Abstract

The low-temperature performance characteristics of a motor oil is highly dependent on the extent, and type, of microcrystallite formation in the paraffinic components of the product. We have utilized solid-state ^{2}H NMR to observe the formation of crystallites in various base oils by observing the behavior of 1 wt% of a perdeuterated probe molecule blended into a number of different classes of base oil. Different cooling cycles were utilized, one involving a fairly rapid cycle (+20 to -35^{o}C in 15 minutes) while the other mimicked the cooling cycle used in an ASTM mini-rotary viscometer (MRV) base oil performance test (+80 to -35^{o}C in 51 hours). The effects of these different cooling cycles on the amount, and type (whether orthorhombic or hexagonal crystal-packing), of crystalline domain will be presented, along with the solid/liquid, and mobility profiles that can be obtained from the data for the different base oils. Finally, the effect of addition of pour-point depressant additives will be discussed.

Background

During the course of lubricant property testing in the formulation of both diesel and gasoline lubricants certain base oil stocks have become associated with poor low temperature pumpability due to the formation of wax crystallization gels. Specific tests have been developed to identify these poor low temperature properties (mini-rotary viscometer (MRV)) which manifest themselves as large increases in viscosity and shear stress (the motivating force per unit area for fluid flow). The MRV test will be described later.

Two contrasting oils have been obtained:-

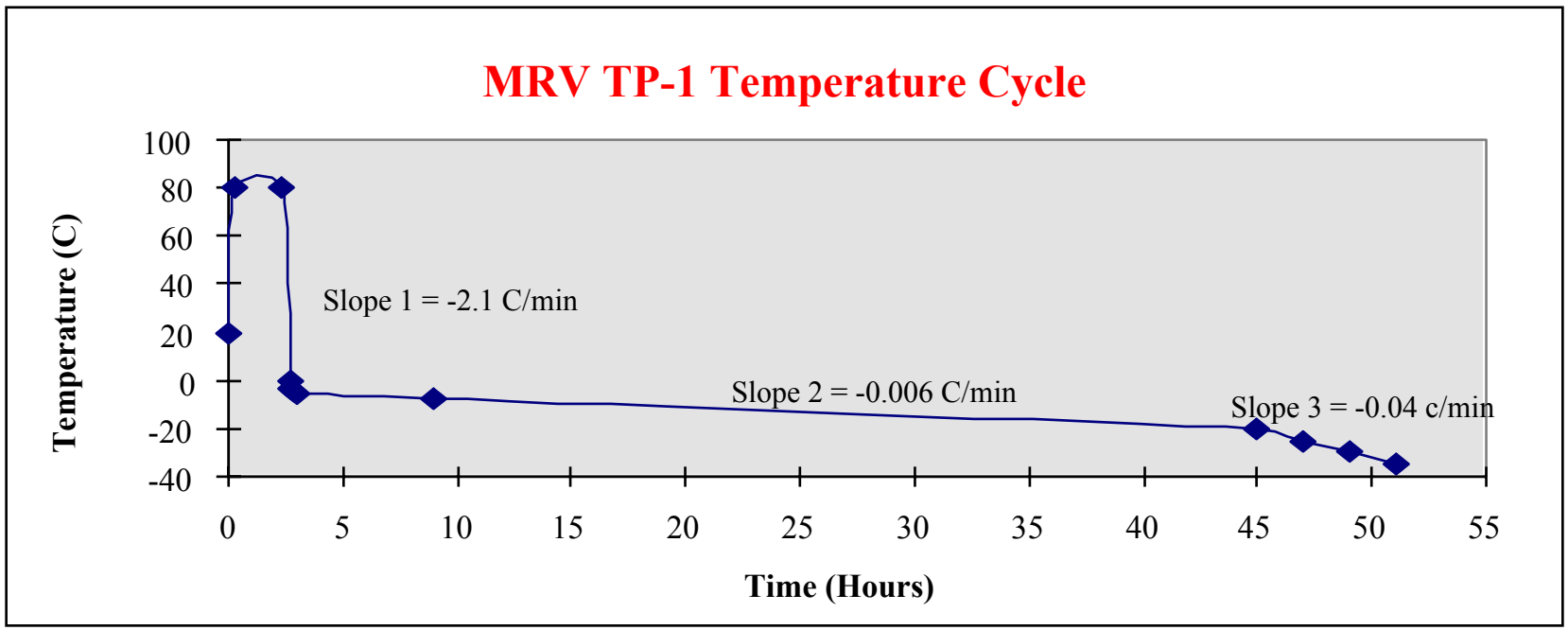
Oil A : readily passes the MRV test with an acceptable viscosity increase (< 30,000 cP), and no measurable shear stress.

