should be noted however, that usually the cloud points of the surfactants exhibited a downward trend with aging, the possible instrument fluctuations make the extent of the real changes uncertain. Correlation with structural changes found later in the study will still be attempted on all of the surfactants, in order to support or contradict the observed changes and the method.

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CHAPTER III

Use of Surface Tension in Surfactant Aging

III.A. Introduction

Surface tension changes with surfactant aging have been measured for the ionic surfactants, Fluorad FC-754 and Rhodafac PL-620. These measurements are valuable in many studies related to oil recovery, since surface tension is often the asset of the surfactant that is most important to EOR processes. Surfactant decomposition caused by the severe conditions of our study results in a loss of surface activity. This loss of surface activity is easily observed by an increase in the surface tension of the solution. The unknown active concentration of a surfactant solution after thermal aging is typically estimated by comparing its surface tension value to known values of surface tension vs. concentration. Since only the loss of surface activity is measurable by this method, molecular degradation in regions of the surfactant molecule that do not significantly alter surface activity are not detected. The results of this type of study can also be affected by certain degradation products (ex. alcohols) that significantly lower the surface tension of water themselves. The Neodol series was not studied by this method because the separation of head and tail necessary to significantly reduce the surface tension not only would result in the production of alcohols, but also was not thought to be the most prominent degradation mechanism.

III.B. Experimental Methods and Procedures

Surfactant/Sea water solutions were prepared for the two ionic surfactants as described in chapter II, with the exception that a lower concentration (250 ppm) was chosen for this part of the study for reasons detailed in the following paragraph. These stock solutions were divided into 7 samples, nitrogen-flushed in glass ampoules, and sealed as previously described. The 7 samples were for 3, 7, 21, 35 , and 77 days of oven aging at 131 C, and one for room temperature aging. After each sample was removed from the oven, it was stored at room temperature until all other members of the test series were ready for measurement. This was done so that the conditions under which the surface tension of the samples were measured would be consistent, and to obviate any instrumental drift. The room temperature aged sample was used to show what changes would occur at room temperature, whether from surfactant decomposition or equilibrium changes such as those discussed in chapter 2.

Because cloud points do not occur below the critical micelle concentration(CMC), and analytical evaluation requires a significant amount of sample, the other studies required the use of higher concentrations. The concentration of 250 ppm was arbitrarily chosen for these studies as a concentration below the CMCs of the two surfactants. A plot of surface tension versus concentration for a typical surfactant will show that above the concentration value at which micelles begin to form (CMC), the surface tension changes very little with concentration. For this reason it was necessary to choose a concentration below the surfactants' CMCs if any accuracy was to be obtained in the estimations of active concentration change with aging.

The instrument used was a SensaDyne Surface Tensionmeter 6000. This instrument operates on the principal of the maximum bubble pressure method.

This method avoids the effects of the solution surface environment such as surface contaminants and surface foam by measuring the surface tension within the body of the test fluid. This is done by blowing bubbles of inert gas into the body of fluid through two probes of different orifice size and measuring the difference in the maximum bubble pressure of each (Figure 3.1). The differential pressure signal that results is directly related to the fluid surface tension.

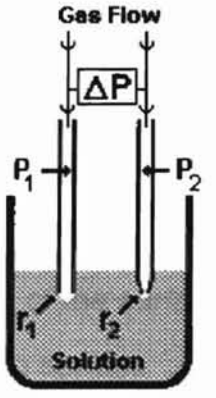

Figure 3.1

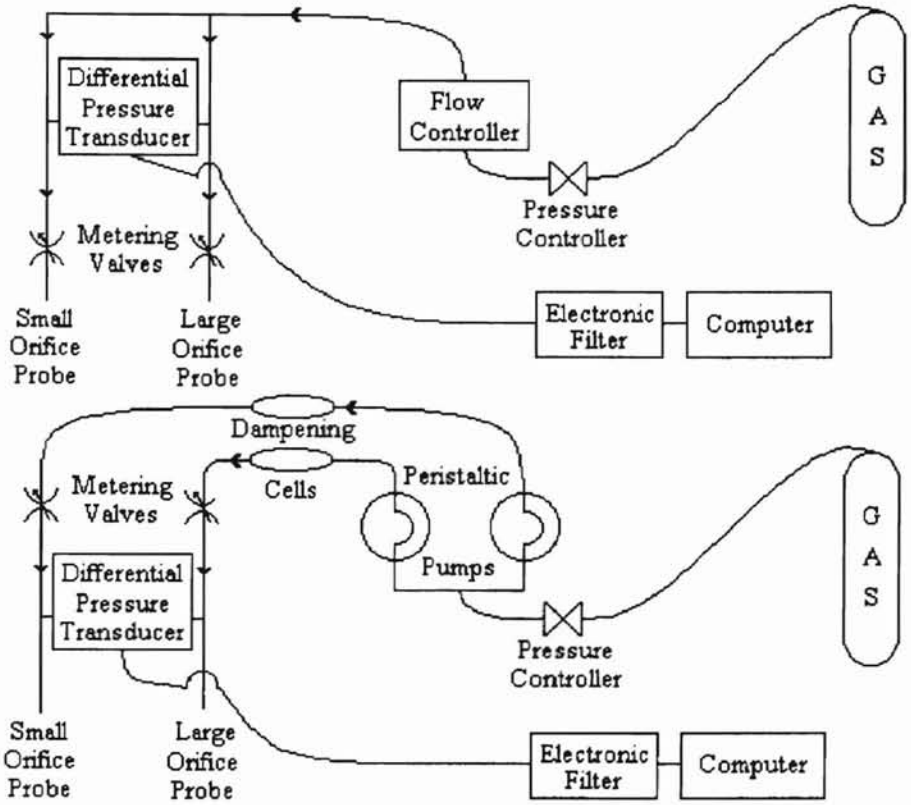

Figure 3.2 SensaDyne Diagram: Before and After Changes

The instrument was modified by the addition of peristaltic pumps, which provided a more consistently regulated nitrogen flow and yielded slower bubble rates than those realized using the instrument's original gas restriction valves

(Figure 3.2). Any minute pulses from the pumps were then controlled for by dampening coils and the restriction valves. Although only the changes in surface tension values were necessary for this study, the instrument modifications were made because greater accuracy can be achieved in solution surface tension measurements by allowing longer migration times of the surface active agent to the air/solution interface. Bubble rates ranged with surface tension from 32 seconds at 39.9 Dynes/cm to 71 seconds at 74.1 Dynes/cm. Fresh surfactant/sea water solutions were prepared over a range of concentrations and their surface tensions were measured to create graphs for comparison to the aged samples.

III.C. Results and Discussion

The surface tension values of the aged Rhodafac samples, while initially agreeing with unaged samples, fluctuated by only a few Dynes/cm over the whole study and proved to be partially uninterpretable since they seemed to have lower surface tension values than unaged samples (see Table 3.1). These results suggest that the Rhodafac surfactant is very stable under these conditions. The Rhodafac half-life appears much longer than the aging period of 77 days.

The surface tension values found for fresh specimens of Fluorad FC-754 at various concentrations were plotted in Figure 3.3. By locating the surface tension values found for the aged Fluorad specimens(shown as straight lines) on the curve, the effective concentrations of the Fluorad after aging can be found.

The surface tension values of the aged Fluorad samples and the corresponding effective concentrations are shown in Table 3.1. These values show that the Fluorad surfactant was relatively stable at room temperature, changing from an effective concentration of 250 ppm to 220 ppm over the course of the study. However, Fluorad decomposed rapidly at reservoir temperature undergoing approximately three half-lives of decomposition in the first three day aging period.

Fluorad	Days Aged*	0	3	7	21	35	77
	Eff. Conc. (ppm)	220	33.0	29.5	25.0	23.5	21.0
	S.T. (Dyne/cm)	46.6	70.4	71.4	72.6	72.9	73.5
Rhodafac	S.T. (Dyne/cm)	42.8	41.5	40.4	38.5	39.9	40.2

* At reservoir conditions, samples then stored at RT until all collected for ST measurement.

Table 3.1. Surface tension values of Aged Fluorad and Rhodafac samples.

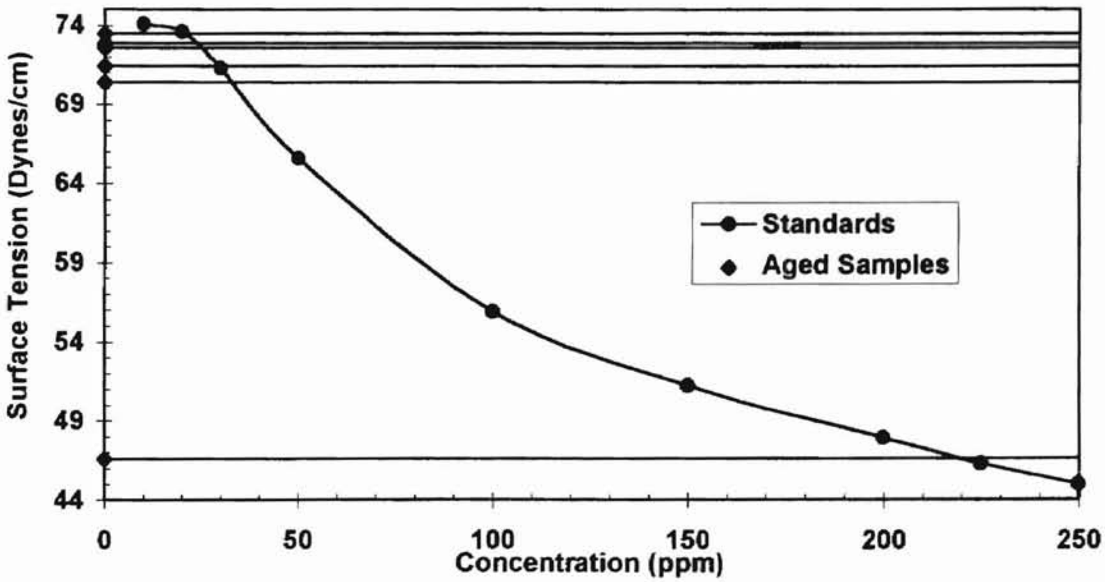

Figure 3.3. Surface Tension vs. Concentration for Fluorad FC-754

CHAPTER IV

Structural Effects of Surfactant Aging

IV.A. Introduction

The structural changes taking place among the surfactants as they are aged were analyzed where appropriate using analytical techniques such as ^1H and ^{13}C NMR, IR, and Headspace gas chromatography/mass spectrometry (Headspace GC/MS) . As discussed previously, it is well known that surfactant cloud points are a function of both their concentration and more importantly to this discussion, their structure. These analytical techniques were employed in attempt to correlate structural changes in the surfactant to the observed changes in the surfactant cloud points. The goal is to assess the mechanisms of aging effects and cloud point changes for the surfactants of interest.

Because large numbers of structural combinations are the norm in industrial surfactant blends, identifying changes in the structure due to aging are not nearly as straightforward as identifying structural changes in a structurally pure sample. Nonetheless, if major structural changes occur during aging, such as a change in functionality, traditional methods such as NMR and IR should prove to be useful.

In surfactants such as the Neodol series (general structure $R\text{-}(\text{-}OCH_2CH_2)_n\text{-}OH)$, fragmentation of a surfactant molecule does not necessarily lead to a new and therefore readily identifiable structure in the blend, but could likely result in a molecule that already exists in the blend, plus a smaller fragment of a volatile nature and, consequently, one absent from our solution during standard analytical evaluations.

NMR and IR were used to look for general changes in structure or functionality, and headspace GC/MS was used to identify some of the more volatile decomposition products.

IV.B. Analytical Methods

IV.B.1 ^{1}HNMR & ^{C}NMR

IV.B.1.a Introduction

The NMR spectra with surfactant aging was acquired for the four nonionic Neodol surfactants and the anionic surfactant Rhodafac PL-620. Unfortunately, the equipment was not available at either facility for the acquisition of fluorine NMR. NMR is one of the most useful instruments in identifying molecular structure in organic compounds because of it's ability to provide data about the environment of the two principle organic elements, hydrogen and carbon. Any significant changes in the general structure of the surfactants due to thermal degradation should be readily identified by this method. Besides the obvious usefulness of NMR in this respect, as mentioned earlier, many possible degradations could occur without changing the general structure (ex. lowering of n or R). We therefore chose to show changes in the average n and R values of the nonionic surfactant mixtures with aging by this method.

IV.B.1.b Experimental Methods and Procedures

Surfactant/Sea water solutions were prepared and aged for the surfactants as described in Chapter II. For many of the following techniques, the water, and/or the sea salts present in the samples prevented the acquisition of proper spectra. Therefore, unless otherwise specified, the samples were vacuum dried and the majority of the salts were removed by extracting the surfactant with ethanol. Each sample was extracted with 20, 10, and 10 ml of absolute ethanol in succession. The three extracts were decanted, filtered with a 0.45 micron nylon filter, and combined before being vacuum dried.

The fresh, 0 age, and 3 week ^{1}H and ^{13}C NMR were obtained at Phillips laboratories on a JEOL GX270 NMR instrument with a Tecmag LIBRA data acquisition system and a Power Macintosh 7100 controlling computer. The ethanol extracted residues were dissolved in D_2O with a final solute content of 15-18 wt%. Approximately 4 ml of each solution was placed into a separate 10 mm NMR tube for analysis. A 1 mm capillary tube containing tetramethylsilane in $CDCl_3$ was centered in the 10 mm tube for chemical shift reference.

The 11 week specimen spectra were carried out using the Varian XL-400 instrument at the facilities of Oklahoma State University. Samples were prepared as above except that a) 5 mm tubes were used instead of the 10mm tubes, and b) deuterated Sodium 3-trimethylsilylpropionate or TSP was used for chemical shift reference.

IV.B.1.c Discussion of Results

IV.B.1.c.1. Neodols

The four Neodol samples were analyzed by both ^{1}H and ^{13}C NMR. The samples were extracted and analyzed at zero, 3-week, and 11-week aging periods, fresh samples were also analyzed for three of the Neodols. There are no significant differences in the spectra of the fresh, unaged, 3-week, or 11-week aged samples, although there are small differences in the relative peak areas of the various peaks in the spectra. Because the Neodol series all have the same general structure, the obtained spectra for each series member are very similar. Figures 4.1 and 4.2 are a representative of the zero aged and 3 week aged ^1H NMR and Figures 4.3 and 4.4 are representative of the zero aged and 3 week aged ^{13}C NMR respectively of these structures. All Neodol spectra for each sample age can be found in Appendix A.

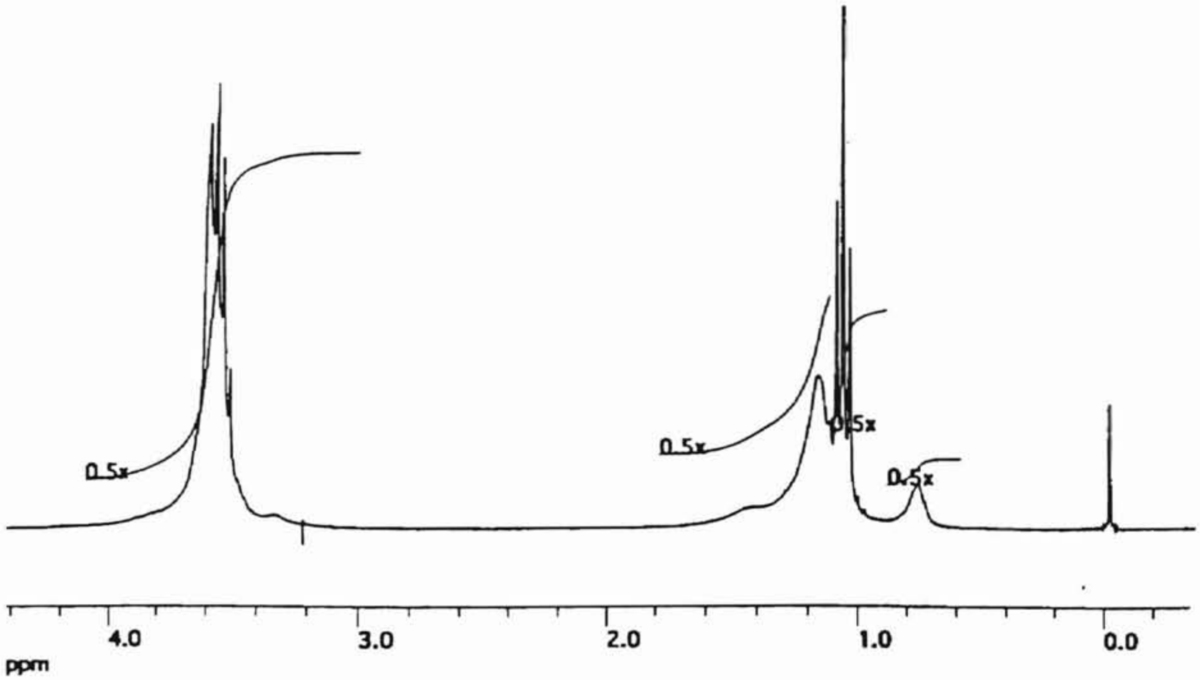

Figure 4.1. ^1H NMR spectrum of zero aged Neodol 25-7.

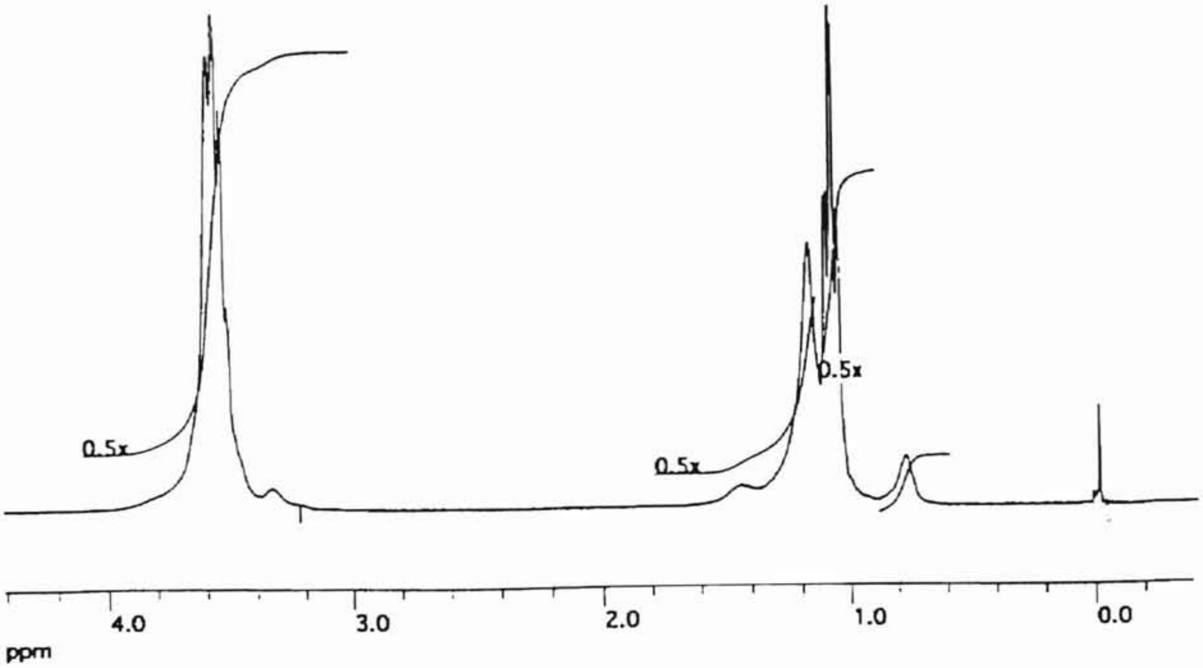

Figure 4.2. ^{1}H NMR spectrum of 3 week aged Neodol 25-7.

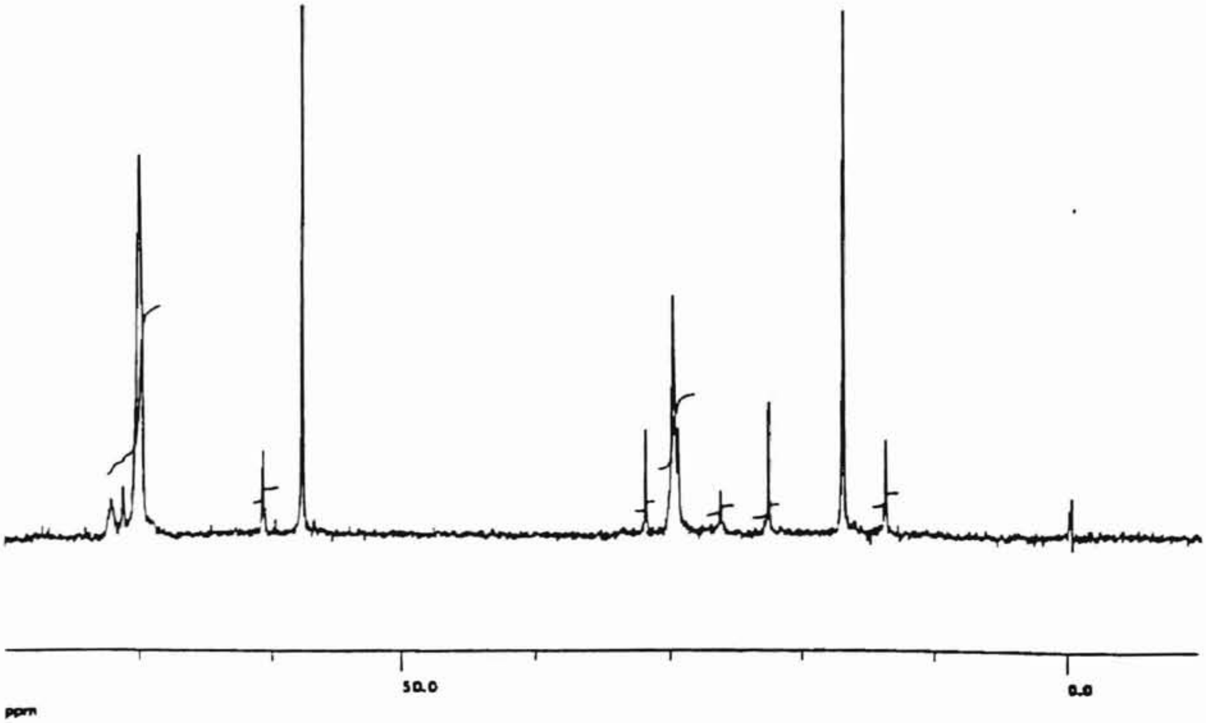

Figure 4.3. ^{13}C NMR spectrum of zero aged Neodol 25-7.

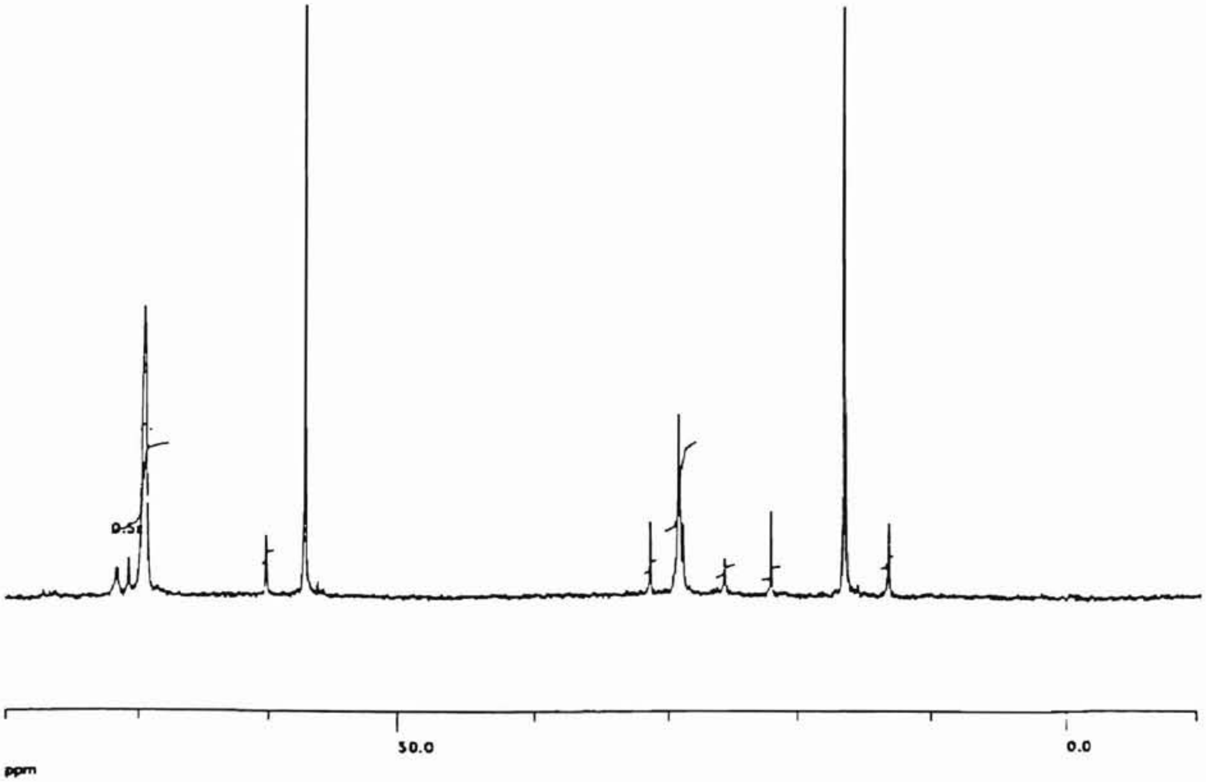

Figure 4.4. ^{13}C NMR spectrum of 3 week aged Neodol 25-7.

	Integrated Region (ppm)	Integral Value
A (-OCH2)	75-65	100
B (-OCH2-*CH2-OH)	63-58	6.86
C (S3)	34-31	9.28
D (-CH2-)	31-28	44.42
E (OCH2-CH2-*CH2-)	28-24	6.72
F (S2)	24-21	8
G (S1)	15.5-12	7.1

Avg. 13C Integration

(C+E+F+G+B)/5 = 7.6

n=(((A - 7.6) / 7.6)+1)/2

n= 6.6

R = (D / 7.6) + 5

R= 10.9

$$\overset{\mathbf{G}}{CH_3}\text{-}\overset{\mathbf{F}}{CH_2}\text{-}\overset{\mathbf{C}}{CH_2}\text{-}\overset{\mathbf{D}}{(CH_2)_{R-5}}\ \text{-}\overset{\mathbf{E}}{CH_2}\text{-}\overset{\mathbf{D}}{CH_2}\text{-}\overset{\mathbf{A}}{CH_2}\text{-}(\text{-}\overset{\mathbf{A}}{OCH_2}\text{-}\overset{\mathbf{B}}{CH_2}\text{-})_n\text{-}OH$$

Table 4.1. Sample of n and R calculation based on ^{13}C peak integrations.

	Integral Region	Integral Value
OCH2(**A,B,I**)	2.8 - 4.1	105.13
CH2(**C,D,E,F**)	1.15 - 1.8	50.8
CH3(**H**)	0.90 - 1.15	38.8
CH3(**G**)	0.3 - 0.9	8.6

	Mole Fraction
W OCH2	39.63
X CH2	25.40
Y Etoh	12.93
Z CH3	2.87
Total MF	80.83

n= ((W / Z) -1) / 2
n= 6.41

R= ((X / Z)+ 2
R= 10.86

G F C D E D A A B
CH_3-CH_2-CH_2-$(CH_2)_{R-5}$ -CH_2-CH_2-CH_2-(-OCH_2-CH_2-$)_n$-OH

H I
CH_3-CH_2-OH

Table 4.2. Sample of n and R calculation based on ^{1}H peak integrations.

Sample/ Neodol	C-13 R	H-1 R	C-13 n	H-1 n
Fresh 25-7	10.9	8.1	6.6	5.6
zero aged 25-7	10.7	10.9	6.3	6.4
3 week 25-7	11.5	11.2	6.6	6.4
11 week 25-7	11.8	7.2	8.5	4.7
zero aged 25-12	13.0	11.3	13.6	9.9
3 week 25-12	11.8	12.9	11.8	10.3
11 week 25-12	14.5	9.4	20.6	9.1
Fresh 45-20	12.0	11.1	19.3	15.5
zero aged 45-20	12.4	11.1	20.1	14.3
3 week 45-20	12.9	14.3	22.8	16.0
11 week 45-20	10.9	15.6	17.4	23.3
Fresh 91-20	9.3	8.8	19.3	17.4
zero aged 91-20	10.0	9.6	22.8	17.2
3 week 91-20	9.2	9.5	18.9	16.0
11 week 91-20	9.5	5.6	25.8	10.8

Table 4.3. R and n values for the Neodol surfactants from ^{13}C and ^{1}H spectra.

The integral values of the peaks were used in an Excel spreadsheet to calculate the values of n and R for the various samples from both the ^{1}H and ^{13}C spectra. A sample of these calculations containing appropriate peak assignments for ^{13}C , Table 4.1, and for ^{1}H Table 4.2 is attached, and the results for each surfactant sample are summarized in Table 4.3.

Although the ^{13}C data are more consistent than the ^{1}H data, neither set shows any positive trends in the values of n and/or R which would indicate structural changes due to aging. It can however be seen that the reliability of these values obtained from the spectra for the 11 week samples were less than those obtained earlier for the fresh , 0 age and 3 week samples. This is probably due to the smaller samples used in this instrument. The small changes observed for these values in the fresh, 0 age and 3 week samples are within the experimental error of the measurements.

IV.B.2.c.2. Rhodafac

Fresh, zero, 3 week and 11 week aged Rhodafac PL-620 samples were also analyzed by both ^{1}H and ^{13}C NMR, with more positive results than the Neodols. All of the Rhodafac spectra may be found in Appendix A. Calculations of n and R for the Rhodafac surfactant performed similarly to those above revealed an average n of about 16, and an average R of about 12 carbons. Those details of Rhodafac surfactant's structure were formerly unknown to us. Each calculation was in reasonably good agreement with the other age groups, and no definite trends were observed that would indicate a change. The most significant structural difference was found in the ^{13}C spectra. The 3 week (Figure 4.6) and 11 week aged samples have a peak at ~61 ppm that was not present or much smaller in the spectra of the 0 aged (Figure 4.5) and fresh samples. This peak is consistent with one due to the methylene alpha to a terminal OH group. This would seem to indicate the formation of an alcohol or a glycol in the aging process. In attempt to quantify the new alcohol a comparison of it's peak integration to that of the polyoxyethylene carbon integration was made. The approximate ratio of the alcohol groups to the ether groups are shown in Table 4.4, assuming an average n of 16.3, the ratio of the original surfactant to the new alcohol can be found. It can be seen that the number of alcohols eventually becomes larger than the original surfactant. This would indicate multiple fragments from each original molecule, but may be only a result of experimental error.

Sample	Ether/Alcohol	Rhod/Alcohol	% of Original
Fresh	364	22	4.5
RT aged	114	7	13.8
3 week	19	1.2	83.4
11 week	13	.8	141.0

Table 4.4. Quantization of 61ppm alcohol peak.

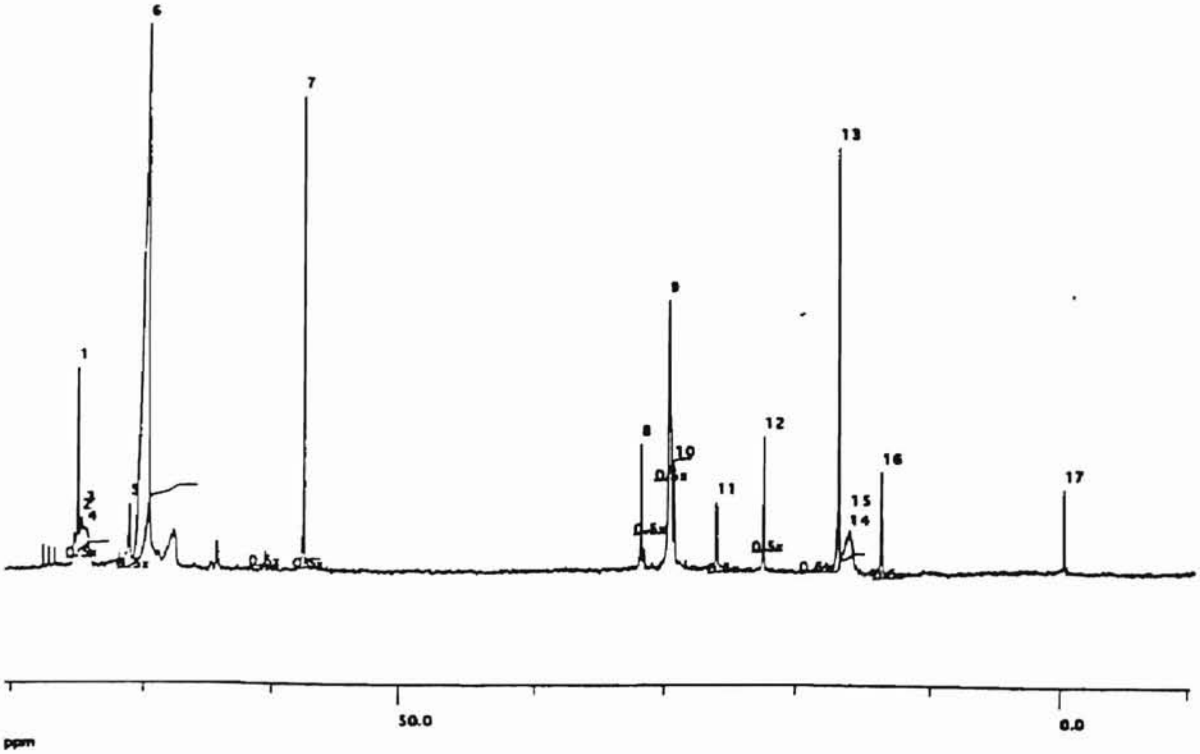

Figure 4.5. Zero aged ^{13}C NMR spectrum of Rhodafac PL-620.

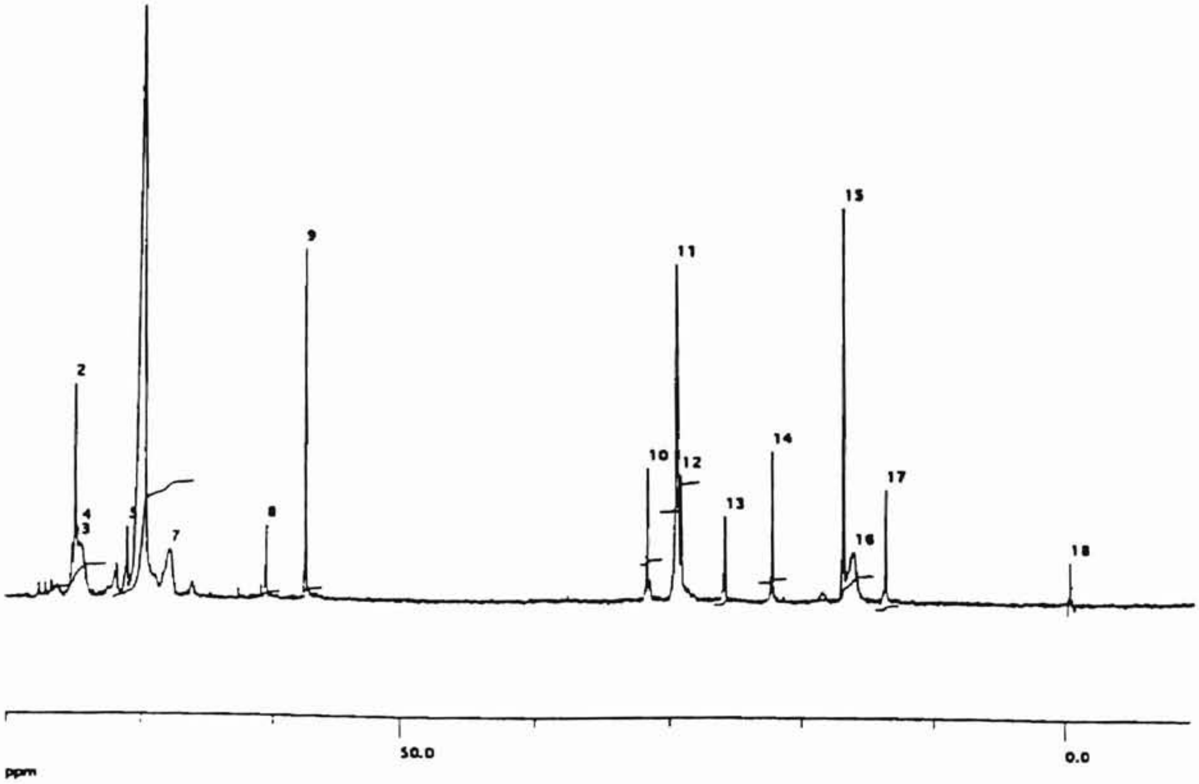

Figure 4.6. Three week aged ^{13}C NMR spectrum of Rhodafac PL-620.

IV.B.3 IR

IV.B.3.a Introduction

The infrared absorption spectra of the six surfactants were acquired for use in indicating structural changes in the surfactants due to aging. Infrared spectra are generally acknowledged as being very useful indicators of functionality in organic compounds, consequently, this technique is effective in making known any changes in functionality due to aging if modified species occur in high enough quantities.

IV.B.3.b Experimental Methods and Procedures

Surfactant samples were aged as discussed in chapter II. The instrument used was a BIORAD FTIR. Specimen samples were prepared by several

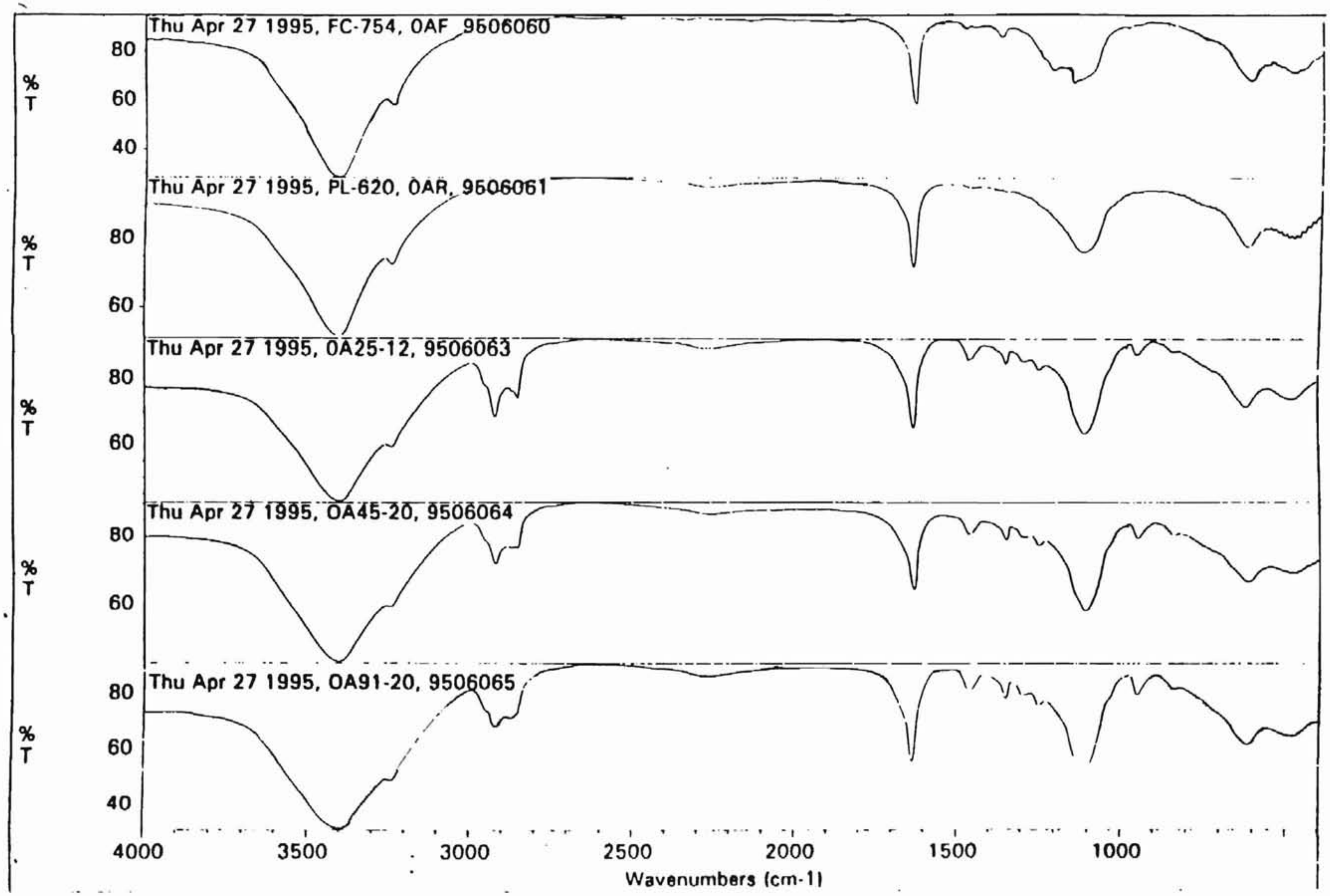

Figure 4.7. FTIR spectra of ethanol extracted surfactant samples.

different methods. Original dried sea water/surfactant samples were run both by pressing with KBr, and by extracting with methylene chloride and film casting on KBr plates. Samples were also extracted with ethanol as described above and were used both by smearing on a KBr plate, and by redissolving in methylene chloride and film casting on a KBr plate.

IV.B.3.c Discussion of Results

The spectra of the original dried samples, Figure 4.7, contain a large number of bands which are mostly due to the sea salt. This sample preparation was therefore not thought to be useful for studying the aging process. The spectra from the ethanol extract smears for zero aged and 3-week aged Neodol

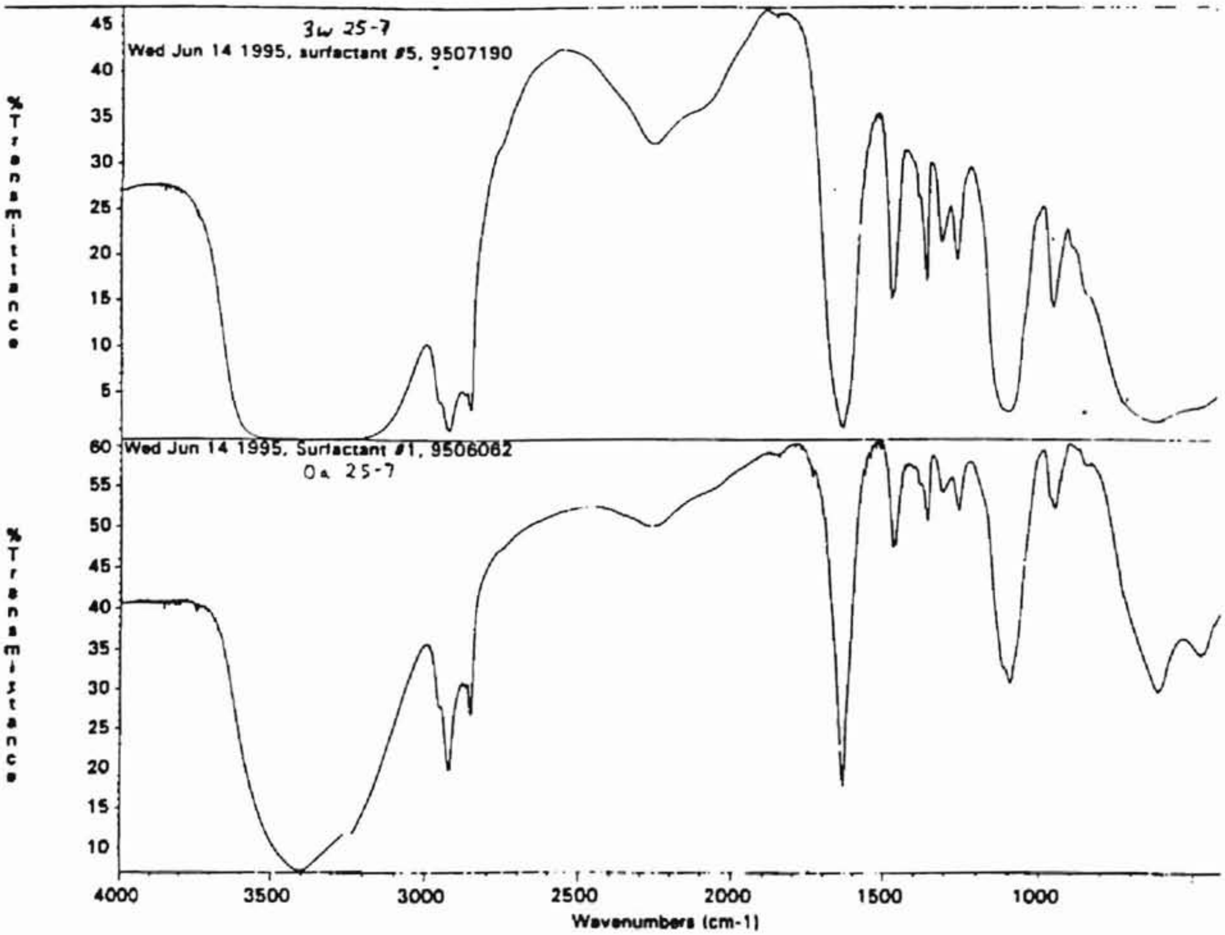

Figure 4.8. FTIR spectra of 3 week and 0 aged ethanol extract of Neodol 25-7.

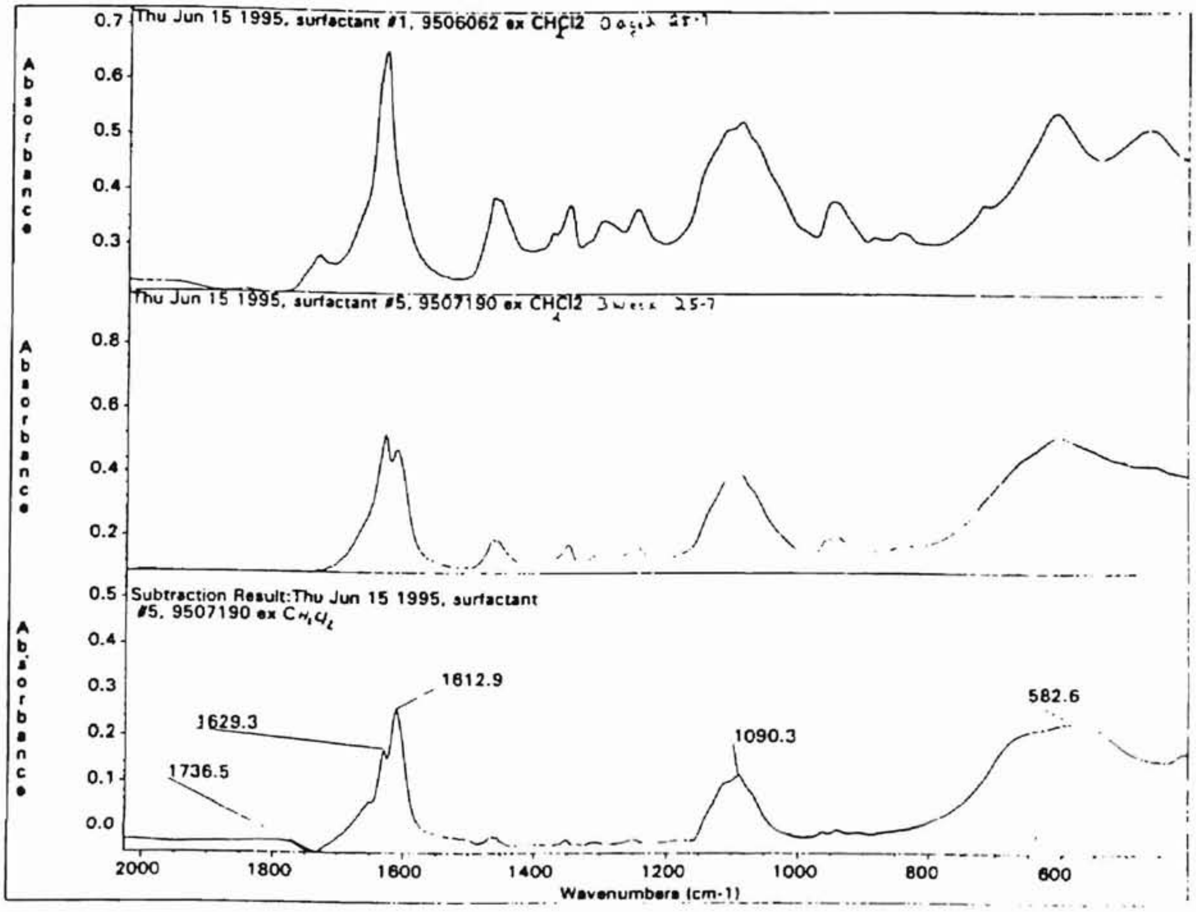

Figure 4.9. FTIR spectra of 0 aged and 3 week CH_2Cl_2 extract of Neodol 25-7.

25-7 is shown in figure 4.8. These spectra both show a strong hydroxyl peak (3100-3600 cm^{-1}), thought to be either retained water or ethanol, and a strong carbonyl peak (1600 cm^{-1}). The methylene chloride extracts (Figure 4.9) did not contain the strong hydroxyl peak but a weaker carbonyl peak is still present. In order to find the source of the carbonyl peaks, a fresh sample of Neodol 25-7 was compared to a methylene chloride extract from the sea water (Figure 4.10). The resulting spectra showed very little difference and no carbonyl peaks. This indicates that the carbonyl peaks in the ethanol extracts were most likely the result of the carbonates in the sea salt. Because no significant difference was found between the spectra of unaged and 3-week aged samples, and because salts, water, and alcohols were interfering with the spectra, IR studies were not continued on other age groups.

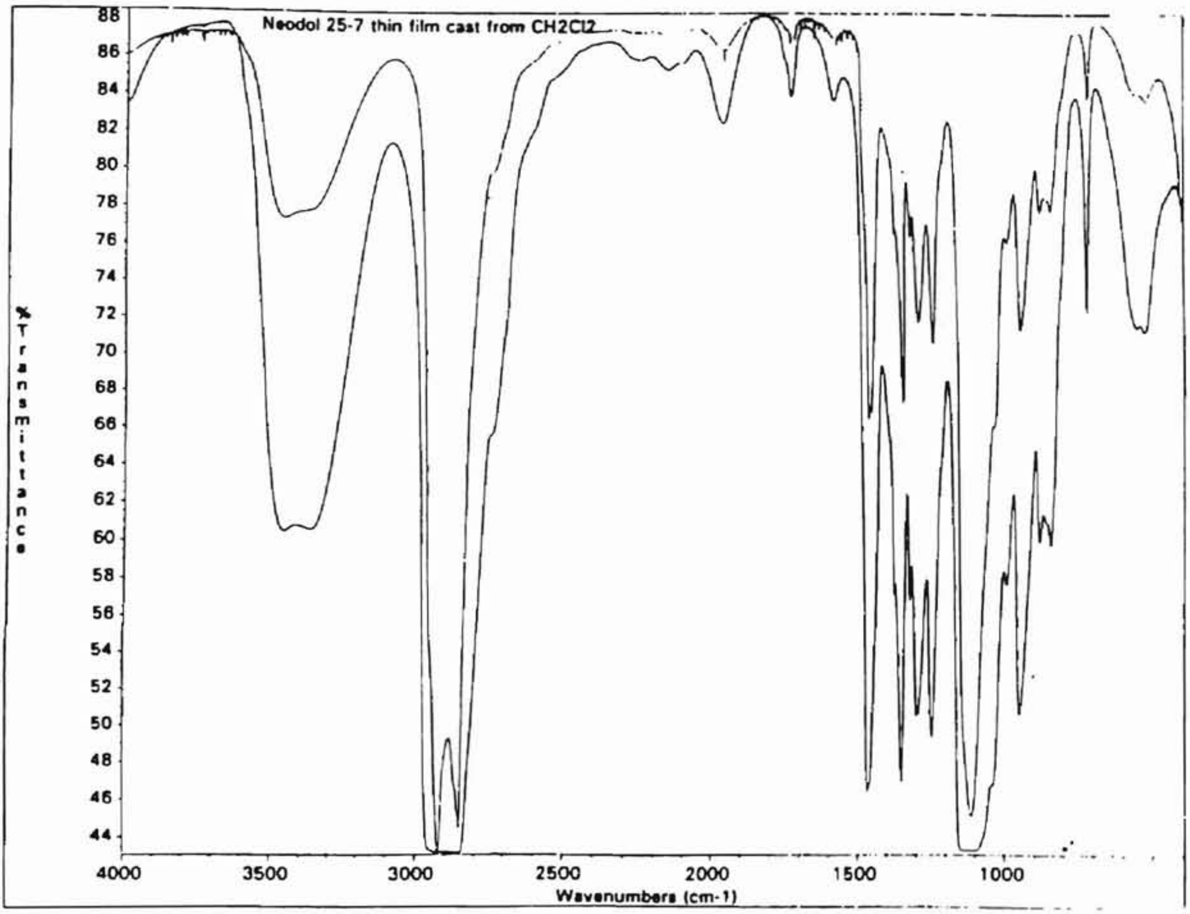

Figure 4.10. FTIR spectra of Fresh and CH_2Cl_2 extract of Neodol 25-7.

IV.B.4 Headspace GC/MS

IV.B.4.a Introduction

The headspace GC/MS was performed for each type of surfactant, the Rhodafac, the Fluorad, and one of the Neodols at zero and 11 weeks of aging.

As discussed in Appendix B, gas chromatography could not be used on our surfactant samples to illustrate shifts in relative composition of the surfactant blends due to salts in the samples. However, gas chromatography has proved to be a useful method for the identification of volatile decomposition products of the aging process. This was possible using a headspace GC/MS, an instrument which samples the volatile components that evolve out of a liquid sample by heating.

IV.B.4.b Experimental Methods and Procedures

Surfactant samples were aged as discussed in Chapter II. In this case, however, the ampoules were not opened and dried prior to sampling. All GC/MS experiments were performed using a Finnigan TSQ70 GC/MS instrument. In each case, about 0.5 ml was sampled directly from the headspace of the sealed ampoules and introduced into the mass spectrometer via a Varian 3400 gas chromatograph with a split ratio of 1:20. Electron ionization (EI, 70 eV) was employed to ionize the sample. The GC injector temperature and the transfer line temperature were set at 280 °C. A J&W Scientific 60 m DB1 column with 0.3 mm ID and 0.33 micron film was used for separation. The oven temperature was initially held at 35 °C for 5 minutes and then ramped to 180 °C.

IV.B.4.c Discussion of Results

The unaged samples of Neodol (Figure 4.11) and Rhodafac contain no significant peaks in the headspace chromatograms.

The 11 week aged sample of Neodol 45-20 (Figure 4.12) shows only six identified decomposition products of sufficient volatility for this method. The identified products were one isomer each of the C4 through C9 alkanes,

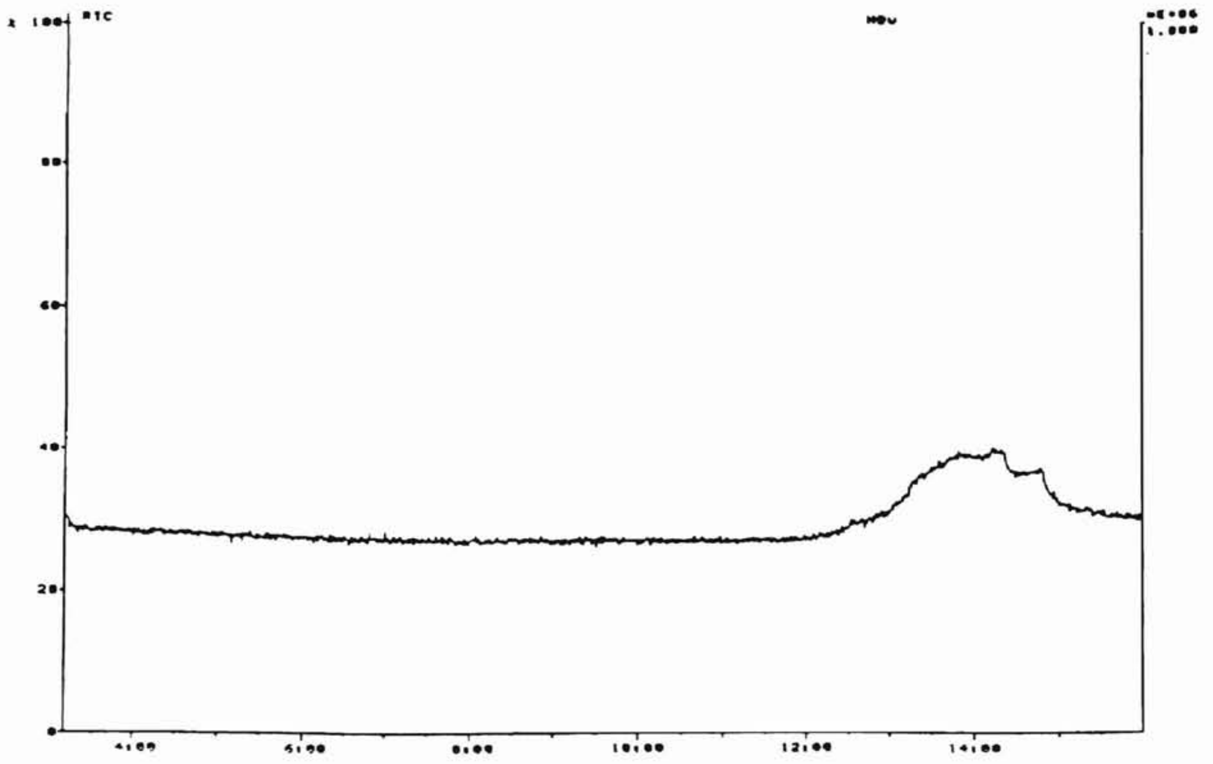

Figure 4.11. Headspace GC of unaged Neodol 45-20.

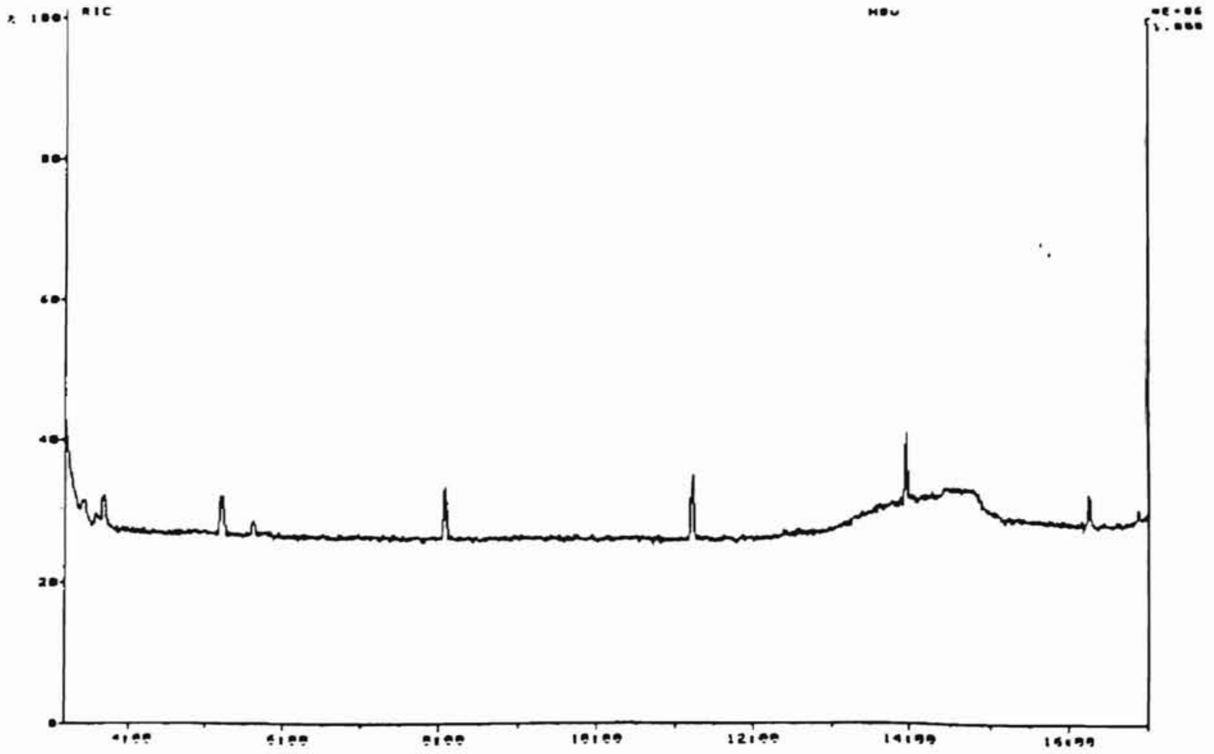

Figure 4.12. Headspace GC of 11 week Neodol 45-20.

correlating with fragments of the tail of the surfactant. No alcohol decomposition products were identified by this method.

The 11 week aged sample of Rodafac PL-620 (Figure 4.13) had a wide variety of identified decomposition products. These included C3 through C10 alkanes of the n-isomer, 2,2-dimethyl propane, and a C5 and two C8 mono-olefins or mono-cyclic hydrocarbons. The products are all consistent with those expected from alkyl chain cleavage of the hydrophobic tail.

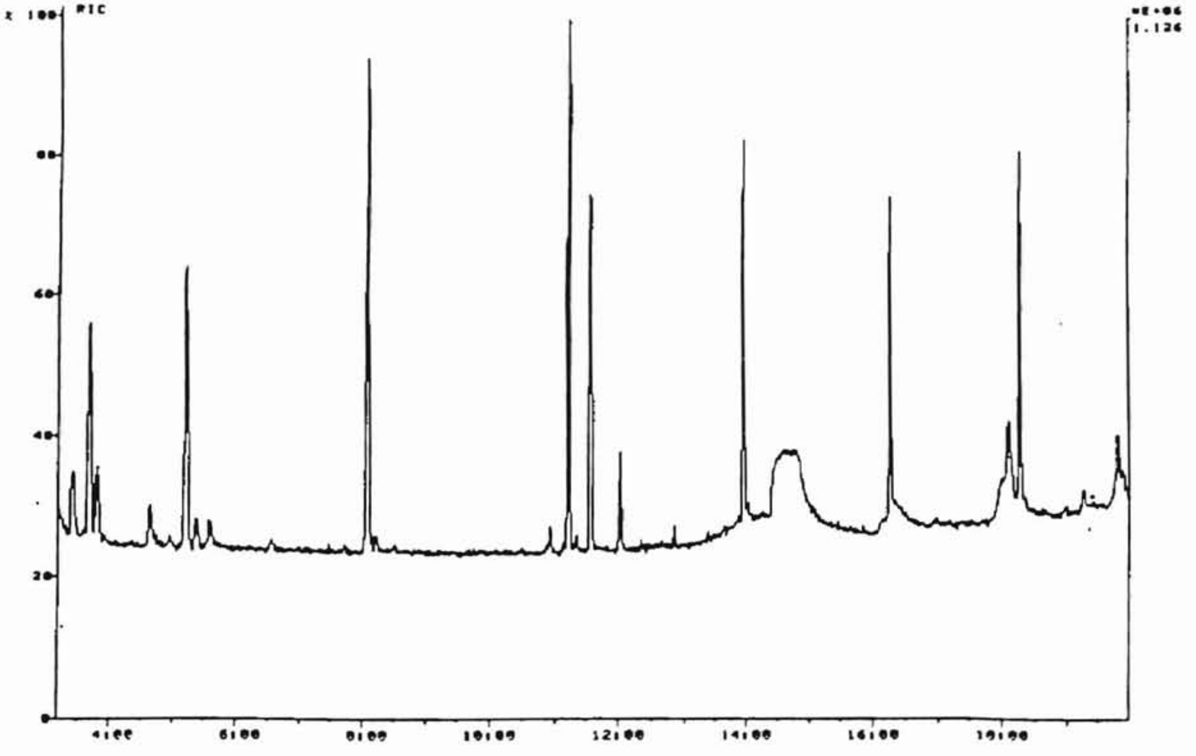

Figure 4.13. Headspace GC of 11 week Rhodafac PL-620.

The zero aged Fluorad surfactant chromatogram (Figure 4.14) exhibited only one small peak which was attributed to isopropanol. It was later determined by alcohols analysis that the as-received Fluorad surfactant contained isopropanol as a solvent.

The 11 week aged Fluorad FC-754 sample (Figure 4.15) contained several decomposition products. Most of these were identified as perfluorinated compounds such as C_6HF_{13}, but also included four C7, and two C8 alkanes, and a C7 and two C8 mono-olefins or mono-cyclic hydrocarbons.

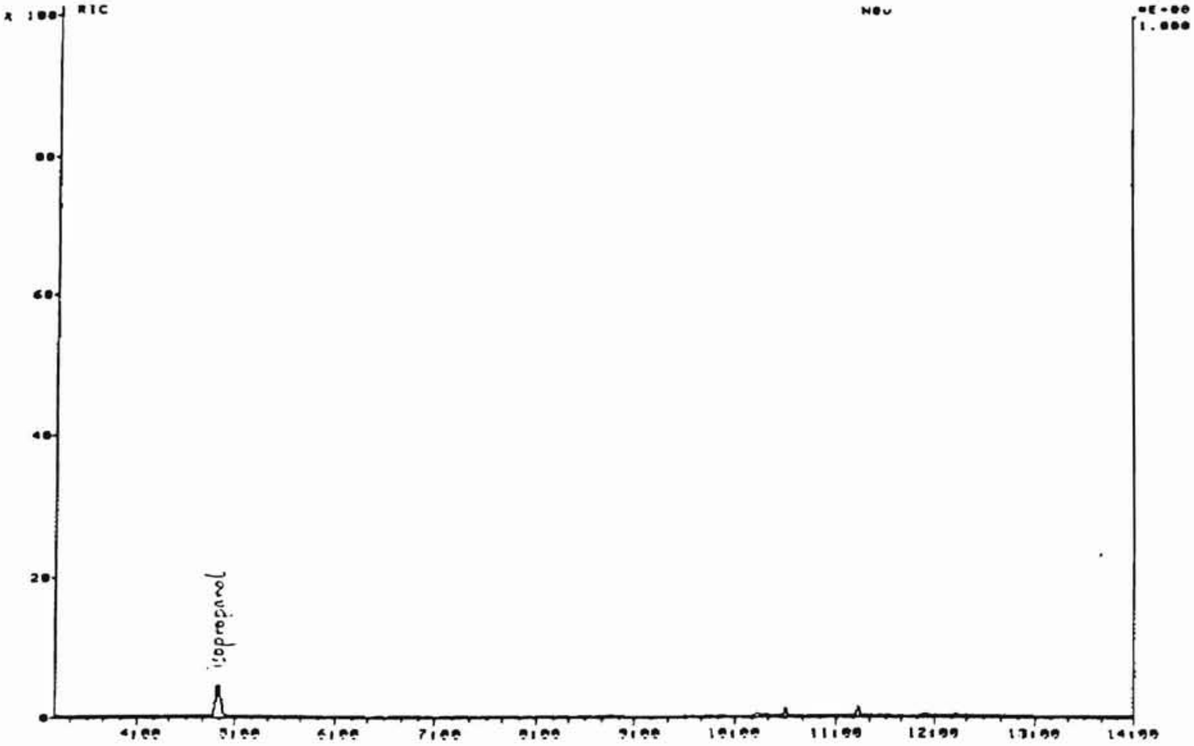

Figure 4.14. Headspace GC of unaged Fluorad FC-754.

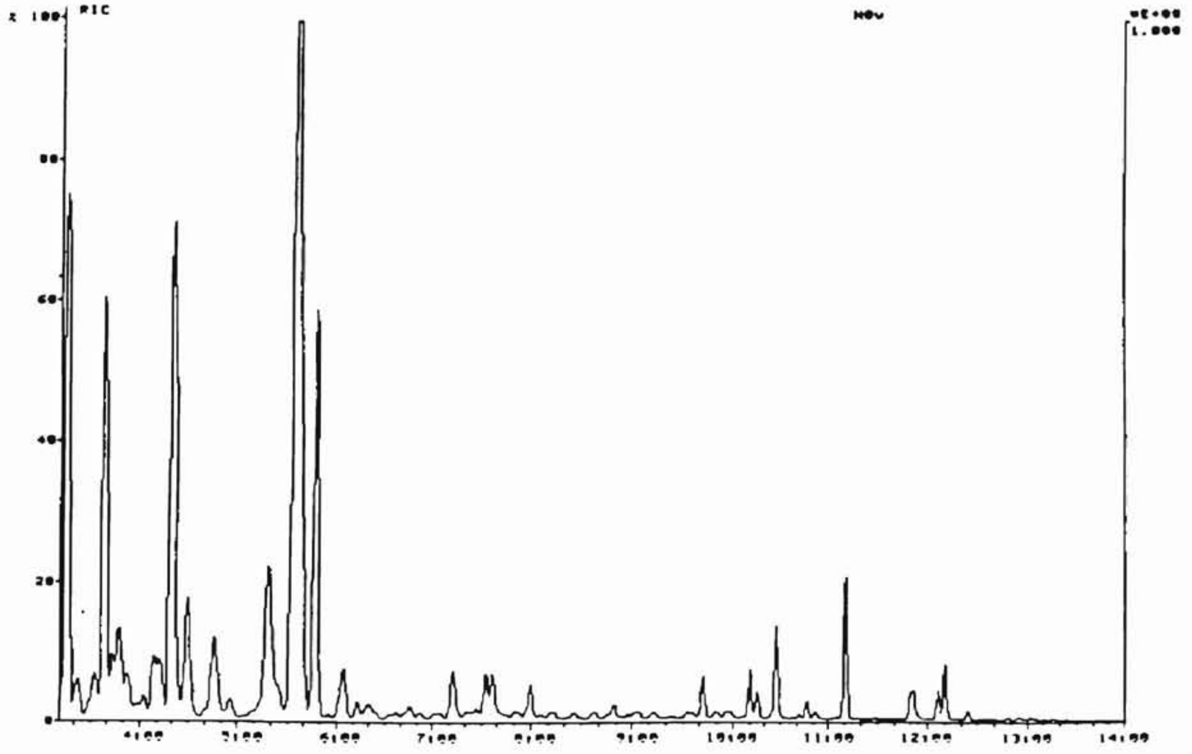

Figure 4.15. Headspace GC of 11 week aged Fluorad FC-754.

IV.D. Discussion and Conclusions

IV.D.1. Structural Changes

The methods utilized identified three major decomposition processes occurring among the surfactants.

Headspace GC/MS identified many hydrocarbon fragments in the Rhodafac and Neodol specimens. These products are consistent with those expected from alkyl chain cleavage of the surfactants hydrophobic tail.

Headspace GC/MS also identified several large perfluorinated fragments in the Fluorad specimens. These products are consistent with those expected from elimination reactions in ammonium chlorides.

The most revealing discovery was the identification of the terminal alcohol in the ^{13}C NMR of aged Rhodafac samples. The alcohol seen by ^{13}C NMR was not evident in the headspace and is therefore probably not a volatile product. It is likely that it was created by head/tail separation of the surfactant due to acid catalyzed hydrolysis. Such a decomposition would result in the formation of a Neodol type surfactant, and phosphoric acid.

No alcohols were identified in the decomposition of Neodol surfactants, therefore alkyl chain cleavage is probably the only decay mechanism.

The headspace of the Fluorad surfactant contained several decomposition products, this would seem to indicate that the surfactant was very unstable under these conditions.

IV.D.2 Effect on Cloud Point

The changes observed in this chapter will have effects on the cloud point as outlined earlier in chapter two. Broader distributions of polyoxyethylene chain have lower cloud points, unfortunately, any changes in distribution were not able to be analyzed because of loss of access to the SFC (see Appendix B). It was seen by ^{13}C NMR that aged Rhodafac surfactant samples began to form terminal alcohols, this probably results in Neodol type surfactants with a maximum n of about 16. The cloud point of such surfactants is lower than that of the parent Rhodafac surfactant, and would therefore probably lower the cloud point of the mixture. Headspace GC MS showed many hydrocarbon tail fragments from both the Neodol and Rhodafac surfactants. The effect of lowering the average tail length should be to raise the cloud point of the surfactant, because of the higher polar to nonpolar ratio. The effect of solubilization of those same hydrocarbon fragments into the micelle core would also be to raise the cloud point. Another possible effect is suggested by the numerous fragments found in the headspace. If the amount of volatile products formed by the decomposition of surfactant is sufficient to raise the pressure in the sample vials, the effect of pressure on the cloud points must be considered. Other aging studies were added in order to establish whether or not a significant pressure change with aging has occurred. These studies and their results are included in chapter five.

CHAPTER V

Other Consequences of Aging

V.A. Introduction

This chapter concerns other consequences of surfactant solution aging, apart from surfactant structural changes, that could be the cause of observed changes in cloud point. Two possible causes include pressure changes in the ampoules during aging, and solution pH changes.

V.B. Aging Consequence

V.B.1. Pressure

V.B.1.a. Introduction

In Chapter 4, it was shown that some of the decomposition products which arise during aging of the surfactants are volatile species. The question arose as to whether an increase in pressure in the ampoules would result and what effect such a change would have on the cloud point. It has been shown in nonionic Neodol type surfactant systems that an increase in pressure leads to an increase in the cloud point. Such changes occur because the volume change associated with the formation of water/ether hydrogen bonds is negative[1]. LeChatlier's principle says that under increase in pressure, an increase in hydration of ether oxygens should occur. An increase in hydration counteracts the effect of temperature, and leads to the increase in cloud point.

V.B.1.b Experimental Methods and Procedures

Surfactant solutions for all six surfactants were prepared as discussed in Chapter II. These surfactant solutions were placed in the same glass ampoules as used in the standard aging tests, but were not sealed. These six ampoules, along with a seventh containing seawater, were attached to 1/16" O.D. stainless steel tubing using Swagelok fittings with Teflon ferrules. The ampoules were place within an oven and the 1/16" tubing ran through a port in the oven wall outside to be attached to seven Swagelok stainless steel ball cock valves. A Validyne pressure transducer equipped with a 80 psi maximum diaphragm sensitive to .1 psi, was attached via a three way valve to both the surfactant system, and an dead weight pressure calibrator. The transducer, the valves, and the lines were all filled with distilled water to prevent the loss of pressure in any of the ampoules during measurement due to gas compression in the pressure measuring apparatus. Ampoules were kept inverted, so that any leakage at the fittings would be apparent from salt deposits. Ampoules were flushed with nitrogen, exactly as before, prior to any aging.

Measurements were taken as follows. The oven was allowed to reach reservoir temperature (131 °C) prior to the first measurement. The pressure transducer was calibrated prior to each measurement by the dead weight method. The transducer section of the apparatus was then pressurized to the approximate correct value of the water vapor pressure, 40 psi, directly, then switched to the seawater ampoule for pressurization to exactly that of the vapor pressure of water expected at this temperature. The pressure of each surfactant solution was then measured in turn without significant loss to any built up pressure. Because the most significant changes in cloud point were observed in the first 3 days this experiment was confined to two weeks of aging.

V.B.1.c. Discussion of Results

The pressure measurements were taken at 0,1,2,5,8, and 12 days of aging. The only significant change observed was in the first day of aging, all surfactants had a slight >1psi increase in pressure. Whether this was a result of aging, or of inadequate time for temperature stability in the 0 age measurement is unknown. The following measurements varied only slightly ,.1 psi to .2 psi, in a random manner. In any case reported cloud point changes with increased pressure is on the order of 1 °C raise in CP for about 10 MPa or about 1,450 psi. Therefore we expect no perceptible changes in the cloud point for the observed pressure changes, and any minute changes that did occur would be to raise, not lower the cloud point.

V.B.2. pH and Surfactant Aging

V.B.2.a. Introduction

Another possible solution change that could effect cloud points is the possible pH change accompanying surfactant aging. It was noted in chapter II that H^+ raised cloud points and OH^- lowered cloud points, therefore any change in pH during surfactant aging could be a cause of cloud point changes.

V.B.2.b. Experimental Methods and Procedures

Sample pH's were tested on a Corning pH meter 125 in the ampoules immediately after opening for the Rhodafac, Fluorad, Neodol 45-20, and Neodol 25-7 samples.

V.B.2.c. Discussion of Results

The observed pH's for the four surfactants are shown in Table 5.1. It can be seen that little change occurred in Rhodafac pH's, and that the Neodol pH's are uninterpretable due to their lack of any pattern. The Fluorad pH's however, had a consistent drop with aging, which should lead to a raising in cloud point if the effects noted for nonionics apply here.

	0 (RT)	3 Dys	1 Wk	3 Wks	5 Wks	11 Wks
Rhodafac	2.33	2.38	2.39	2.41	2.35	
Fluorad	6.82	6.20	6.17	6.11	5.78	5.70
Neodol 45-20	8.03	5.90	6.85	6.70		
Neodol 25-7	6.24	7.03	6.99	6.63		

Table 5.1. Changes in solution pH's during aging.

V.C. Summary

Only very minor changes in pressure were observed in the 12 days of surfactant aging. No significant cloud point changes due to pressure effects are expected, because of trivial changes in the pressure, and because of the small magnitude of the effect. Minor changes in Fluorad pH would possibly lead to a raising of the cloud point.

V.D. Bibliography

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CHAPTER VI

Summary, Conclusions, and Suggestions for Additional Study

VI.A. Summary

It was found that the surfactant solutions all exhibited a downward trend in cloud point upon aging. While some of these changes are questionable due to possible instrument fluctuations, it was noted that the downward trend was repeated in some additional studies that were performed as well. It should also be noted that on different studies the initial unaged cloud points of a given surfactant often disagreed by as much as about 15 °F, but that on the three day aged samples the cloud points were often in close agreement. This would lend some support to the possibility that micellar equilibrium had not been reached upon our 0 age cloud points. However, it should also be understood that even though identical samples showed good agreement in cloud points, that some random fluctuations did occasionally occur in the cloud points (see Neodol 500 ppm and Rhodafac 1000 ppm in 3 day aging study).

Taking all of this into consideration, the Rhodafac surfactant had a dramatic change in cloud point, the Fluorad had an apparently moderate downward change, and the Neodols all had either a small and therefore questionable change or were uninterpretable.

Surface tension studies suggested that Fluorad was very unstable under these conditions, but the Rhodafac surfactant remained very stable with regards to surface activity and therefore was thought to be very stable.

Headspace GC revealed small quantities of the hydrocarbon tails of the Neodol surfactant, and the Rhodafac surfactant, and a surplus of fragments of the Fluorad surfactant. Lessening of hydrocarbon tail/solvation of hydrocarbon in the Neodol and Rhodafac surfactants both should result in the raising of the surfactants cloud point, however the magnitude of the effect suggested by our studies was small. The apparent destruction of the Fluorad surfactant has an unknown effect on cloud point, loss of solubility should lower the cloud point, but should eventually result in the absence of a cloud point.

^{13}C NMR revealed a terminal alcohol in the Rhodafac surfactant that, while signifying the destruction of Rhodafac surfactant, probably results in the formation of Neodol type surfactants. Because the Neodol surfactants have a significantly lower cloud point than the Rhodafac a downward trend is expected.

No significant cloud point changes due to pressure effects are expected. Both because of trivial changes in the pressure, and because of the small magnitude of the effect. Minor changes in Fluorad pH would possibly lead to a raising of the cloud point.

VI.A. Conclusions

The cloud point method of surfactant stability prediction had both it's successes and failures. The method's biggest success was in the case of Rhodafac surfactant. The traditional technique of surfactant stability testing, surface tension, would predict a highly stable Rhodafac surfactant. The cloud point of this solution was found to have had an extreme initial downward change. It was also noted that initially Rhodafac surfactant concentration was directly related to cloud point, but that after aging this relationship reversed. ^{13}C NMR revealed that the Rhodafac surfactant in fact was not stable. The proposed decomposition products from the ^{13}C NMR would have both of the effects observed on the Rhodafac cloud point.

The near total destruction of Fluorad surfactant as indicated by surface tension and headspace GC, only amounted to moderate if any change in the cloud point of the samples. The Neodol surfactants had no significant structural changes noted that would severely lesson their surface activity or change their cloud point, likewise only small changes if any were noted in their cloud points.

While this study is by no means a full examination of the possible application of cloud points in predicting surfactant stability, these preliminary results indicate some degree of success. Probably the best argument against the practicality of using cloud points for surfactant stability prediction at this point lies in the fact that few ionic surfactants exhibit any cloud points whatsoever.

VI.A. Suggestions for Additional Study

Several suggestions for continuing the present study arise from problems occurring in this study. Structurally pure samples would provide easier characterization of structural changes and therefore better correlation with observed cloud point changes. An alternative study to one using stucturally pure samples could be based on the idea of looking for changing R and n distributions as suggested by the preliminary data taken by SFC in Appendix B. Some standard for instrument calibration/testing purposes would be advisable. A wider range of surfactant types would also prove useful in the method's evaluation. Testing should be conducted to see if the structural and environmental changes affect the cloud points of ionic surfactants similarly to their effect on nonionics. Many of the cloud point affecting structural and environmental changes should be gauged on the magnitude of the effect to see which changes are worth considering.

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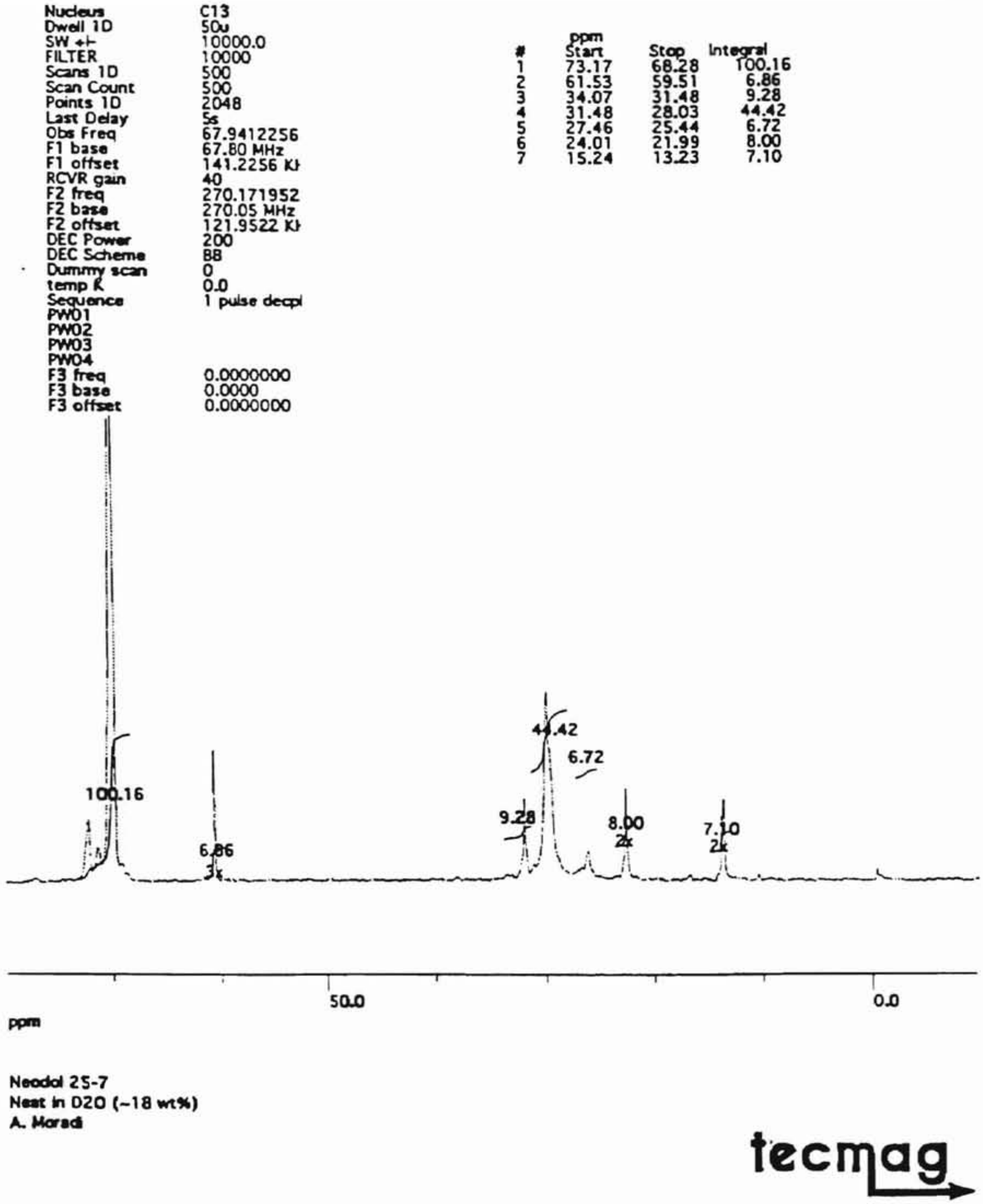
APPENDIX A

^{1}H NMR AND ^{13}C NMR



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Points 1D	2048
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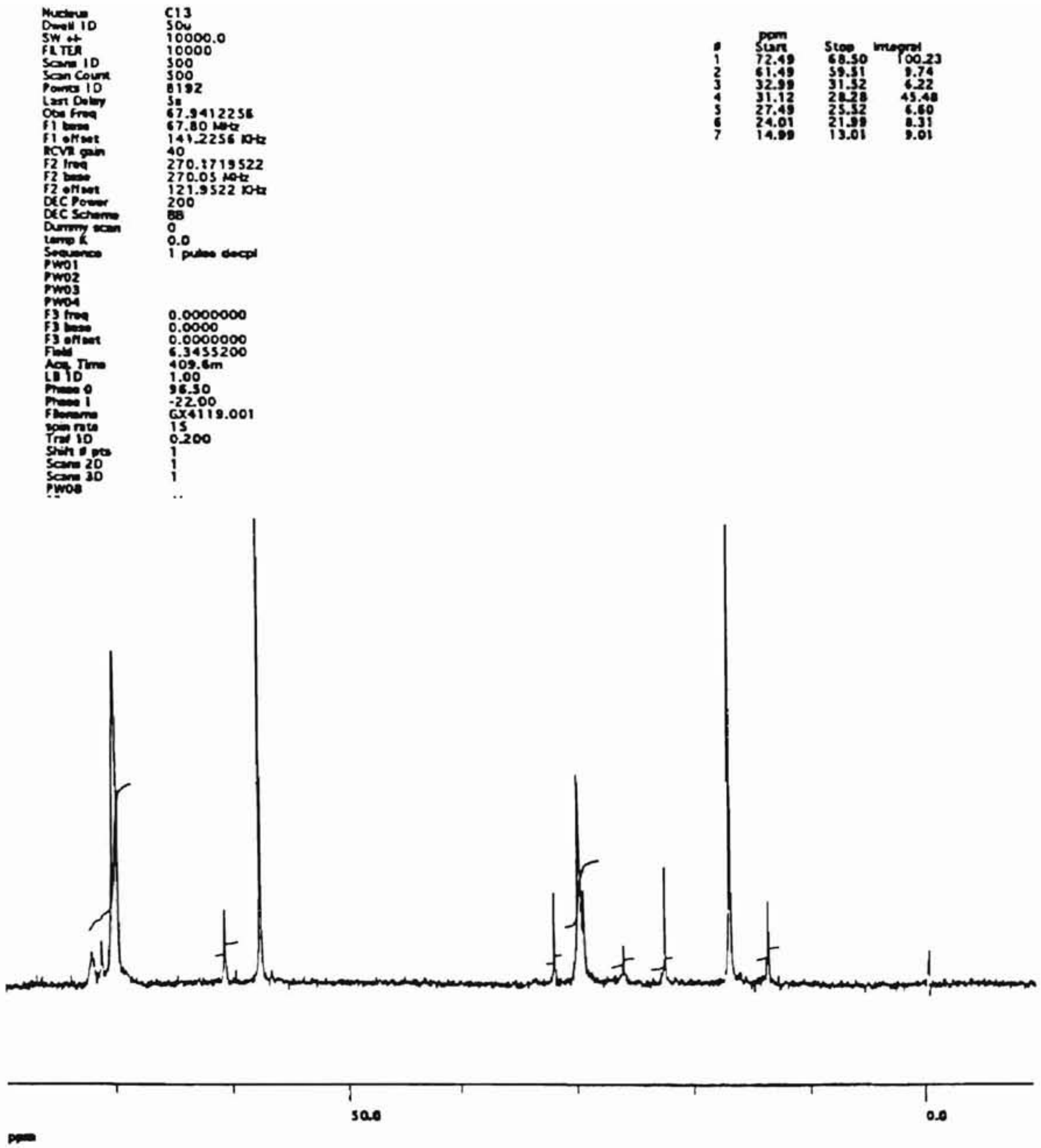
F1 base	67.80 MHz
F1 offset	141.2256 KH
RCVR gain	40
F2 freq	270.171952
F2 base	270.05 MHz
F2 offset	121.9522 KH
DEC Power	200
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse decpl
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000

#	ppm Start	Stop	Integral
1	73.17	68.28	100.16
2	61.53	59.51	6.86
3	34.07	31.48	9.28
4	31.48	28.03	44.42
5	27.46	25.44	6.72
6	24.01	21.99	8.00
7	15.24	13.23	7.10

Neodol 25-7
Neat in D2O (~18 wt%)
A. Moradi

Figure A.1. ^{13}C NMR spectrum of Neodol 25-7 surfactant.



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F1 base        67.80 MHz
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Temp K         0.0
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PW02
PW03
PW04
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Phase 1        -22.00
Filename       GX4119.001
spin rate      15
Traf 1D        0.200
Shift # pts    1
Scans 2D       1
Scans 3D       1
PW08
               ..
```

```
      ppm
#     Start     Stop    integral
1     72.49     68.50     100.23
2     61.49     59.51       9.74
3     32.99     31.52       6.22
4     31.12     28.28      45.48
5     27.49     25.52       6.60
6     24.01     21.99       8.31
7     14.99     13.01       9.01
```

GO-37274-59-0A25-7E
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ETOH EXTRACTED

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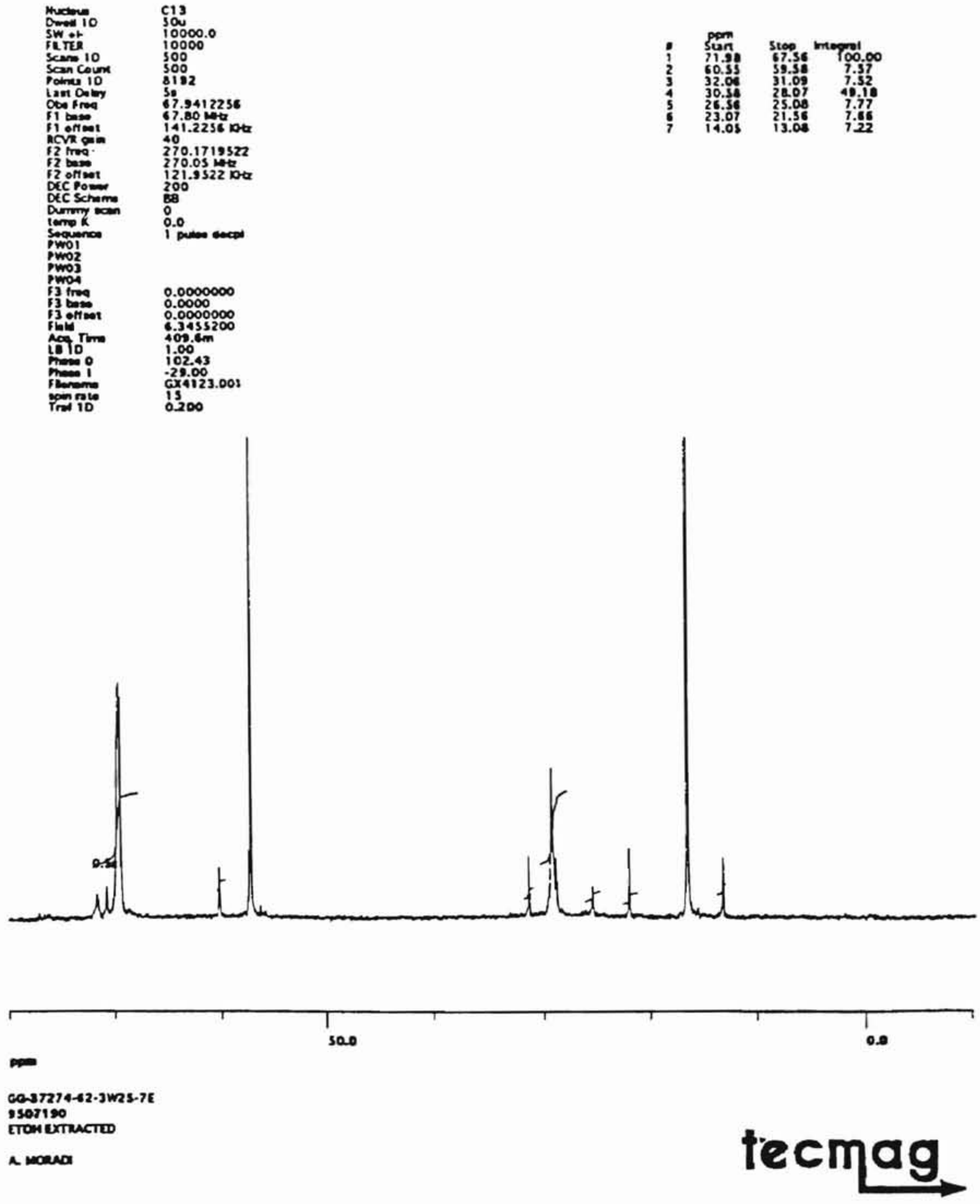
Figure A.2. ^{13}C NMR spectrum of 0 aged Neodol 25-7.



Nucleus	C13
Dwell 1D	50u
SW +/-	10000.0
FILTER	10000
Scans 1D	500
Scan Count	500
Points 1D	8192
Last Delay	5s
Obs Freq	67.9412256
F1 base	67.80 MHz
F1 offset	141.2256 KHz
RCVR gain	40
F2 freq	270.1719522
F2 base	270.05 MHz
F2 offset	121.9522 KHz
DEC Power	200
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse decpl
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	409.6m
LB 1D	1.00
Phase 0	102.43
Phase 1	-29.00
Filename	GX4123.001
spin rate	15
Trel 1D	0.200

#	ppm Start	Stop	Integral
1	71.98	67.56	100.00
2	60.55	59.58	7.37
3	32.08	31.09	7.52
4	30.58	28.07	49.18
5	26.56	25.08	7.77
6	23.07	21.56	7.66
7	14.05	13.08	7.22

GG-37274-62-3W25-7E
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Figure A.3. ^{13}C NMR spectrum of 3 week aged Neodol 25-7.

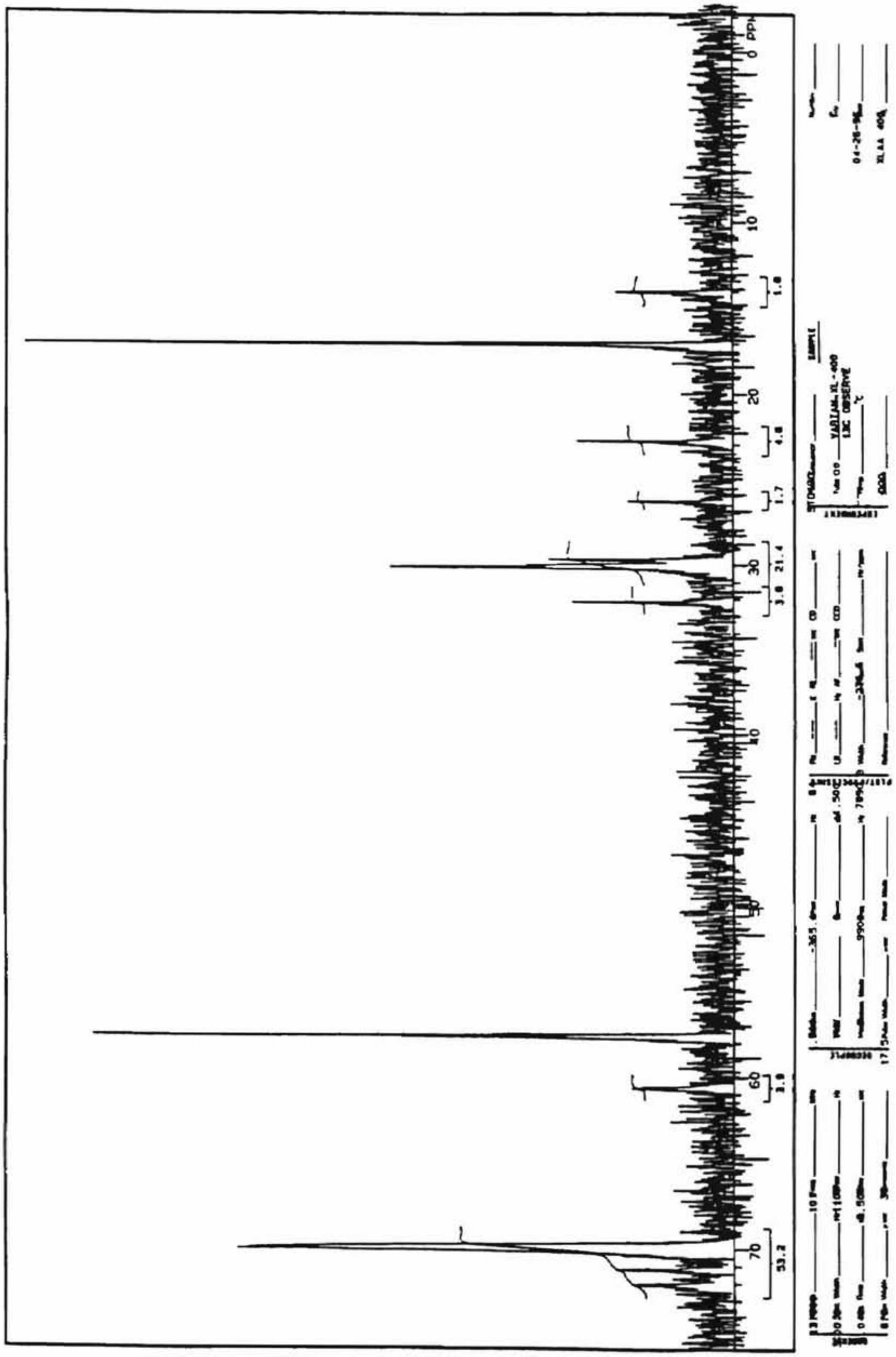
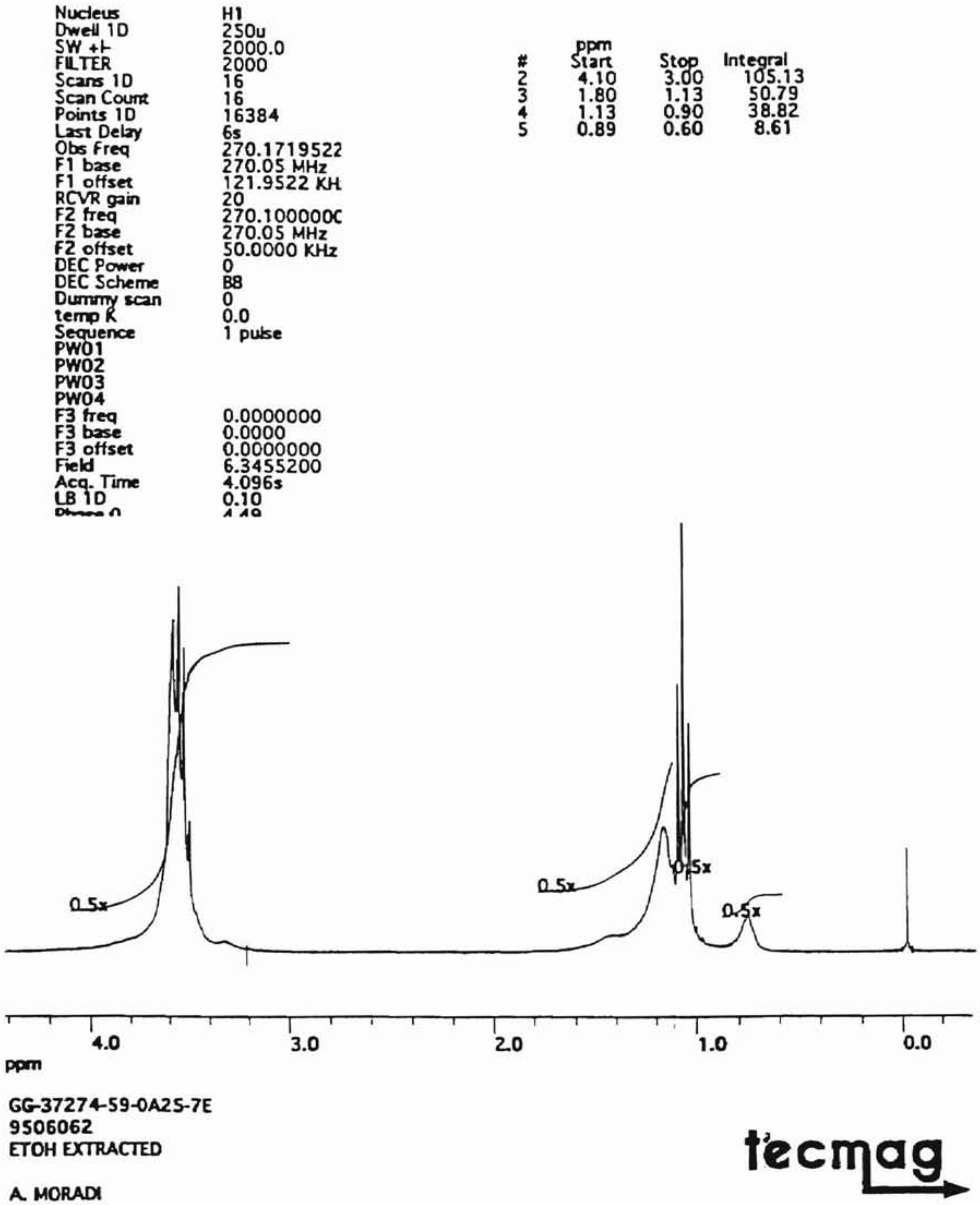


Figure A.4. ^{13}C NMR spectrum of 11 week aged Neodol 25-7.



Nucleus	H1
Dwell 1D	250u
SW +-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.1719522
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000C
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	B8
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10
Phase 0	4.49

#	ppm Start	Stop	Integral
2	4.10	3.00	105.13
3	1.80	1.13	50.79
4	1.13	0.90	38.82
5	0.89	0.60	8.61

GG-37274-59-0A25-7E
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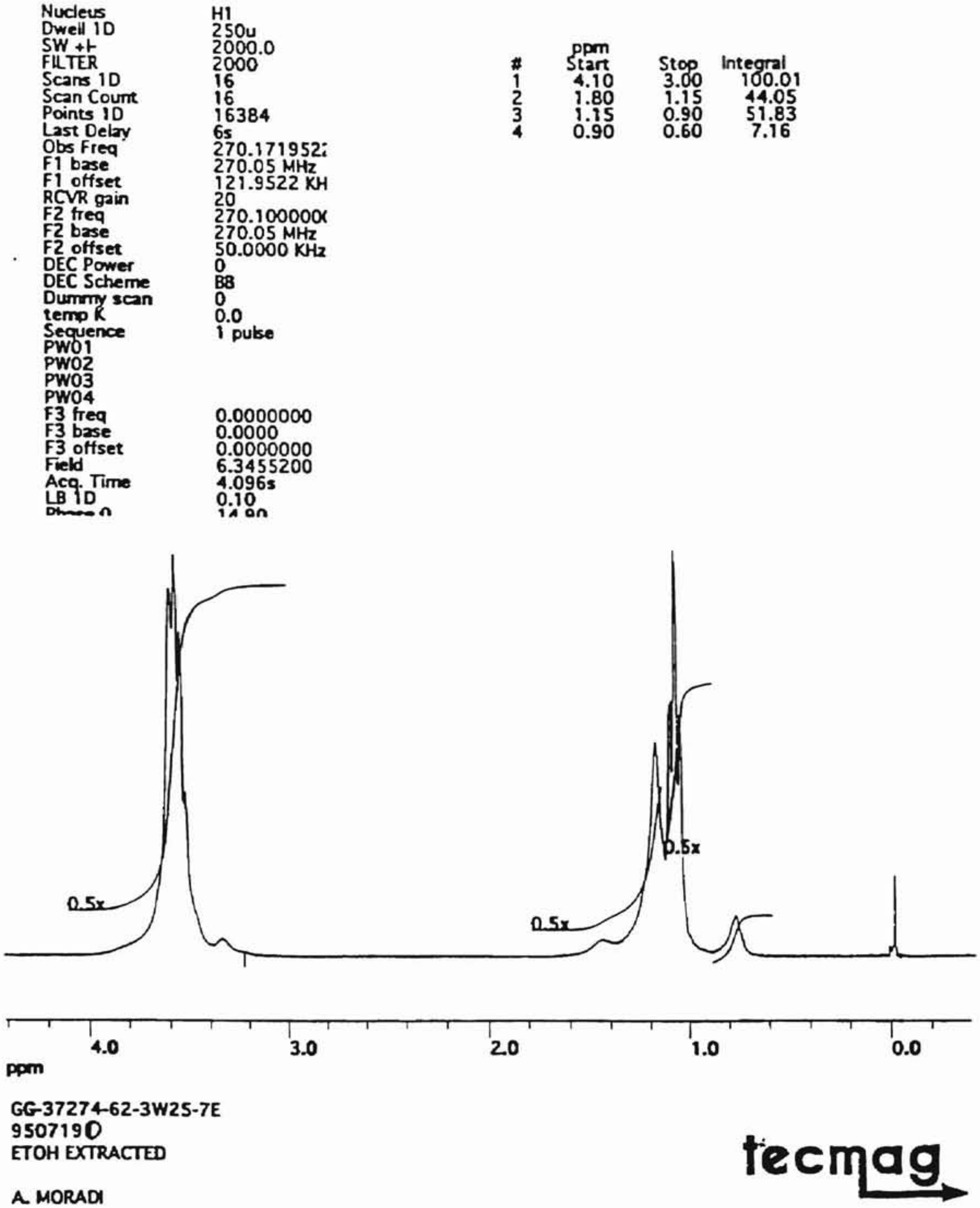
ETOH EXTRACTED

A. MORADI

Figure A.5. ^{1}H NMR spectrum of 0 aged Neodol 25-7.



Nucleus	H1
Dwell 1D	250u
SW +/-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.171952:
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000(
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10
Phase 0	14.90

#	ppm Start	Stop	Integral
1	4.10	3.00	100.01
2	1.80	1.15	44.05
3	1.15	0.90	51.83
4	0.90	0.60	7.16

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ETOH EXTRACTED

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Figure A.6. ^{1}H NMR spectrum of 3 week aged Neodol 25-7.

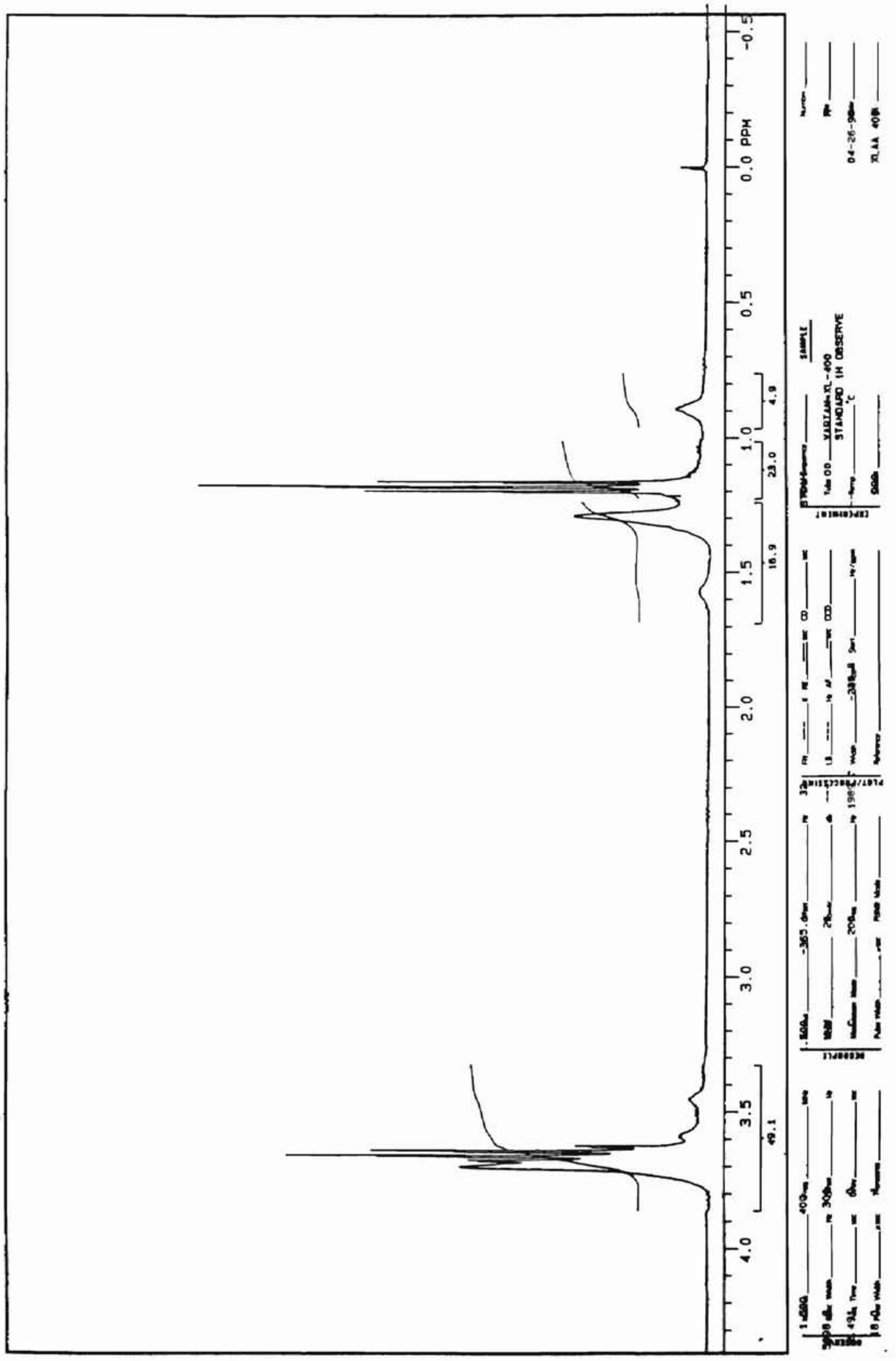
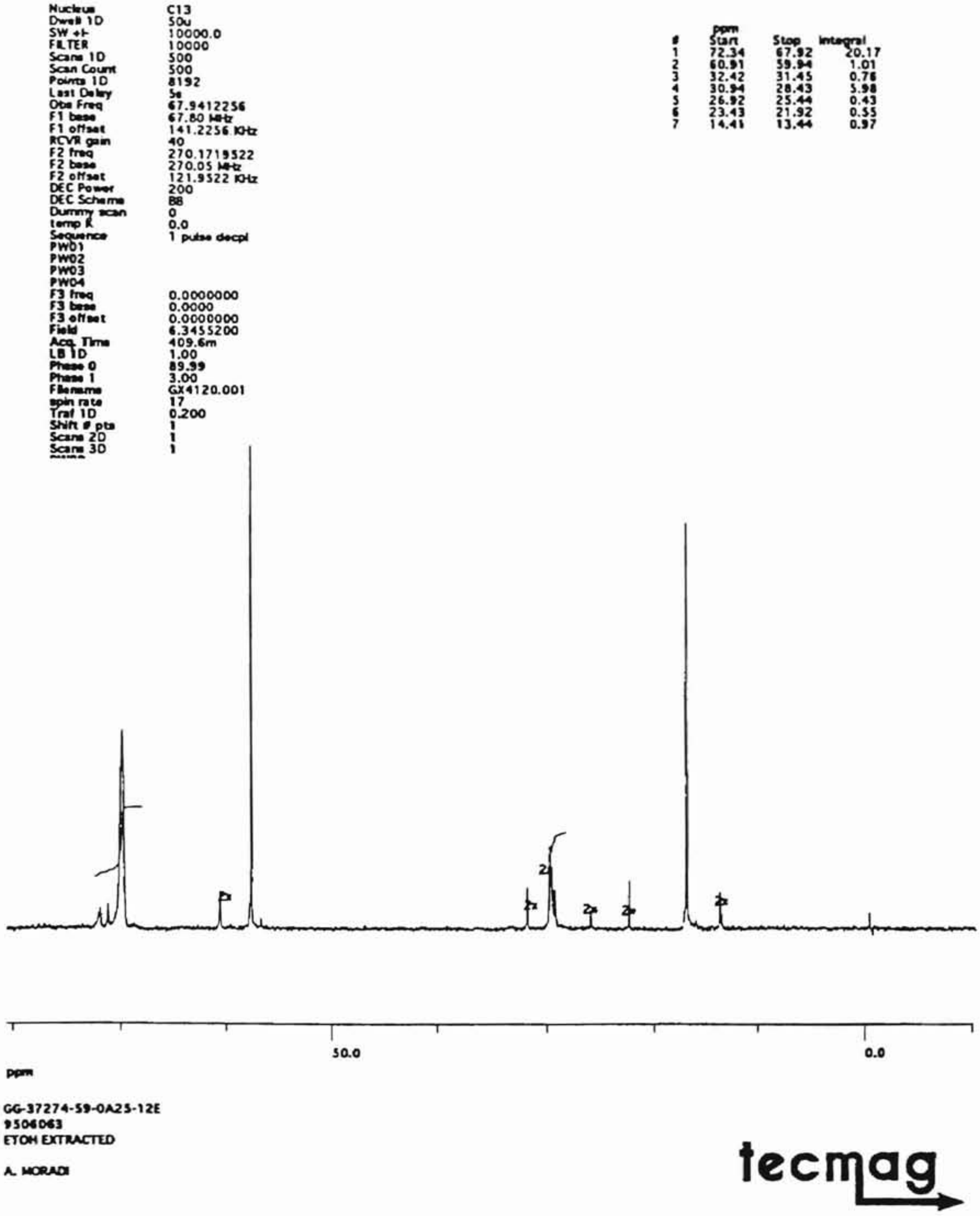
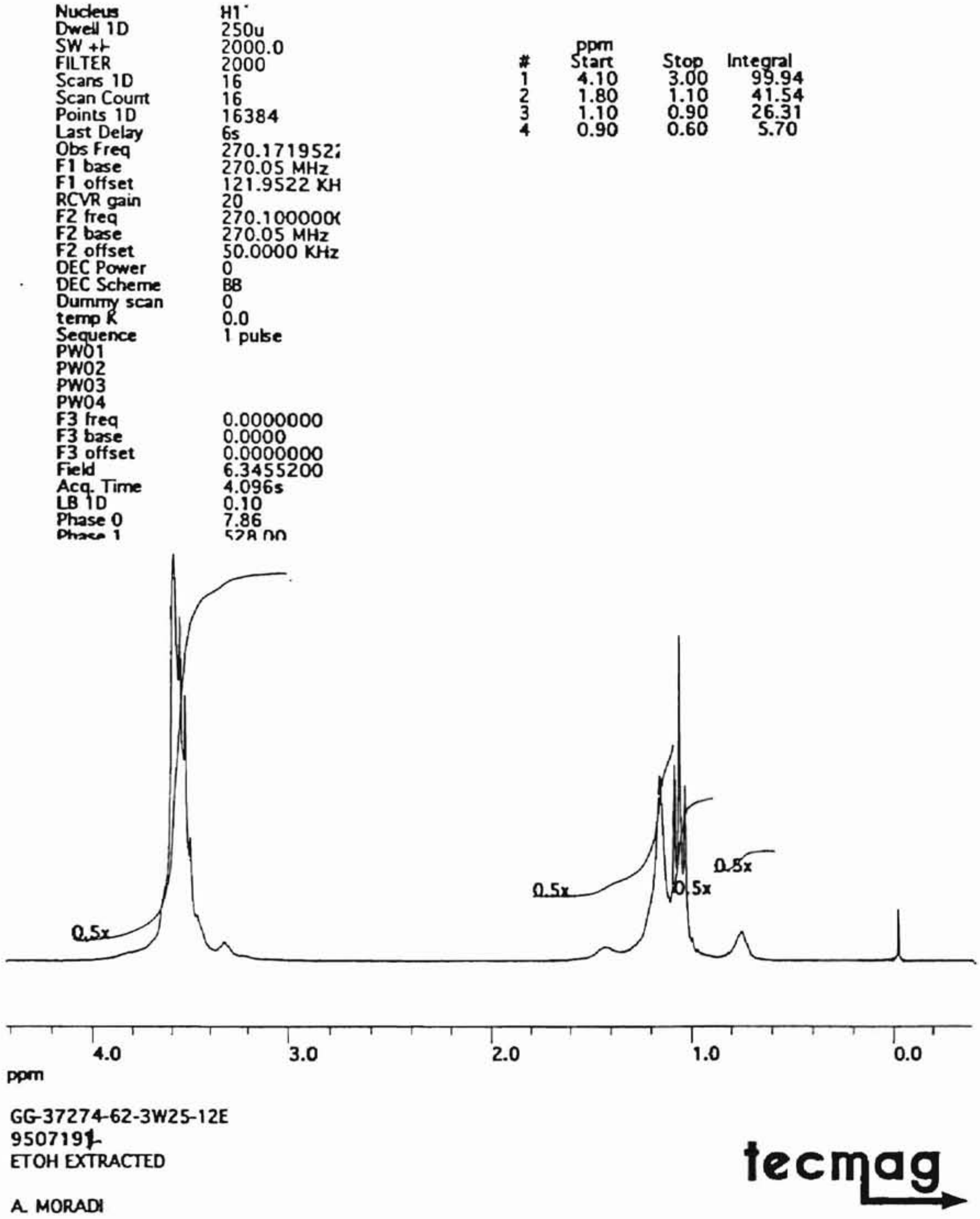


Figure A.7. ^{1}H NMR spectrum of 11 week aged Neodol 25-7.





Nucleus	H1
Dwell 1D	250u
SW +/-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.171952
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10
Phase 0	7.86
Phase 1	528.00

#	ppm Start	Stop	Integral
1	4.10	3.00	99.94
2	1.80	1.10	41.54
3	1.10	0.90	26.31
4	0.90	0.60	5.70

GG-37274-62-3W25-12E
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ETOH EXTRACTED

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Figure A.9. ^{13}C NMR spectrum of 3 week aged Neodol 25-12.

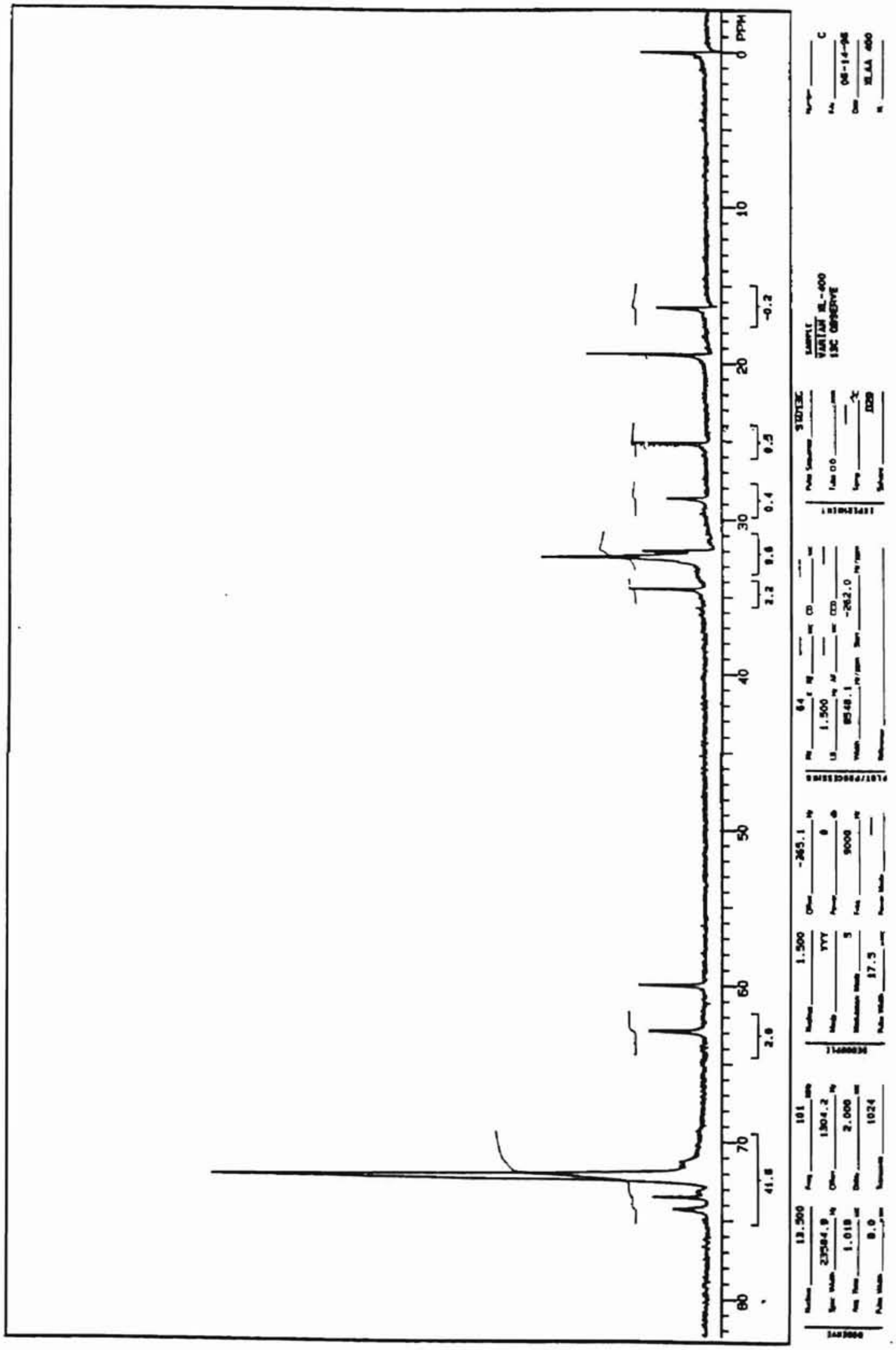
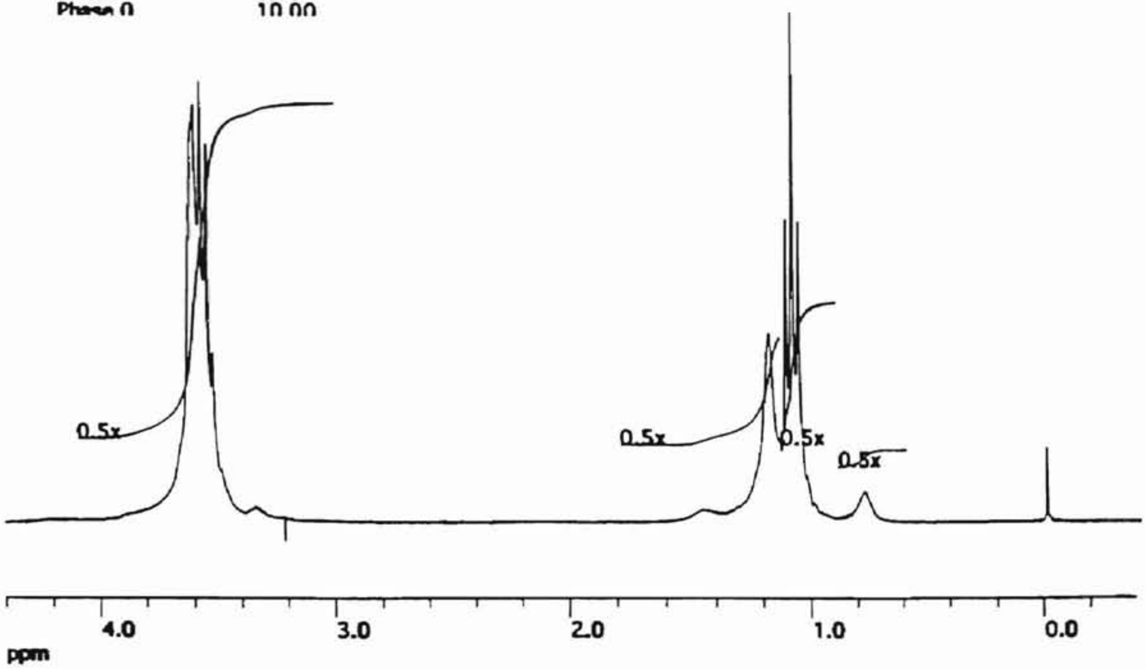


Figure A.10. ^{13}C NMR spectrum of 11 week aged Neodol 25-12.

Nucleus	H1
Dwell 1D	250u
SW +I-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.1719522
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000C
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10
Phase 0	10.00

#	ppm Start	Stop	Integral
1	4.10	3.00	103.61
2	1.80	1.14	33.19
3	1.14	0.90	44.01
4	0.90	0.60	5.35



GG-37274-59-0A25-12E
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ETOH EXTRACTED

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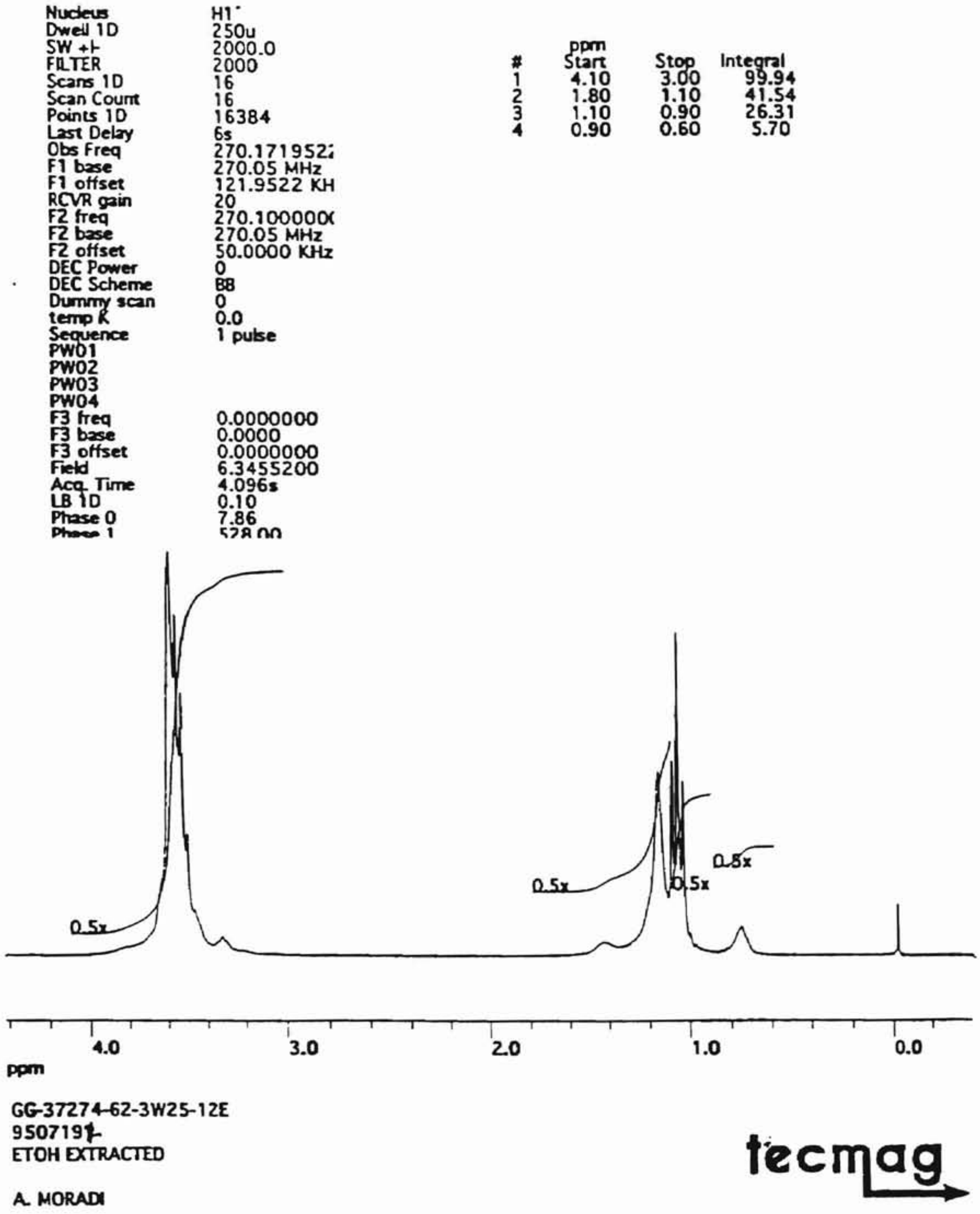
Figure A.11. ¹H NMR spectrum of 0 aged Neodol 25-12.



Nucleus	H1
Dwell 1D	250u
SW +-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.171952
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10
Phase 0	7.86
Phase 1	528.00

#	ppm Start	Stop	Integral
1	4.10	3.00	99.94
2	1.80	1.10	41.54
3	1.10	0.90	26.31
4	0.90	0.60	5.70

GG-37274-62-3W25-12E
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ETOH EXTRACTED

A. MORADI

Figure A.12. ^{1}H NMR spectrum of 3 week aged Neodol 25-12.

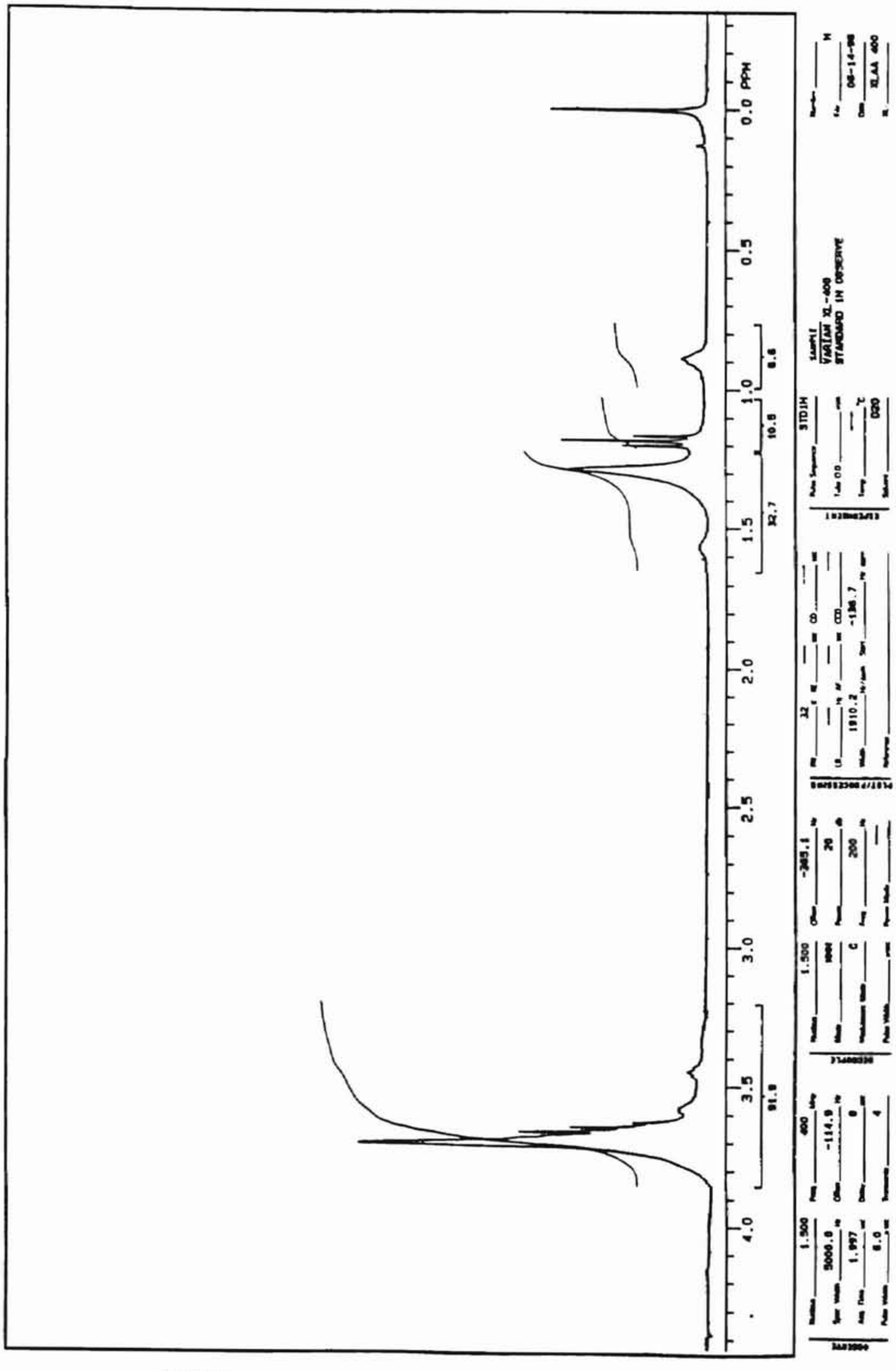
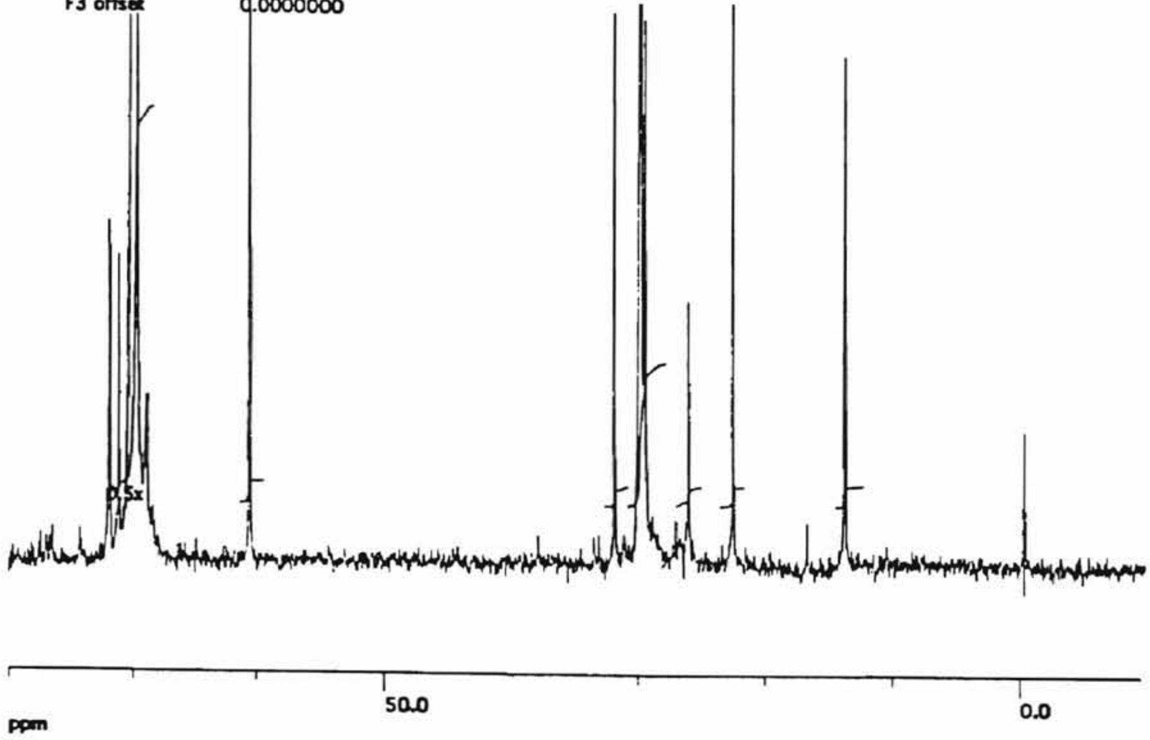


Figure A.13. ^{1}H NMR spectrum of 11 week aged Neodol 25-12.

Nucleus	C13
Dwell 1D	50u
SW +/-	10000.0
FILTER	10000
Scans 1D	500
Scan Count	500
Points 1D	8192
Last Delay	5s
Obs Freq	67.9412256
F1 base	67.80 MHz
F1 offset	141.2256 KH
RCVR gain	40
F2 freq	270.171952
F2 base	270.05 MHz
F2 offset	121.9522 KH
DEC Power	200
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse decpl
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000

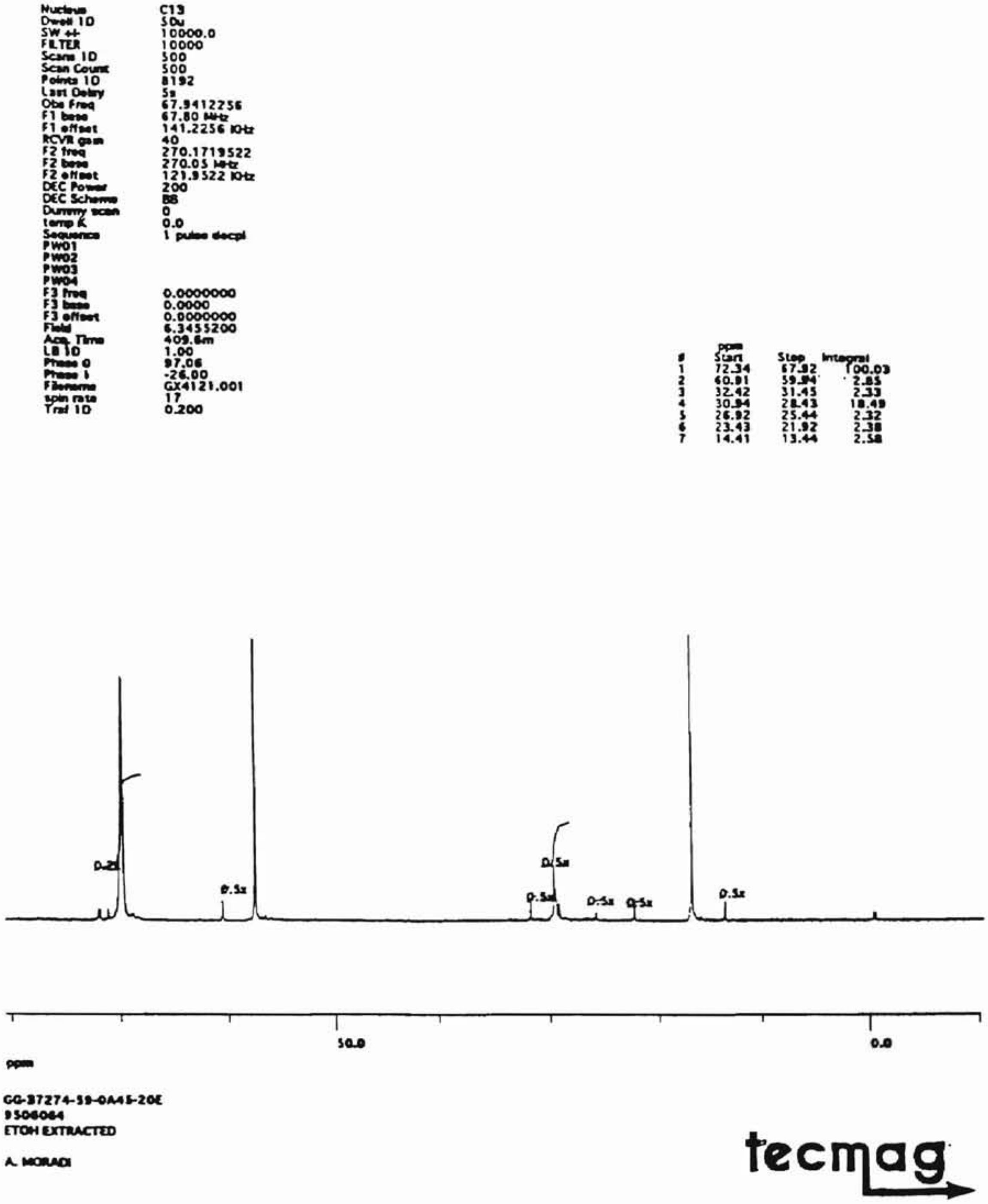
#	ppm Start	Stop	Integral
1	72.34	68.35	100.25
2	61.35	59.37	2.83
3	32.99	31.01	2.53
4	31.01	28.00	18.09
5	27.35	25.37	2.49
6	23.86	21.85	2.49
7	14.84	12.87	2.67



Neodol 45-20
Neat in D2O (~18 wt%)
A. Morad

tecmag

Figure A.14. ^{13}C NMR spectrum of Neodol 45-20 surfactant.



```
Nucleus         C13
Dwell 1D        50u
SW +-           10000.0
FILTER          10000
Scans 1D        500
Scan Count      500
Points 1D       8192
Last Delay      5s
Obs Freq        67.9412256
F1 base         67.80 MHz
F1 offset       141.2256 KHz
RCVR gain       40
F2 freq         270.1719522
F2 base         270.05 MHz
F2 offset       121.9522 KHz
DEC Power       200
DEC Scheme      BB
Dummy scan      0
temp K          0.0
Sequence        1 pulse decpl
PW01
PW02
PW03
PW04
F3 freq         0.0000000
F3 base         0.0000
F3 offset       0.0000000
Field           6.3455200
Acq. Time       409.6m
LB 1D           1.00
Phase 0         97.06
Phase 1         -26.00
Filename        GX4121.001
spin rate       17
Trd 1D          0.200
```

```
     ppm
#    Start     Stop    Integral
1    72.34     67.92    100.03
2    60.91     59.94      2.85
3    32.42     31.45      2.33
4    30.94     28.43     18.49
5    26.92     25.44      2.32
6    23.43     21.92      2.38
7    14.41     13.44      2.58
```

GG-37274-59-0A45-20E
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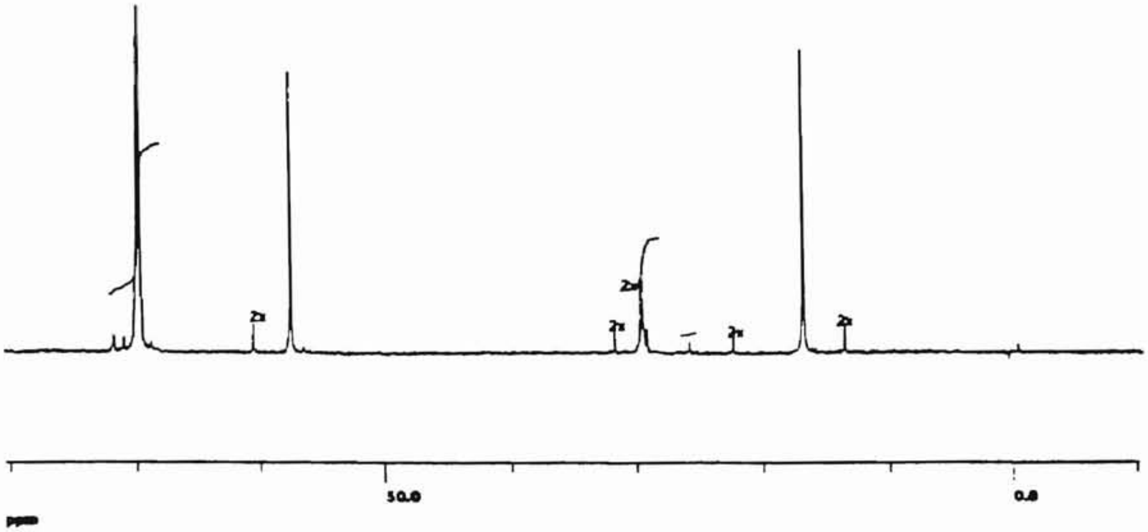
ETOH EXTRACTED

A. MORADI

Figure A.15. ^{13}C NMR spectrum of 0 aged Neodol 45-20.

Nucleus	C13
Dwell 1D	50u
SW +/-	10000.0
FILTER	10000
Scans 1D	500
Scan Count	500
Points 1D	8192
Last Delay	5s
Obs Freq	67.9412256
F1 base	67.80 MHz
F1 offset	141.2256 KHz
RCVR gain	40
F2 freq	270.1719522
F2 base	270.05 MHz
F2 offset	121.9522 KHz
DEC Power	200
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse decpl
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	409.6m
LB 1D	1.00
Phase 0	105.57
Phase 1	-29.00
Filename	GX4125.001
spin rate	15
Tref 1D	0.200

#	ppm Start	Stop	Integral
1	72.31	67.99	103.00
2	60.88	59.91	2.91
3	32.49	31.52	2.35
4	31.52	28.50	17.94
5	26.85	25.70	1.36
6	23.04	22.14	1.67
7	14.48	13.51	3.00



GG-37274-62-3W45-20E
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ETOH EXTRACTED

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Figure A.16. ^{13}C NMR spectrum of 3 week aged Neodol 45-20.

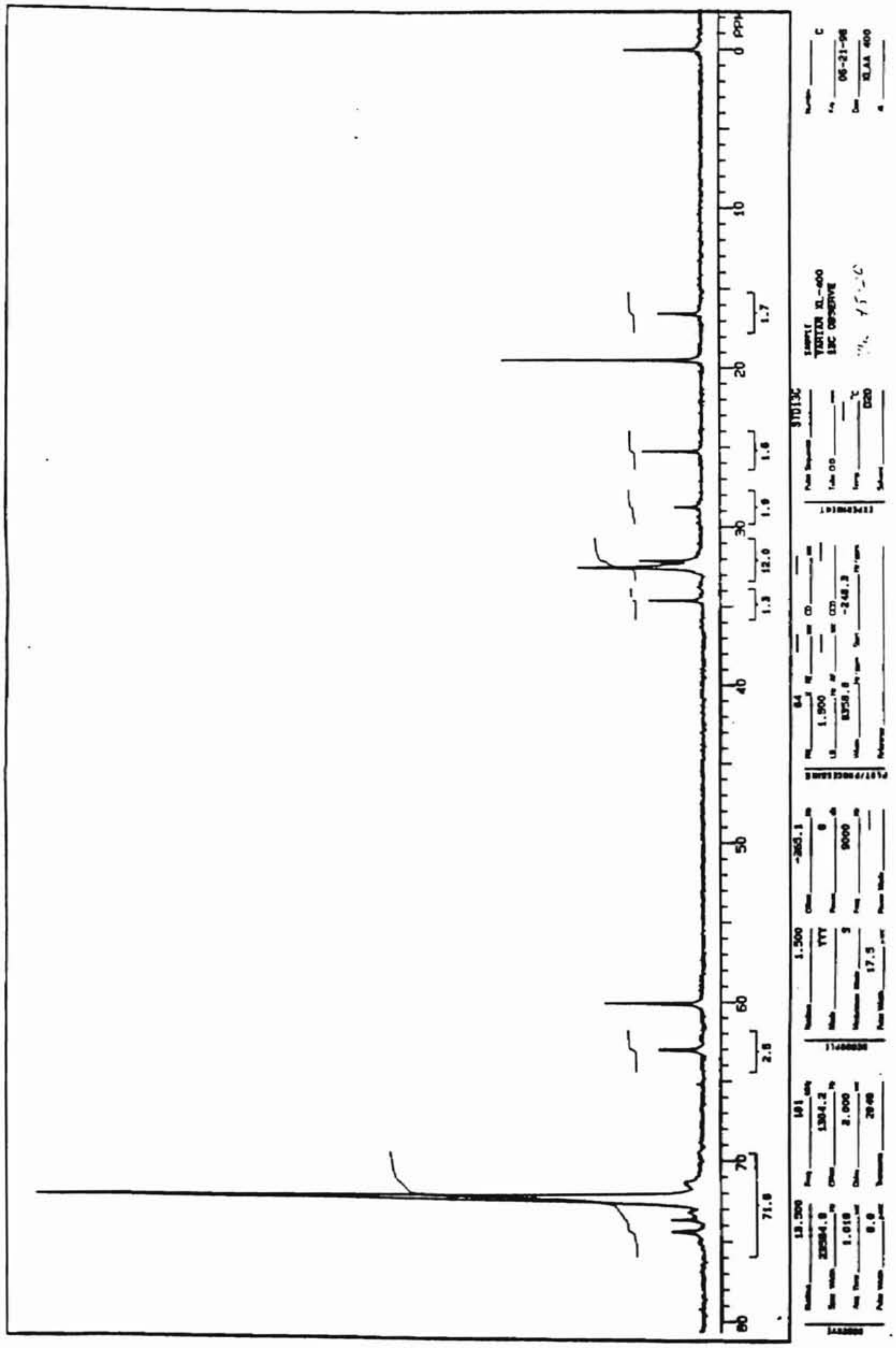
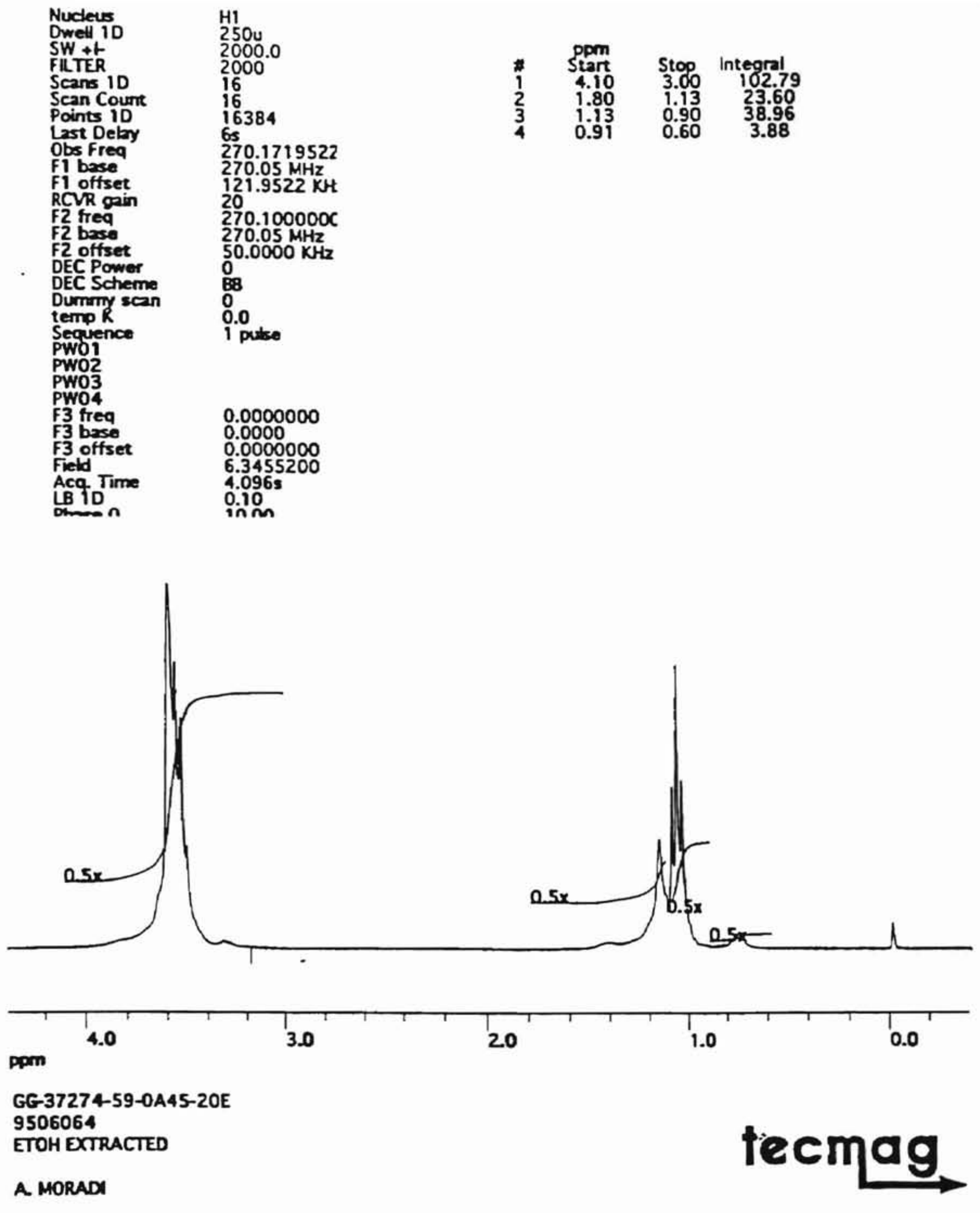


Figure A.17. ^{13}C NMR spectrum of 11 week aged Neodol 45-20.



Nucleus	H1
Dwell 1D	250u
SW +/-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.1719522
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000C
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10
Phase 0	10.00

#	ppm Start	Stop	Integral
1	4.10	3.00	102.79
2	1.80	1.13	23.60
3	1.13	0.90	38.96
4	0.91	0.60	3.88

GG-37274-59-0A45-20E
9506064
ETOH EXTRACTED

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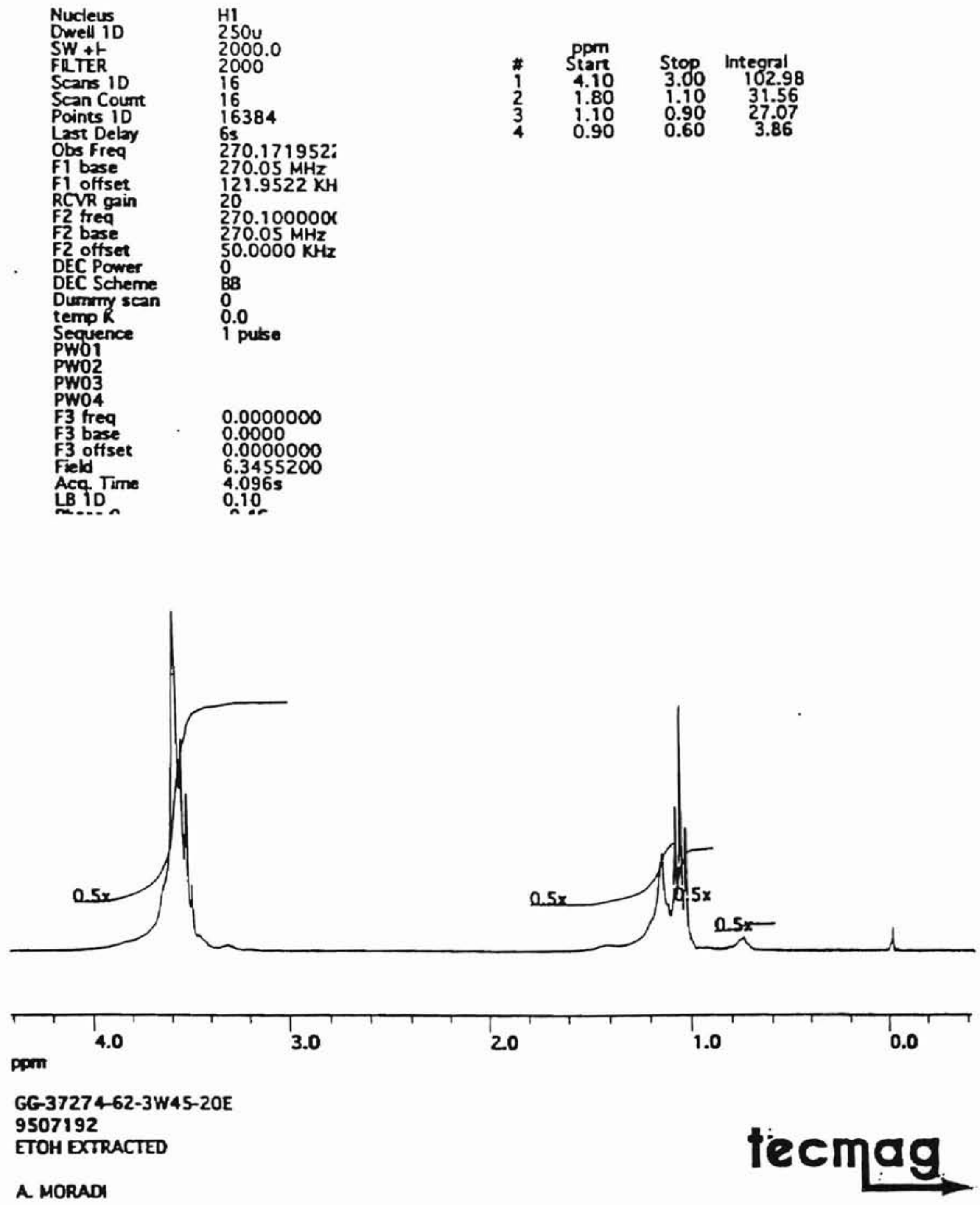
Figure A.18. ^{1}H NMR spectrum of 0 aged Neodol 45-20.



Nucleus	H1
Dwell 1D	250u
SW +-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.171952
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10

#	ppm Start	Stop	Integral
1	4.10	3.00	102.98
2	1.80	1.10	31.56
3	1.10	0.90	27.07
4	0.90	0.60	3.86

GG-37274-62-3W45-20E
9507192
ETOH EXTRACTED

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Figure A.19: ^{1}H NMR spectrum of 3 week aged Neodol 45-20.

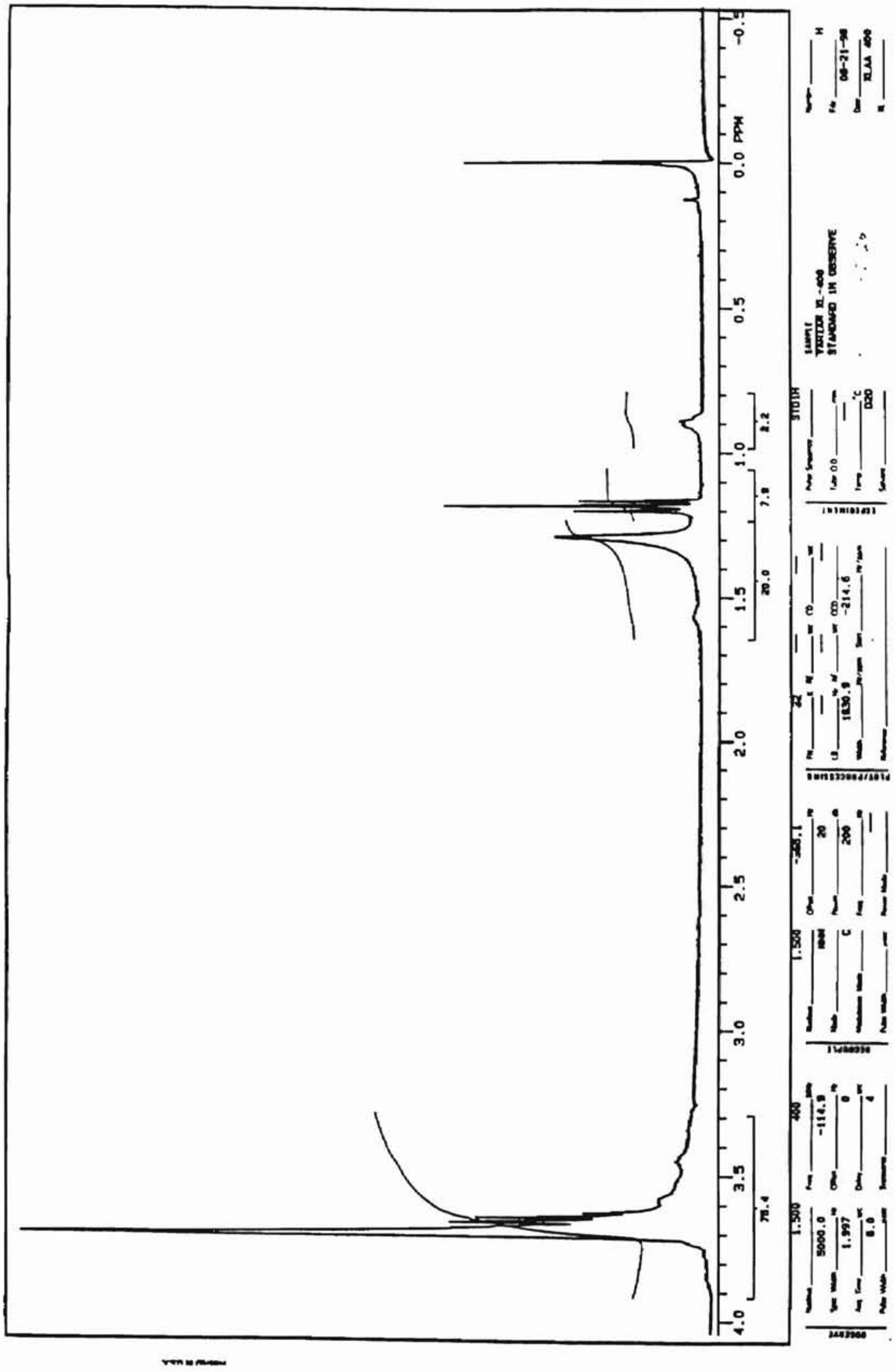
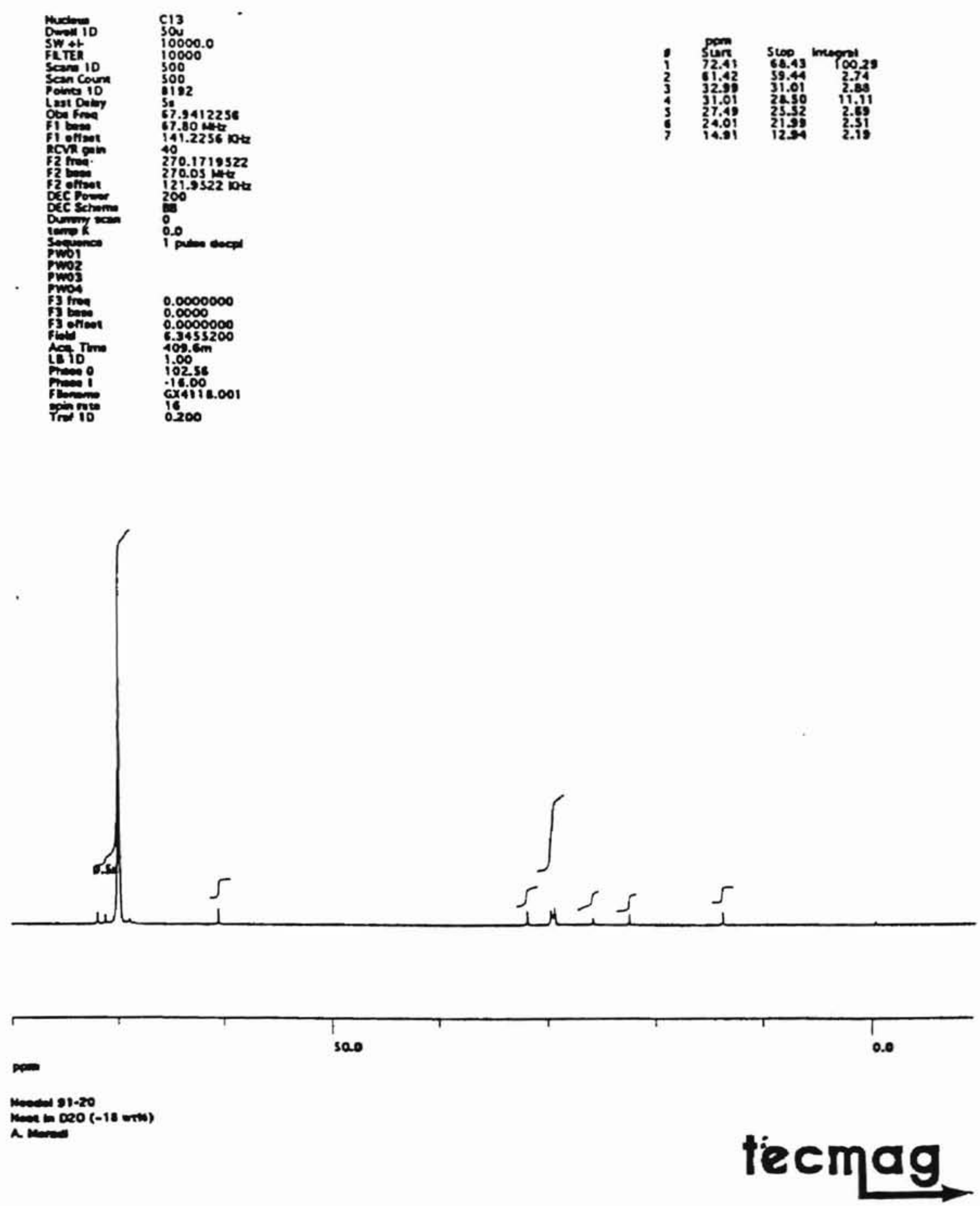


Figure A.20. ^{1}H NMR spectrum of 11 week aged Neodol 45-20.



Nucleus	C13
Dwell 1D	50u
SW +/-	10000.0
FILTER	10000
Scans 1D	500
Scan Count	500
Points 1D	8192
Last Delay	5s
Obs Freq	67.9412256
F1 base	67.80 MHz
F1 offset	141.2256 KHz
RCVR gain	40
F2 freq	270.1719522
F2 base	270.05 MHz
F2 offset	121.9522 KHz
DEC Power	200
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse decpl
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	409.6m
LB 1D	1.00
Phase 0	102.56
Phase 1	-16.00
Filename	GX4118.001
spin rate	16
Tref 1D	0.200

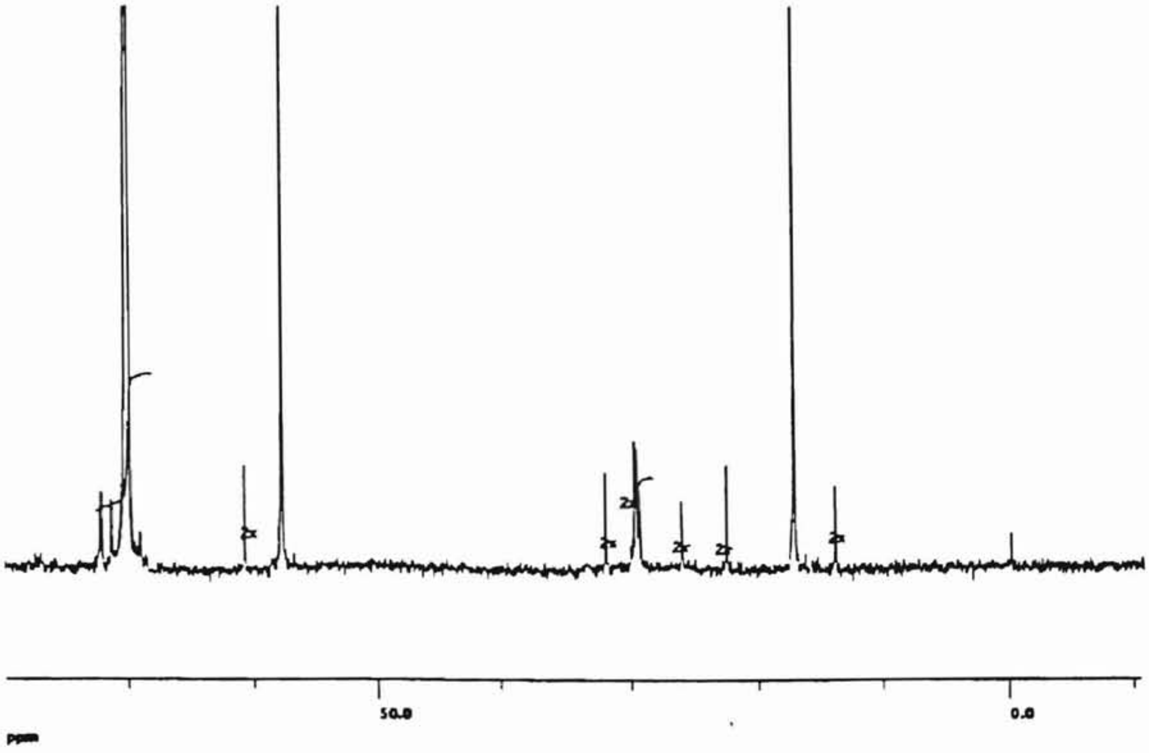
#	ppm Start	Stop	Integral
1	72.41	68.43	100.29
2	61.42	59.44	2.74
3	32.99	31.01	2.88
4	31.01	28.50	11.11
5	27.49	25.52	2.89
6	24.01	21.99	2.51
7	14.91	12.94	2.19

Neodol 91-20
Neat in D2O (~18 wt%)
A. Moradi

Figure A.21. ^{13}C NMR spectrum of Neodol 91-20 surfactant.

Nucleus	C13
Dwell 1D	50u
SW +/-	10000.0
FILTER	10000
Scans 1D	500
Scan Count	500
Points 1D	8192
Last Delay	5s
Obs Freq	67.9412256
F1 base	67.80 MHz
F1 offset	141.2256 KHz
RCVR gain	40
F2 freq	270.1719522
F2 base	270.05 MHz
F2 offset	121.9522 KHz
DEC Power	200
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse decpl
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	409.6m
LB 1D	1.00
Phase 0	102.67
Phase 1	-29.00
Filename	GX4122.001
spin rate	17
Traf 1D	0.200

#	ppm Start	Stop	Integral
1	72.52	68.10	33.77
2	61.09	60.12	0.79
3	32.60	31.63	0.65
4	31.12	28.61	3.70
5	27.10	25.62	0.94
6	23.61	22.10	0.69
7	14.59	13.62	0.64



GG-37274-59-OA91-20E
9506065
ETOH EXTRACTED

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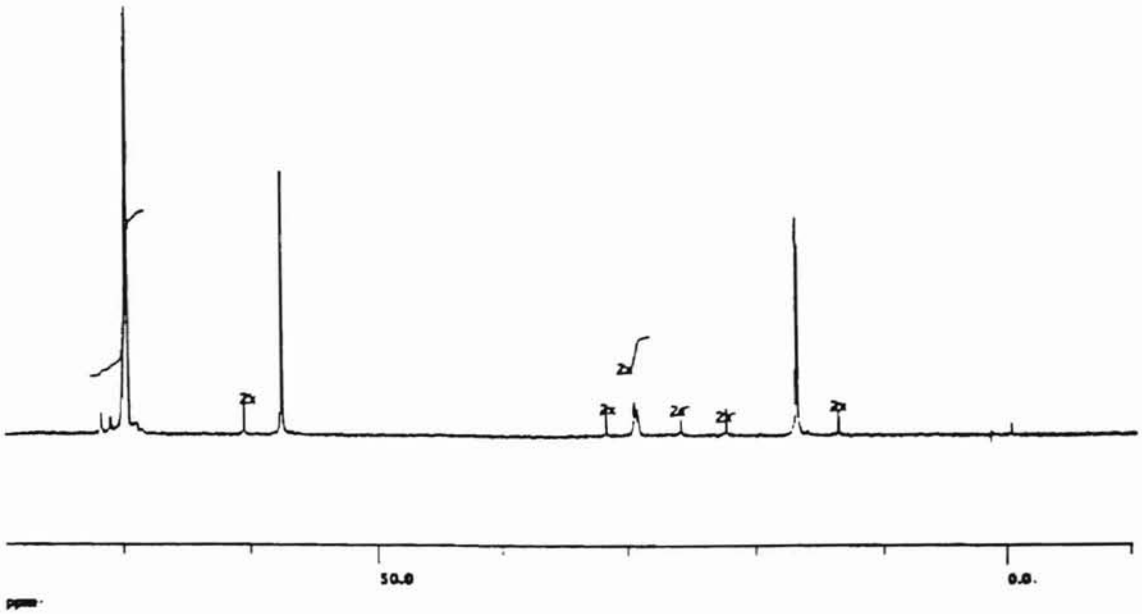
Figure A.22. ^{13}C NMR spectrum of 0 aged Neodol 91-20.

Nucleus	C13
Dwell 1D	50u
SW +/-	10000.0
FILTER	10000
Scans 1D	500
Scan Count	500
Points 1D	8192
Last Delay	5s
Obs Freq	67.9412236
F1 base	67.80 MHz
F1 offset	141.2256 KHz
RCVR gain	40
F2 freq.	270.1719522
F2 base	270.05 MHz
F2 offset	121.9522 KHz
DEC Power	200
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse decpl
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	409.6m
LB 1D	1.00
Phase 0	105.57
Phase 1	-29.00
Filename	GX4126.001
spin rate	17
Traf 1D	0.200
Shift # pts	1
Scans 2D	1
Scans 3D	1
PW08	

#	ppm Start	Stop	Integral
1	72.74	68.21	40.47
2	60.95	59.98	1.16
3	32.49	31.32	0.85
4	31.05	28.39	4.55
5	26.92	25.34	1.10
6	23.50	21.85	1.13
7	14.45	13.48	1.03



GG-37274-42-3W91-20E
9507193
ETOH EXTRACTED

A. MORADI

Figure A.23. ^{13}C NMR spectrum of 3 week aged Neodol 91-20.

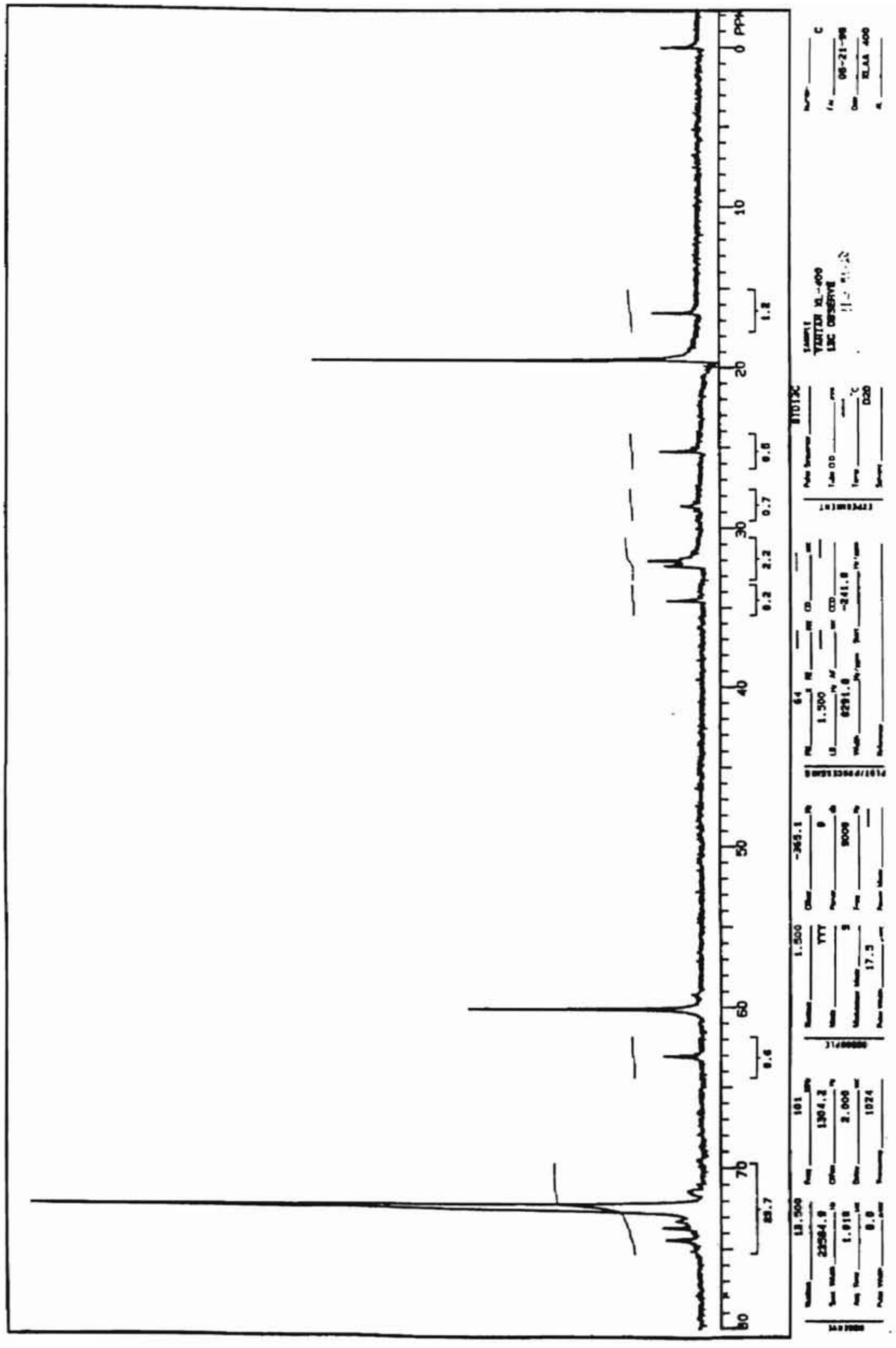
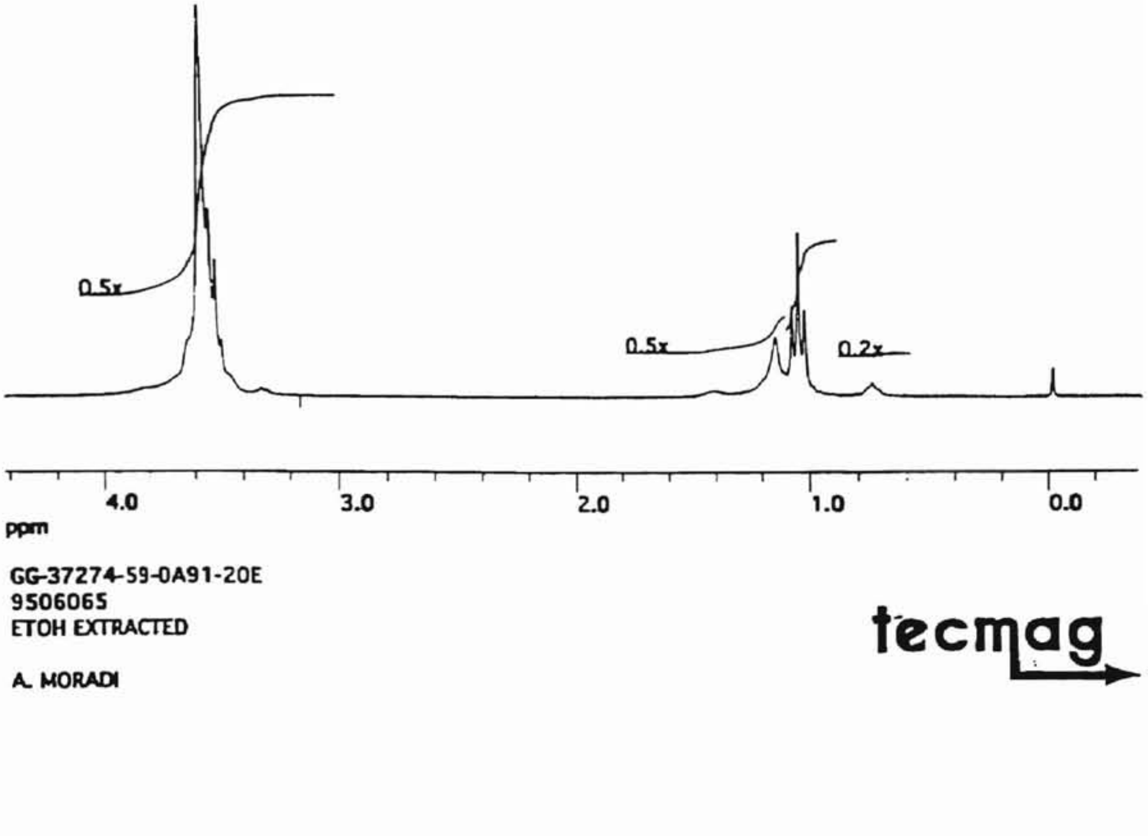


Figure A.24. ^{13}C NMR spectrum of 11 week aged Neodol 91-20.

Nucleus	H1
Dwell 1D	250u
SW +/-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.1719522
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000C
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10

#	ppm Start	Stop	Integral
1	4.10	3.00	100.38
2	1.80	1.11	18.40
4	1.11	0.90	22.32
3	0.90	0.60	3.63



GG-37274-59-0A91-20E
9506065
ETOH EXTRACTED

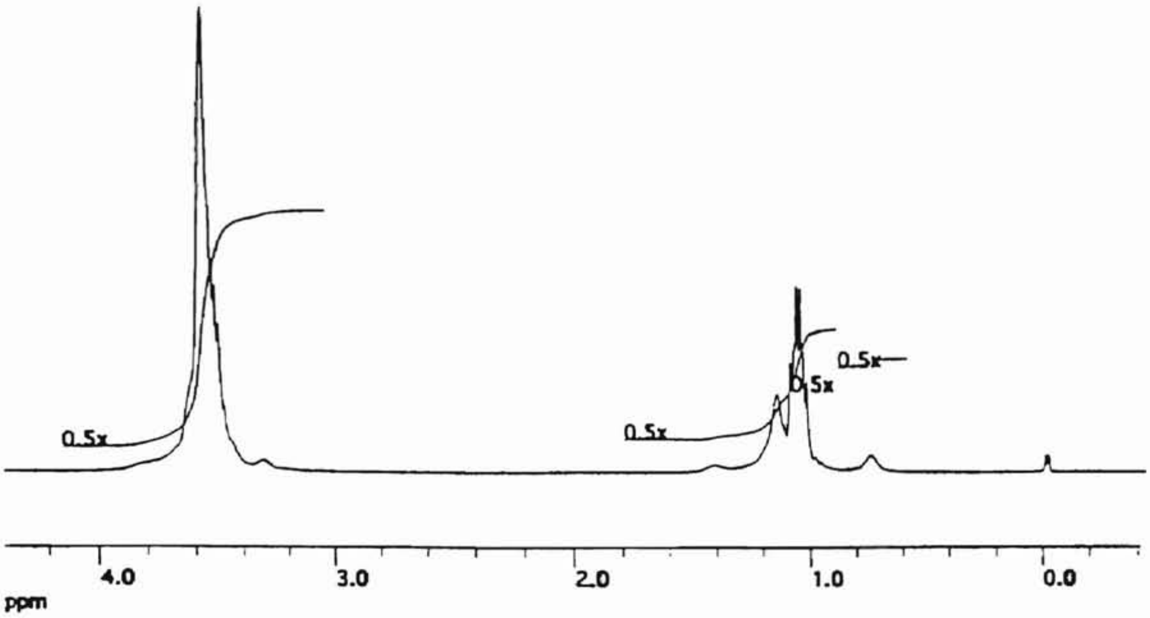
A. MORADI

tecmag

Figure A.25. ^{1}H NMR spectrum of 0 aged Neodol 91-20.

Nucleus	H1
Dwell 1D	250u
SW +/-	2000.0
FILTER	2000
Scans 1D	16
Scan Count	16
Points 1D	16384
Last Delay	6s
Obs Freq	270.171952
F1 base	270.05 MHz
F1 offset	121.9522 KH
RCVR gain	20
F2 freq	270.100000
F2 base	270.05 MHz
F2 offset	50.0000 KHz
DEC Power	0
DEC Scheme	BB
Dummy scan	0
temp K	0.0
Sequence	1 pulse
PW01	
PW02	
PW03	
PW04	
F3 freq	0.0000000
F3 base	0.0000
F3 offset	0.0000000
Field	6.3455200
Acq. Time	4.096s
LB 1D	0.10

#	ppm Start	Stop	Integral
1	4.14	3.04	100.00
2	1.80	1.10	18.78
3	1.10	0.90	26.47
4	0.90	0.60	3.74



GG-37274-62-3W9 -20E
9507193
ETOH EXTRACTED

A. MORADI

tecmag

Figure A.26. ^{1}H NMR spectrum of 3 week aged Neodol 91-20.

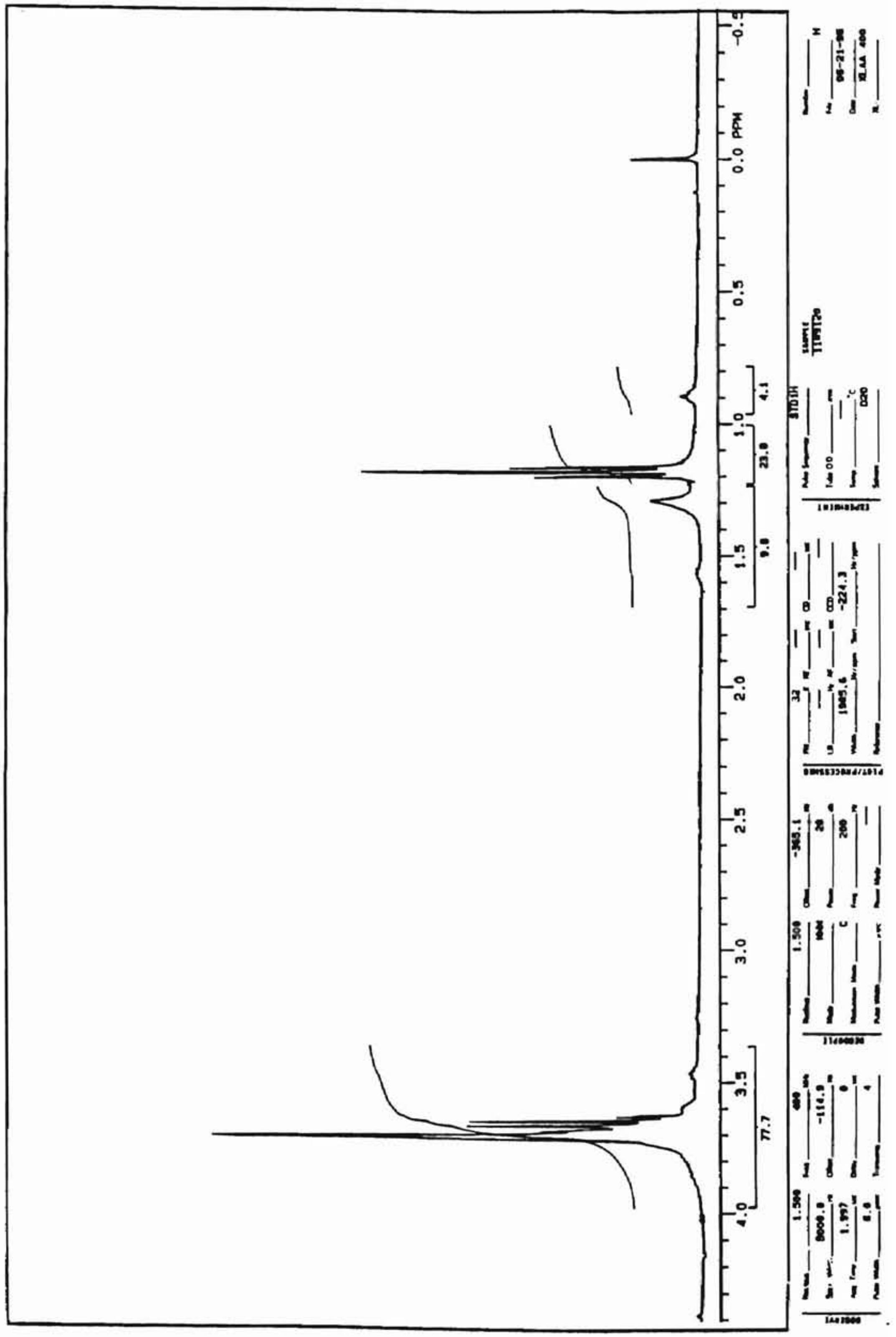
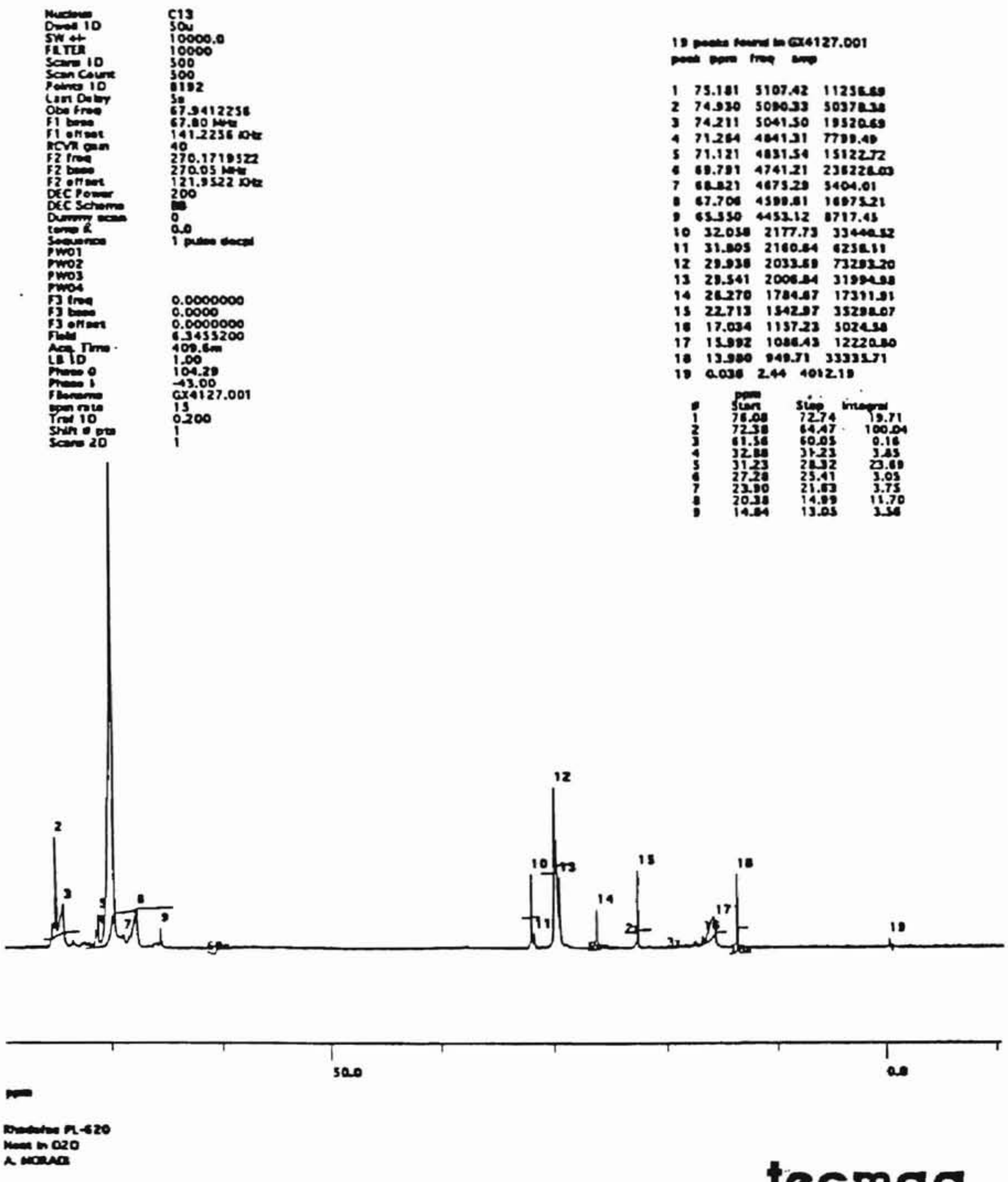


Figure A.27. ^1H NMR spectrum of 11 week aged Neodol 91-20.



```
Nucleus        C13
Dwell 1D       50u
SW +/-         10000.0
FILTER         10000
Scans 1D       500
Scan Count     500
Points 1D      8192
Last Delay     5s
Obs Freq       67.9412256
F1 base        67.80 MHz
F1 offset      141.2256 KHz
RCVR gain      40
F2 freq        270.1719522
F2 base        270.05 MHz
F2 offset      121.9522 KHz
DEC Power      200
DEC Scheme     BB
Dummy scans    0
temp K         0.0
Sequence       1 pulse decpl
PW01
PW02
PW03
PW04
F3 freq        0.0000000
F3 base        0.0000
F3 offset      0.0000000
Field          6.3455200
Acq. Time      409.6m
LB 1D          1.00
Phase 0        104.29
Phase 1        -43.00
Filename       GX4127.001
spin rate      15
Trel 1D        0.200
Shift # pts    1
Scans 2D       1
```

```
19 peaks found in GX4127.001
peak ppm    freq     amp

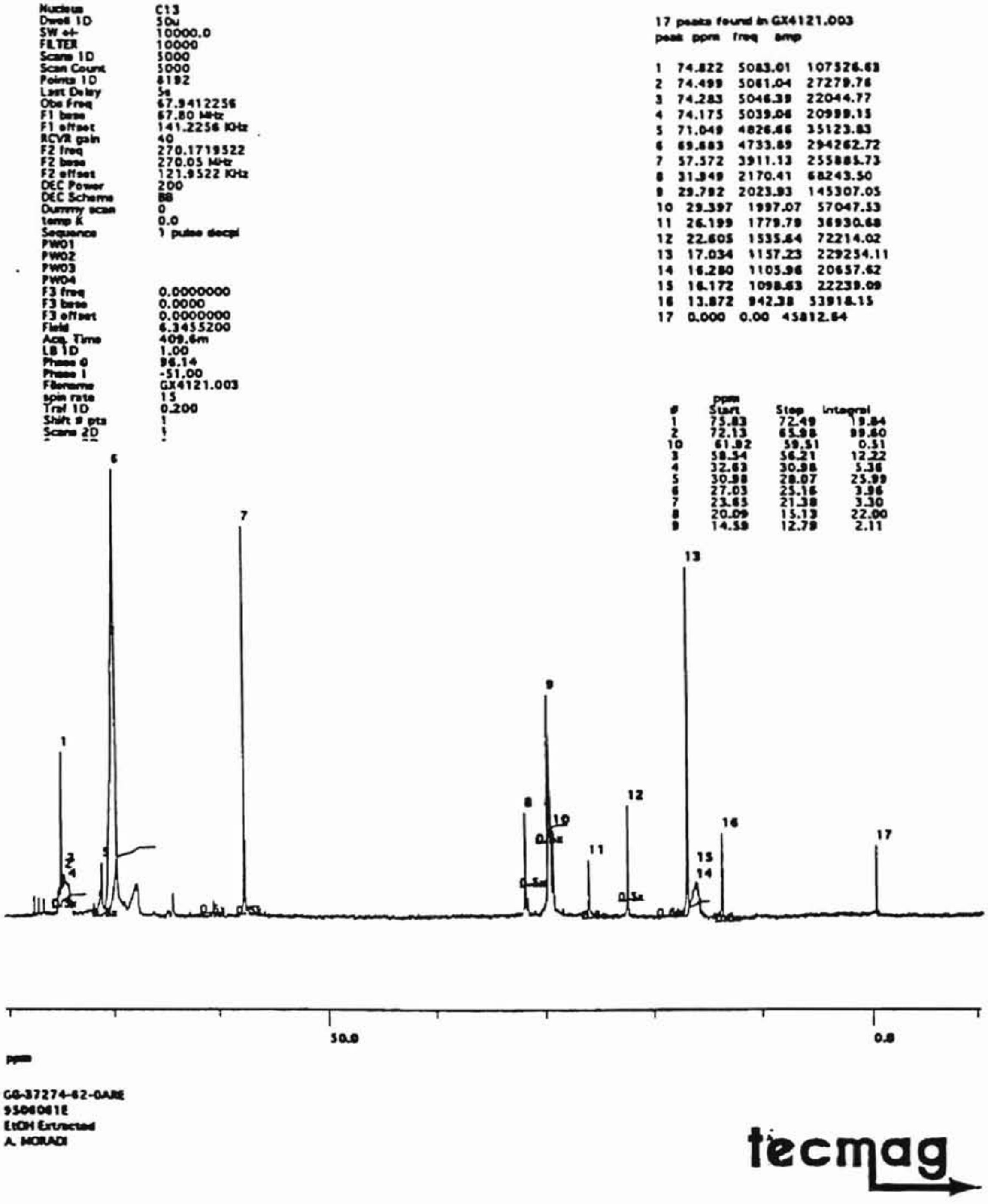
1  75.181   5107.42  11256.89
2  74.930   5090.33  50378.38
3  74.211   5041.50  19520.69
4  71.264   4841.31  7799.49
5  71.121   4831.54  15122.72
6  69.791   4741.21  238226.03
7  68.821   4675.29  5404.01
8  67.706   4599.81  16975.21
9  65.550   4453.12  8717.45
10  32.058  2177.73  33440.52
11  31.805  2160.84  6258.11
12  29.938  2033.69  73293.20
13  29.541  2006.84  31994.98
14  26.270  1784.87  17311.91
15  22.713  1542.97  35298.07
16  17.034  1157.23  5024.58
17  15.992  1086.43  12220.80
18  13.980  949.71   33335.71
19  0.036   2.44     4012.19

      ppm
#     Start    Stop    Integral
1     76.08    72.74    19.71
2     72.38    64.47   100.04
3     61.56    60.05     0.16
4     32.88    31.23     3.85
5     31.23    28.32    23.69
6     27.28    25.41     3.05
7     23.90    21.83     3.75
8     20.38    14.99    11.70
9     14.84    13.05     3.56
```

Rhodafac PL-620
Neat in D2O
A. MORAG

tecmag

Figure A.28. ^{13}C NMR spectrum of Rhodafac PL-620 surfactant.



```
Nucleus        C13
Dwell 1D       50u
SW +/-         10000.0
FILTER         10000
Scans 1D       5000
Scan Count     5000
Points 1D      8192
Last Delay     5s
Obs Freq       67.9412256
F1 base        67.80 MHz
F1 offset      141.2256 KHz
RCVR gain      40
F2 freq        270.1719522
F2 base        270.05 MHz
F2 offset      121.9522 KHz
DEC Power      200
DEC Scheme     BB
Dummy scan     0
temp K         0.0
Sequence       1 pulse decpl
PW01
PW02
PW03
PW04
F3 freq        0.0000000
F3 base        0.0000
F3 offset      0.0000000
Field          6.3455200
Acq. Time      409.6m
LB 1D          1.00
Phase 0        96.14
Phase 1        -51.00
Filename       GX4121.003
spin rate      15
Traf 1D        0.200
Shift # pts    1
Scans 2D       1
```

```
17 peaks found in GX4121.003
peak  ppm   freq   amp

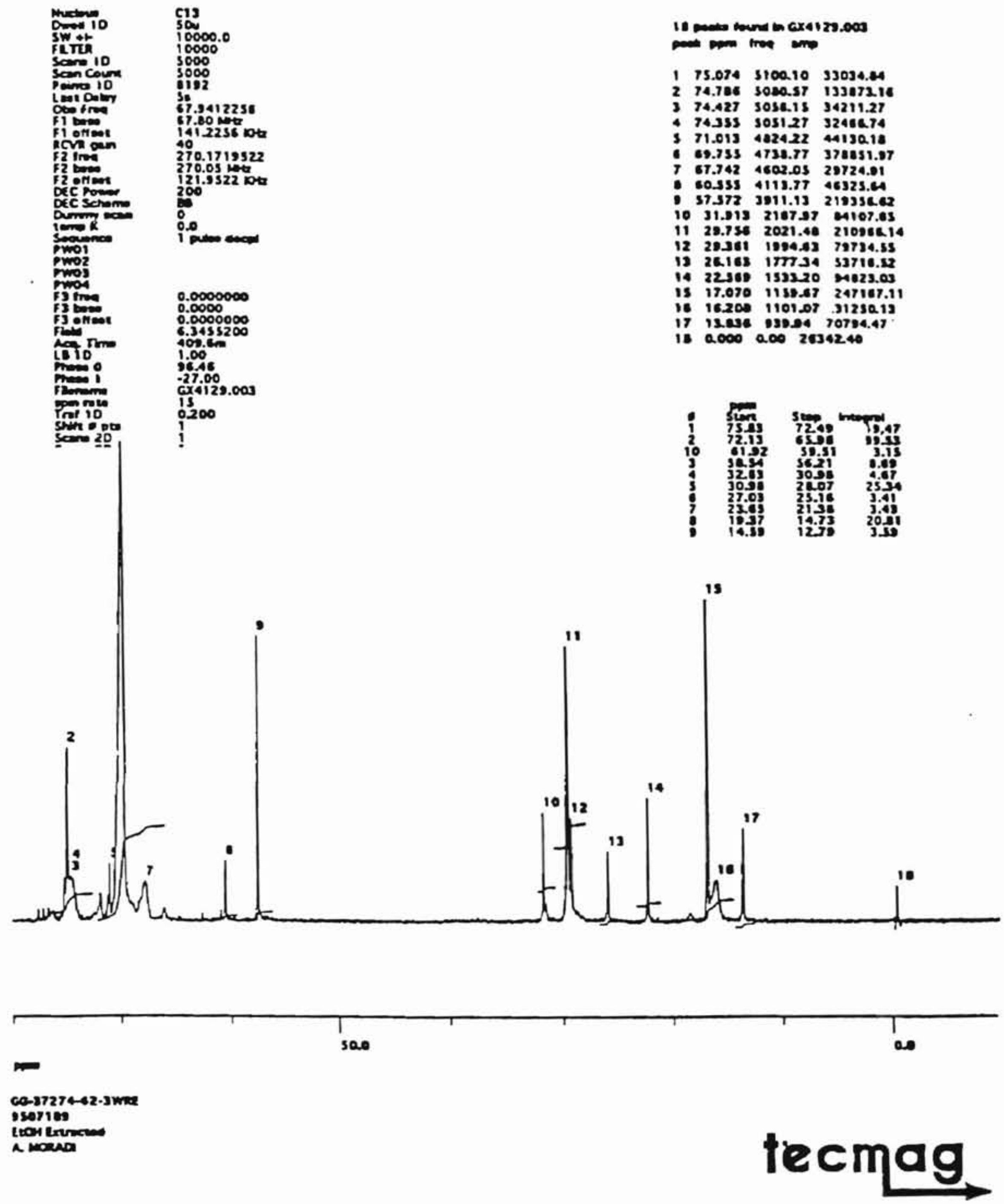
1   74.822  5083.01  107526.63
2   74.499  5061.04  27279.76
3   74.283  5046.39  22044.77
4   74.175  5039.06  20999.15
5   71.049  4826.66  35123.83
6   69.683  4733.89  294262.72
7   57.572  3911.13  255885.73
8   31.949  2170.41  68243.50
9   29.792  2023.93  145307.05
10   29.397  1997.07  57047.53
11   26.199  1779.79  36930.68
12   22.605  1535.64  72214.02
13   17.034  1157.23  229254.11
14   16.280  1105.96  20657.62
15   16.172  1098.63  22239.09
16   13.872  942.38  53918.15
17   0.000  0.00  45812.64
```

```
        ppm
#       Start     Stop    Integral
1       75.83     72.49     19.84
2       72.13     65.98     99.60
10      61.92     59.51      0.51
3       58.54     56.21     12.22
4       32.63     30.98      5.36
5       30.98     28.07     25.99
6       27.03     25.16      3.96
7       23.85     21.38      3.30
8       20.09     15.13     22.00
9       14.58     12.79      2.11
```

GG-37274-62-0ARE
95060061E
EtOH Extracted
A. MORADI

tecmag

Figure A.29. ^{13}C NMR spectrum of 0 aged Rhodafac PL-620.



```
Nucleus          C13
Dwell 1D         50u
SW +/-           10000.0
FILTER           10000
Scans 1D         5000
Scan Count       5000
Points 1D        8192
Last Delay       5s
Obs Freq         67.9412258
F1 base          67.80 MHz
F1 offset        141.2256 KHz
RCVR gain        40
F2 freq          270.1719522
F2 base          270.05 MHz
F2 offset        121.9522 KHz
DEC Power        200
DEC Scheme       BB
Dummy scans      0
Temp K           0.0
Sequence         1 pulse decpl
PWO1
PWO2
PWO3
PWO4
F3 freq          0.0000000
F3 base          0.0000
F3 offset        0.0000000
Field            6.3455200
Acq. Time        409.6m
LB 1D            1.00
Phase 0          96.46
Phase 1          -27.00
Filename         GX4129.003
spin rate        15
Traf 1D          0.200
Shift # pts      1
Scans 2D         1
```

```
18 peaks found in GX4129.003
peak ppm    freq     amp

1  75.074  5100.10  33034.84
2  74.786  5080.57  133873.16
3  74.427  5056.15  34211.27
4  74.355  5051.27  32466.74
5  71.013  4824.22  44130.18
6  69.755  4738.77  378851.97
7  67.742  4602.05  29724.91
8  60.555  4113.77  46325.64
9  57.572  3911.13  219356.62
10  31.913  2167.97  84107.65
11  29.756  2021.48  210966.14
12  29.361  1994.63  79734.55
13  26.163  1777.34  53716.52
14  22.569  1533.20  94823.03
15  17.070  1159.67  247167.11
16  16.208  1101.07  .31250.13
17  13.836  939.94  70794.47
18  0.000  0.00  26342.40
```

```
       ppm
#      Start    Stop    Integral
1      75.83    72.49    19.47
2      72.13    65.98    99.53
10     61.92    59.51     3.15
3      58.54    56.21     8.69
4      32.83    30.98     4.67
5      30.98    28.07    25.34
6      27.03    25.16     3.41
7      23.63    21.38     3.43
8      19.37    14.73    20.81
9      14.59    12.79     3.59
```

GG-37274-62-3WRE
9507189
EtOH Extracted
A. MORADI

Figure A.30. ^{13}C NMR spectrum of 3 week aged Rhodafac PL-620.

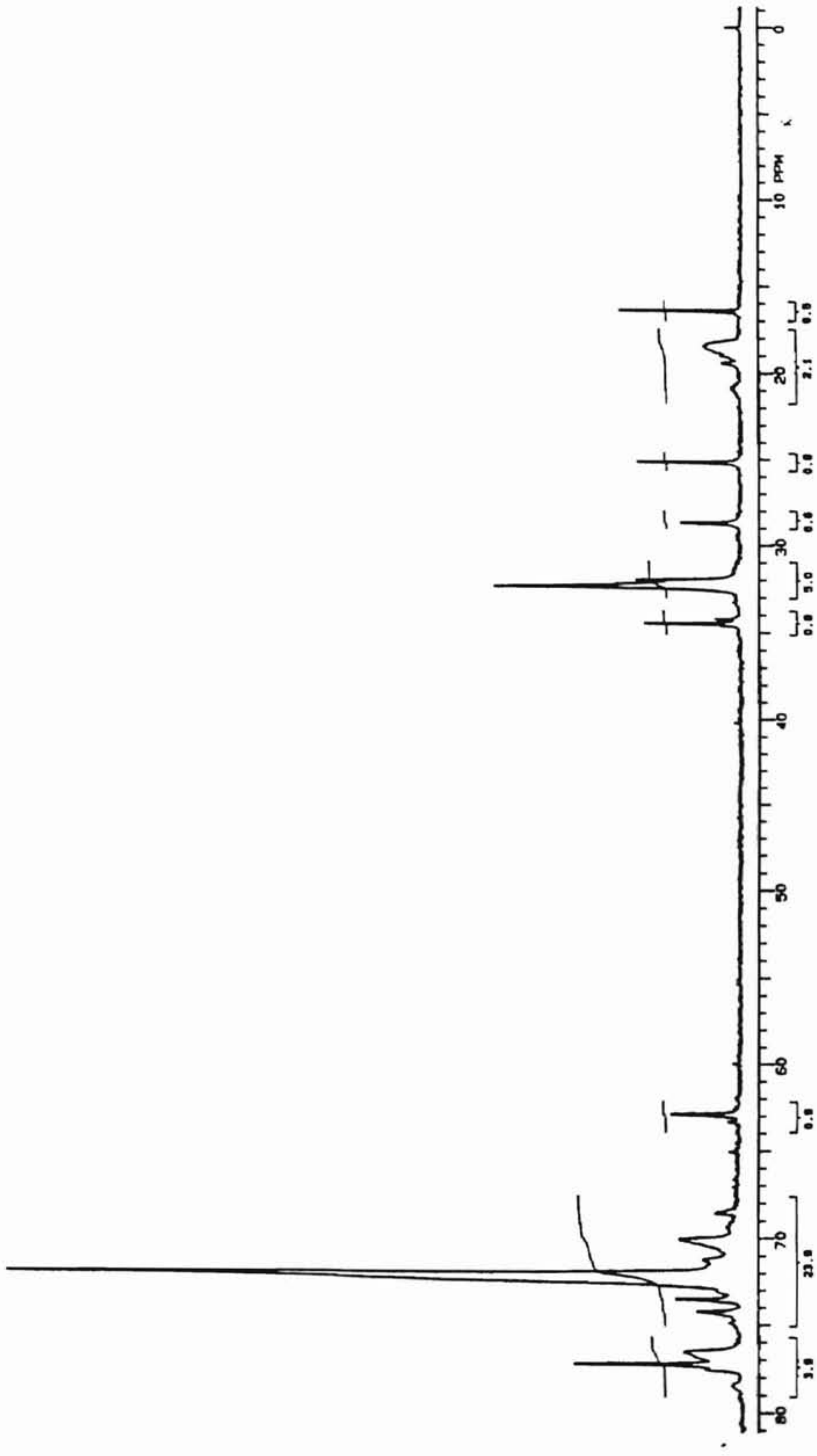
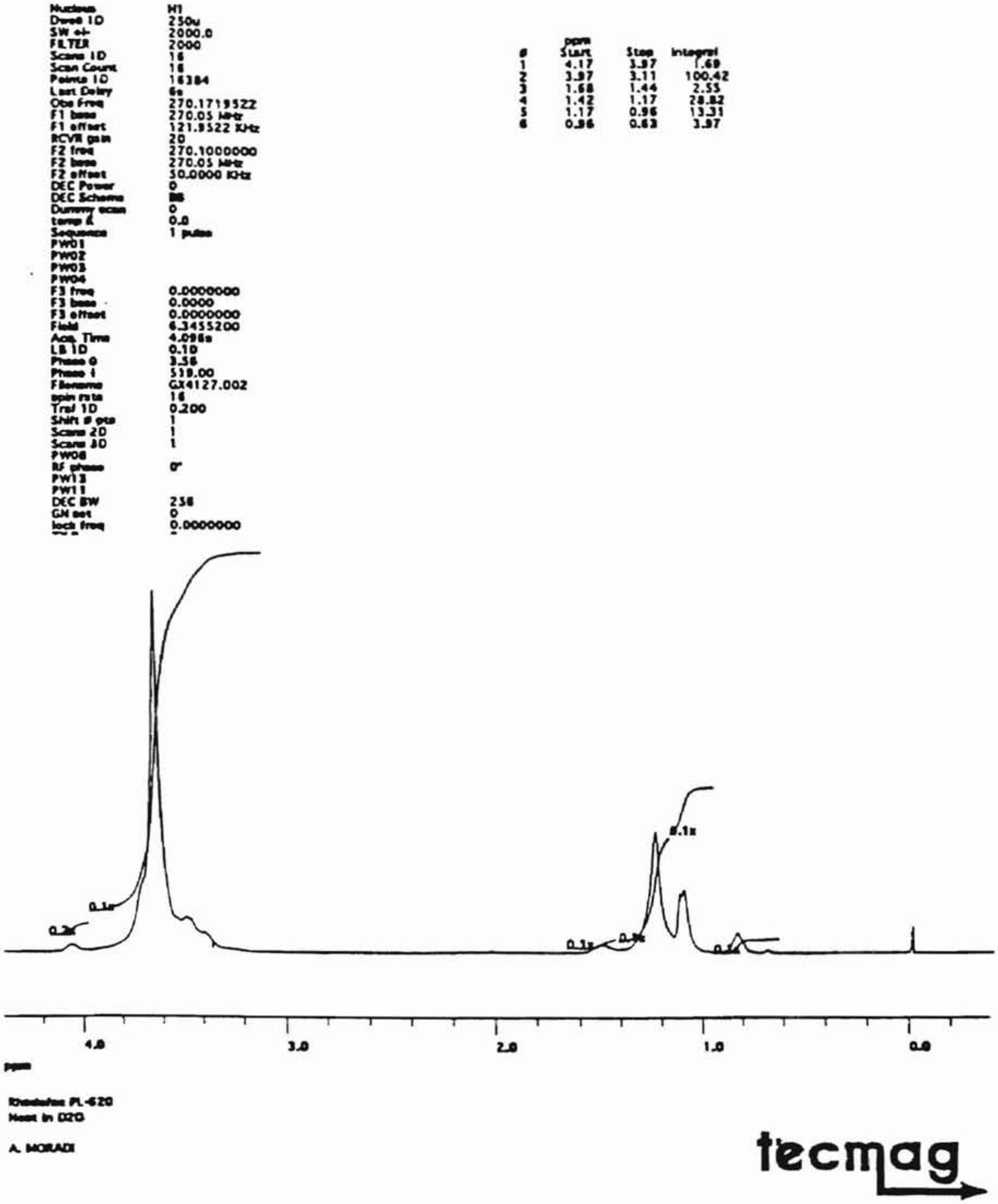


Figure A.31. ^{13}C NMR spectrum of 11 week aged Rhodafac PL-620.



```
Nucleus        H1
Dwell 1D       250u
SW +/-         2000.0
FILTER         2000
Scans 1D       16
Scan Count     16
Points 1D      16384
Last Delay     6s
Obs Freq       270.1719522
F1 base        270.05 MHz
F1 offset      121.9522 KHz
RCVR gain      20
F2 freq        270.1000000
F2 base        270.05 MHz
F2 offset      50.0000 KHz
DEC Power      0
DEC Scheme     BB
Dummy scan     0
temp K         0.0
Sequence       1 pulse
PW01
PW02
PW03
PW04
F3 freq        0.0000000
F3 base        0.0000
F3 offset      0.0000000
Field          6.3455200
Acq. Time      4.096s
LB 1D          0.10
Phase 0        3.56
Phase 1        539.00
Filename       GX4127.002
spin rate      16
Traf 1D        0.200
Shift # pts    1
Scans 2D       1
Scans 3D       1
PW08
RF phase       0°
PW13
PW11
DEC BW         256
GN set         0
lock freq      0.0000000
```

#	ppm Start	Stop	Integral
1	4.17	3.97	1.69
2	3.97	3.11	100.42
3	1.68	1.44	2.55
4	1.42	1.17	28.82
5	1.17	0.96	13.31
6	0.96	0.63	3.97

Rhodafac PL-620
Neat in D2O

A. MORADI

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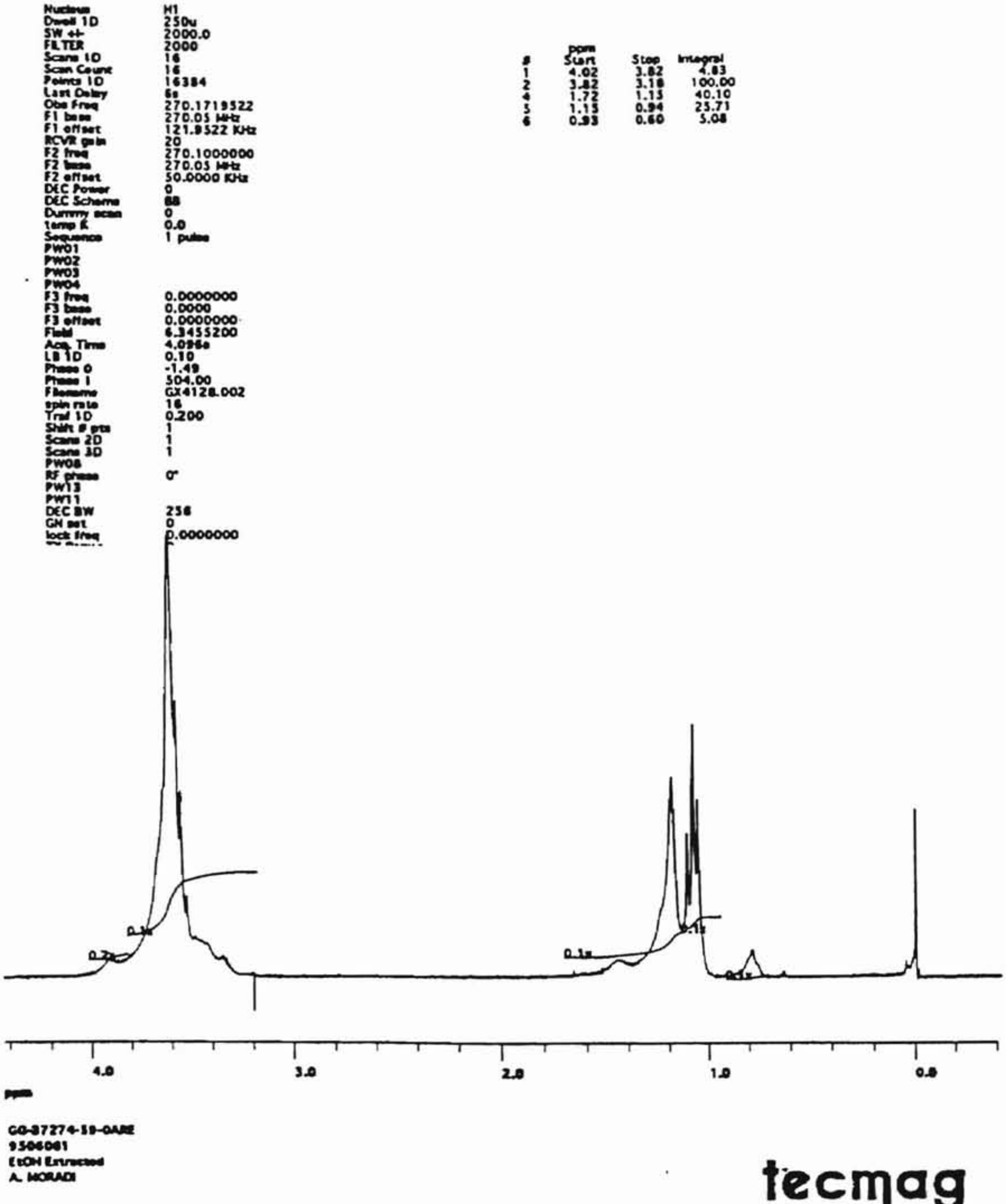
Figure A.32. ¹H NMR spectrum of Rhodafac PL-620 surfactant.

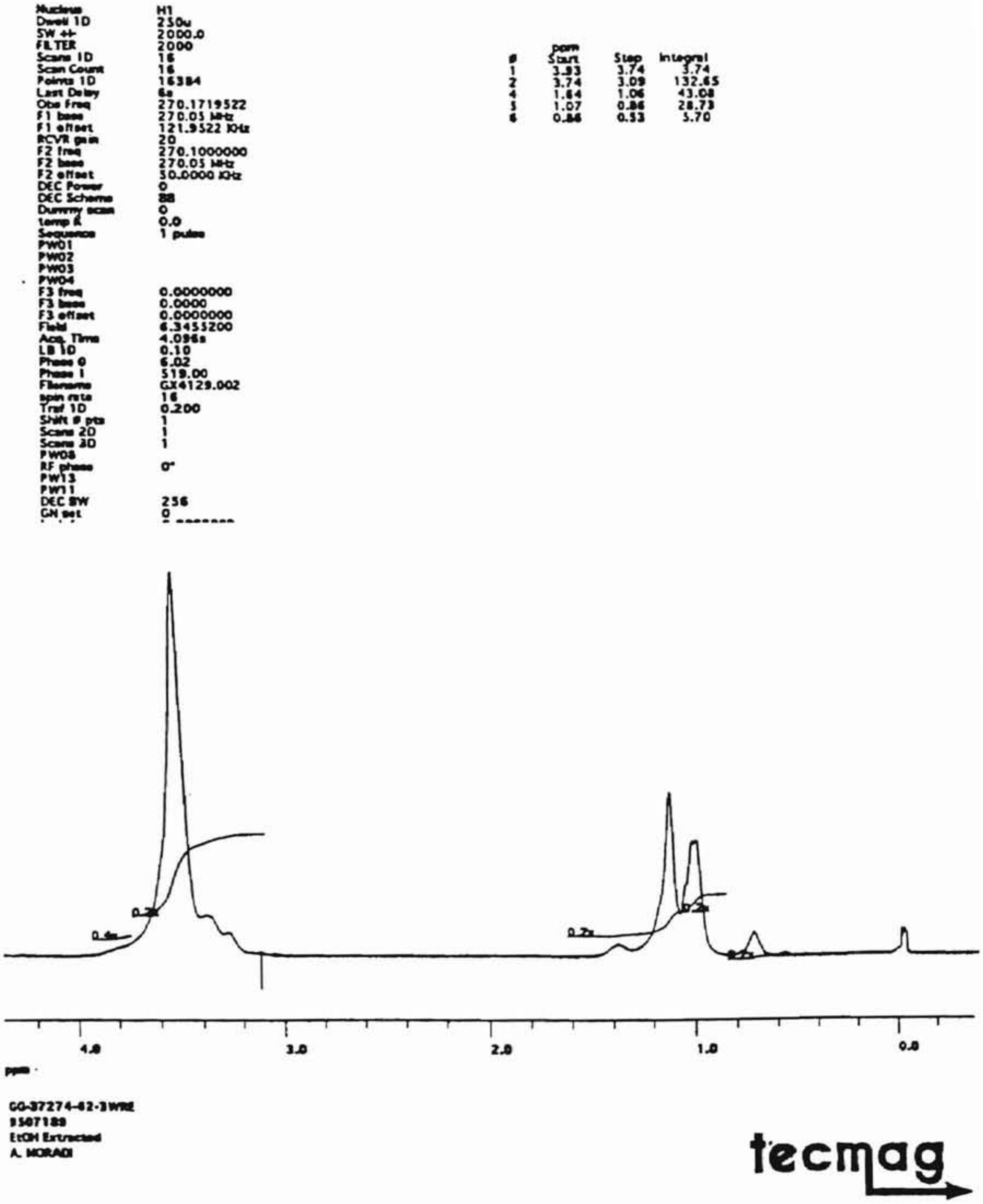


```
Nucleus         H1
Dwell 1D        250u
SW +/-          2000.0
FILTER          2000
Scans 1D        16
Scan Count      16
Points 1D       16384
Last Delay      6s
Obs Freq        270.1719522
F1 base         270.05 MHz
F1 offset       121.9522 KHz
RCVR gain       20
F2 freq         270.1000000
F2 base         270.05 MHz
F2 offset       50.0000 KHz
DEC Power       0
DEC Scheme      BB
Dummy scan      0
temp K          0.0
Sequence        1 pulse
PW01
PW02
PW03
PW04
F3 freq         0.0000000
F3 base         0.0000
F3 offset       0.0000000
Field           6.3455200
Acq. Time       4.096s
LB 1D           0.10
Phase 0         -1.49
Phase 1         504.00
Filename        GX4128.002
spin rate       16
Traf 1D         0.200
Shift # pts     1
Scans 2D        1
Scans 3D        1
PW08
RF phase        0°
PW13
PW11
DEC BW          256
GN set          0
lock freq       0.0000000
```

#	ppm Start	Stop	Integral
1	4.02	3.82	4.83
2	3.82	3.18	100.00
4	1.72	1.15	40.10
5	1.15	0.94	25.71
6	0.93	0.60	5.08

GO-37274-59-OARE
9506061
EtOH Extracted
A. MORADI

Figure A.33. ¹H NMR spectrum of 0 aged Rhodafac PL-620.



```
Nucleus         H1
Dwell 1D        250u
SW +/-          2000.0
FILTER          2000
Scans 1D        16
Scan Count      16
Points 1D       16384
Last Delay      6s
Obs Freq        270.1719522
F1 base         270.05 MHz
F1 offset       121.9522 KHz
RCVR gain       20
F2 freq         270.1000000
F2 base         270.05 MHz
F2 offset       30.0000 KHz
DEC Power       0
DEC Scheme      88
Dummy scans     0
temp K          0.0
Sequence        1 pulse
PWO1
PWO2
PWO3
PWO4
F3 freq         0.0000000
F3 base         0.0000
F3 offset       0.0000000
Field           6.3455200
Acq. Time       4.096s
LB 1D           0.10
Phase 0         6.02
Phase 1         519.00
Filename        GX4129.002
spin rate       16
Traf 1D         0.200
Shift # pts     1
Scans 2D        1
Scans 3D        1
PWO8
RF phase        0°
PW13
PW11
DEC BW          256
GN set          0
```

```
        ppm
#       Start     Stop     Integral
1       3.93      3.74       3.74
2       3.74      3.09     132.65
4       1.64      1.06      43.08
5       1.07      0.86      28.73
6       0.86      0.53       5.70
```

GG-37274-62-3WRE
9507189
EtOH Extracted
A. MORADI

tecmag

Figure A.34. ^{1}H NMR spectrum of 3 week aged Rhodafac PL-620.

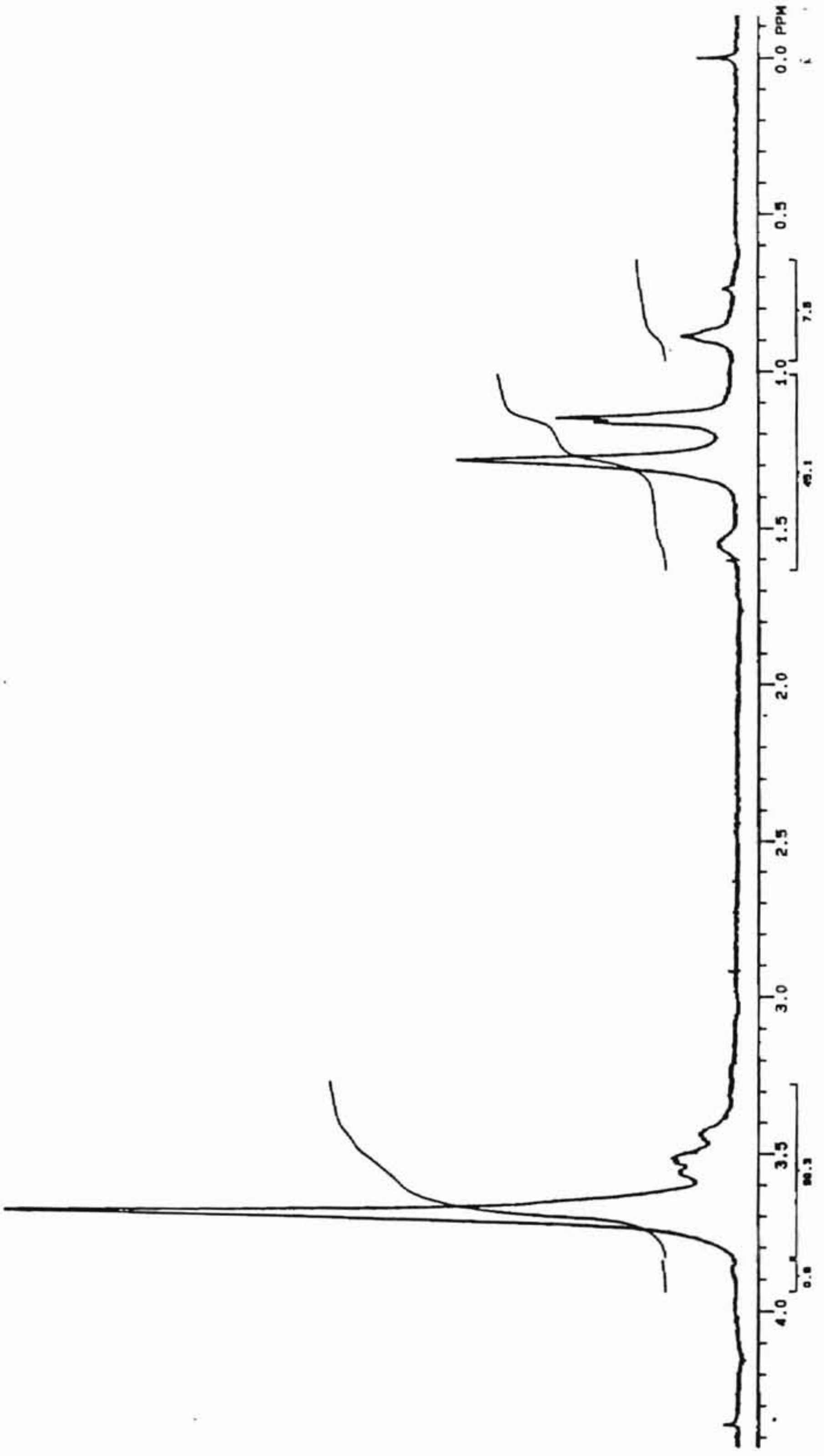


Figure A.35. ^1H NMR spectrum of 11 week aged Rhodafac PL-620.

APPENDIX B

SUPERCRITICAL FLUID CHROMATOGRAPHY

APPENDIX B

SUPERCRITICAL FLUID CHROMATOGRAPHY

Most commercial surfactants available for projects on the scale of enhanced oil recovery, are blends of similar surfactants differing in such things as tail length, R, and in some cases such as the Neodol series, the number of repeat units in the head group, n, where tail refers to the non polar end of the surfactant and head to the polar end.

Any technique capable of separating the components of the mixture and identifying them separately, such as a GC mass spectrometer, would therefore be of great benefit in identifying the decomposition products in these mixtures. The GC MS itself would provide useful results, but at great cost. Unfortunately the salts that were necessarily a part of the aging process of our surfactants would destroy the chromatography coil of the instrument by evaporative deposition of the nonvolatile salts.

It was decided that any analytical method capable of showing changes in the average R and n value would be helpful in the identification of structural change in a surfactant blend. The simplest method available for identifying relative amounts of the components of a mixture is the gas chromatograph, but this technique has already been ruled out. This discussion illustrates why a simple technique for indicating surfactant stability, such as cloud point change, would be useful.

Supercritical fluid chromatography was chosen as one technique available to us with the potential of showing changes in the surfactant blend.

B.1 Supercritical Fluid Chromatography

B.1.a Introduction

Supercritical fluid chromatography was performed on two of the surfactants used in the study, Neodol 45-20 and Neodol 45-7. This method has the capability to separate the surfactant blends into structurally pure samples and indicate the relative amount of each. Any changes in the blend of surfactants with aging would be immediately apparent by comparisons of the shapes of the chromatograms.

B.1.b Experimental Methods and Procedures

The instrument used was a SuperX SFC, with a flame ionization detector. The column was a Deltabrand CN column 10cm x 1mm, with CO_2 used as the carrier. Temperature was constant at 125 °C, pressure was held at 100 bar for 5 minutes followed by linear increase to 450 bar over 20 minutes and then held constant for an additional 10 minutes

B.1.c Discussion of Results

Although the SFC did provide good chromatograms of the surfactant mixtures, and we believed would be useful in indicating any change in surfactant structure either by average value of n and R, or by change in the shape of the chromatograms, the instrument was heavily backlogged, and therefore became unavailable for further use by this project. Chromatograms of two of the unaged Neodols, Neodol 45-7 and Neodol 45-20 are shown in figures B.1 and B.2 respectively. The two chromatograms are useful in illustrating the broad range

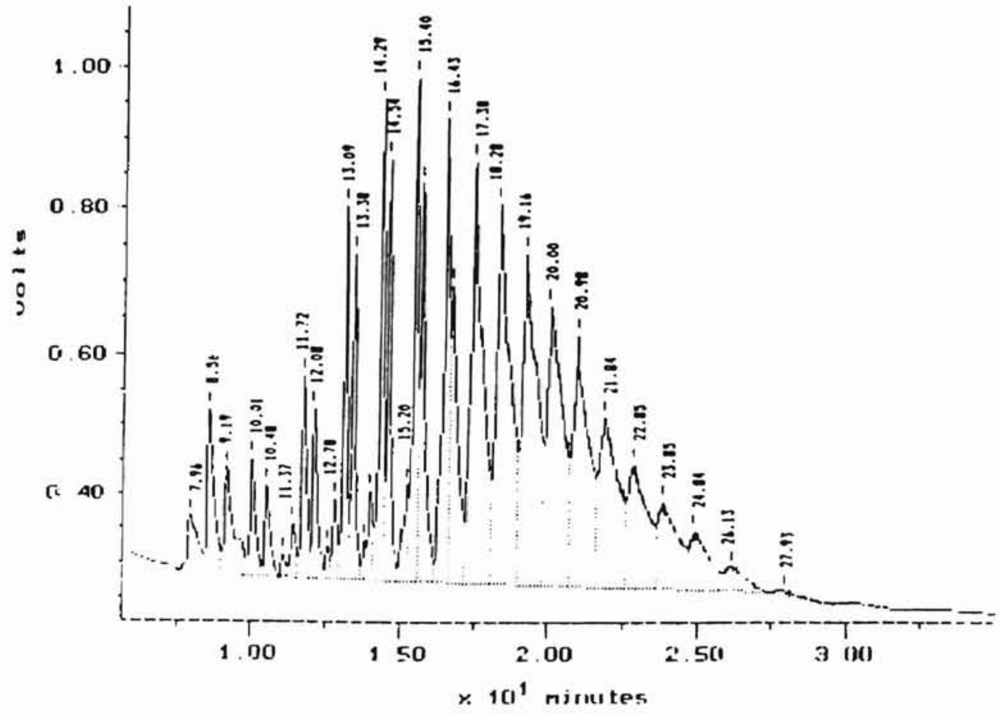


Figure B.1. Chromatogram of Neodol 45-7 by supercritical fluid chromatography.

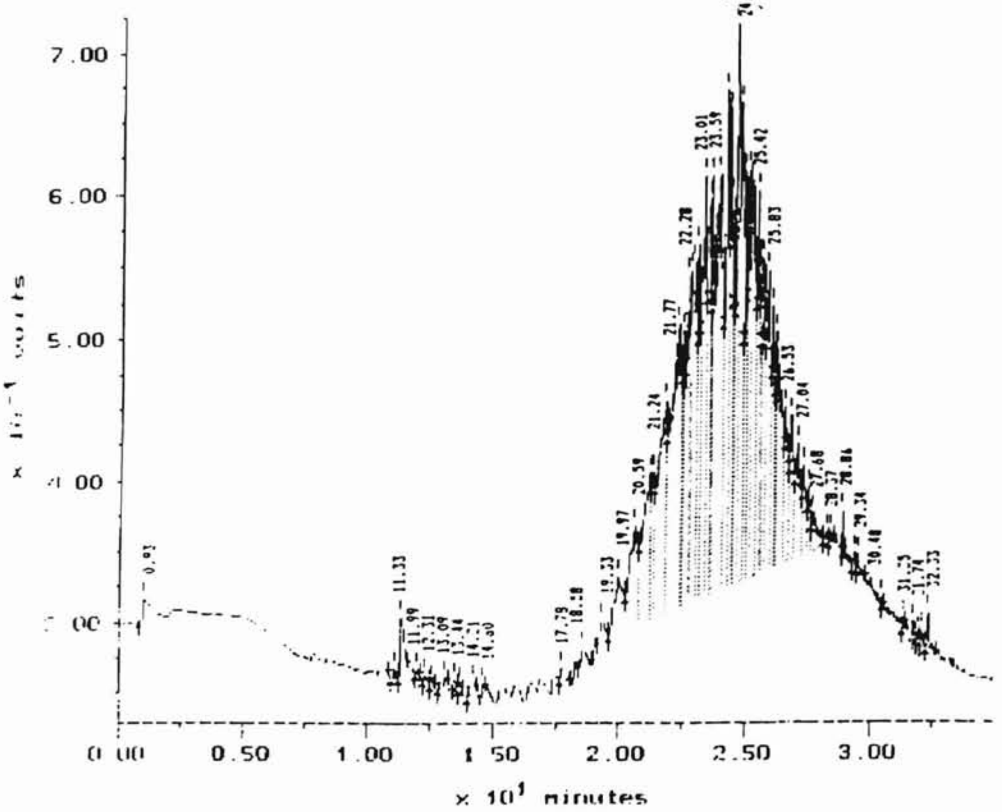


Figure B.2. Chromatogram of Neodol 45-20 by supercritical fluid chromatography.

of combinations of R and n in these commercial surfactants, and are therefore included here for reference.

Many difficulties exist in the characterization of the aging process of a particular surfactant, two of these are especially evident from this section. Foremost are the ruinous effects the sea salts had on any attempt at structural characterization by gas chromatography methods, infrared absorption, and nuclear magnetic resonance. Secondly were the difficulties associated with identifying structural changes in industrial surfactant blends. These blends (see Figure 4.1 or 4.2 for example) are composed of many similar structures which would have the ability to mask many possible decomposition products.

Although some success was made in detecting decomposition products, the success of these methods were limited in part because of the aforementioned reasons.

VITA

James B. Greuel

Candidate for the Degree of

Master of Science

Thesis: COMPARISON OF CLOUD POINT CHANGES AND SURFACTANT DECOMPOSITION UNDER CONDITIONS OF THE EKOFISK RESERVOIR

Major Field: Chemistry

Biographical:

Personal Data: Born in Wagoner, Oklahoma, On January 9, 1970, the son of Paul Greuel and Tom and Joyce Bays.

Education: Graduated from Wagoner High School, Wagoner, Oklahoma in May 1988; received Bachelor of Science in Chemistry, with minors in Mathematics and Engineering Physics from Northeastern State University, Tahlequah, Oklahoma in May 1992. Completed the requirements for the Master of Science degree in Inorganic Chemistry at Oklahoma State University in July, 1998.

Experience: Employed by Oklahoma State University, Department of Chemistry as a graduate research assistant August 1992 to August 1994; participated in collaborative research between OSU, the U.S. Department of Energy, and Phillips petroleum, October 1994 to August 1995; employed as a graduate teaching assistant at OSU August 1995 to May 1998.