Oil B : fails the MRV test due to large viscosity increase (>400,000 cP) and a large shear stress increase (300-500 Pa).

The reasons for the differences in low temperature crystallization behavior are not readily understandable from the basic physical and chemical tests which are performed on the base oils. Thus, a study has been undertaken to attempt to identify differences between the oils that might explain this behavior.

Mini-Rotary Viscometer (MRV) Test [ASTM D4684]

This test method covers the measurement of the yield stress and viscosity of engine oils after cooling at controlled rates over a period exceeding 45 hours. This extended cooling period enhances the formation of wax gel networks in certain oils yielding high yield stress and viscosity measurements at the final measuring temperature (-35°C). This test is used to predict the failure of engine oils in the field due to loss of oil pumpability. The following is the temperature profile performed during the test.

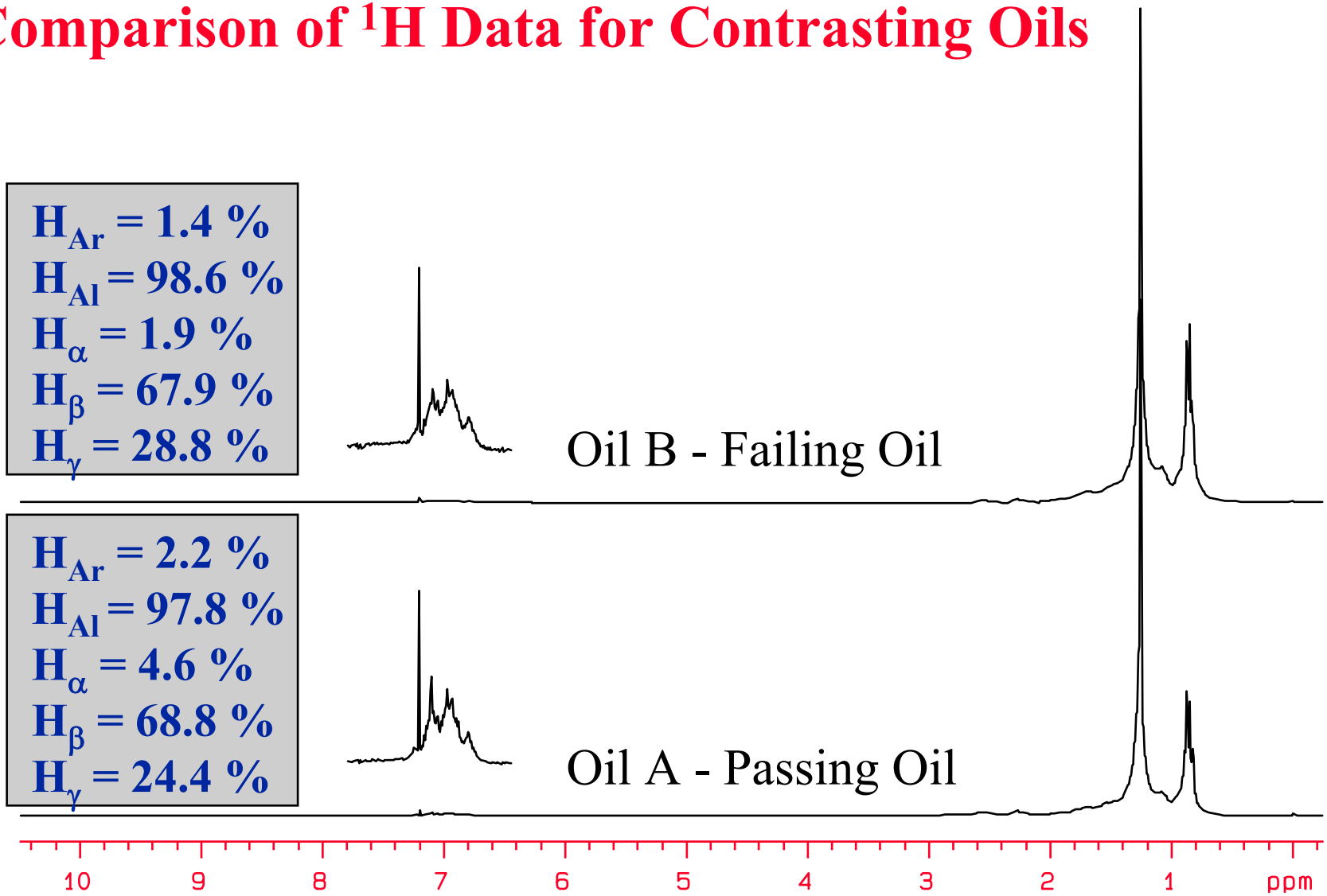


Physical and Chemical Properties of Contrasting Oils

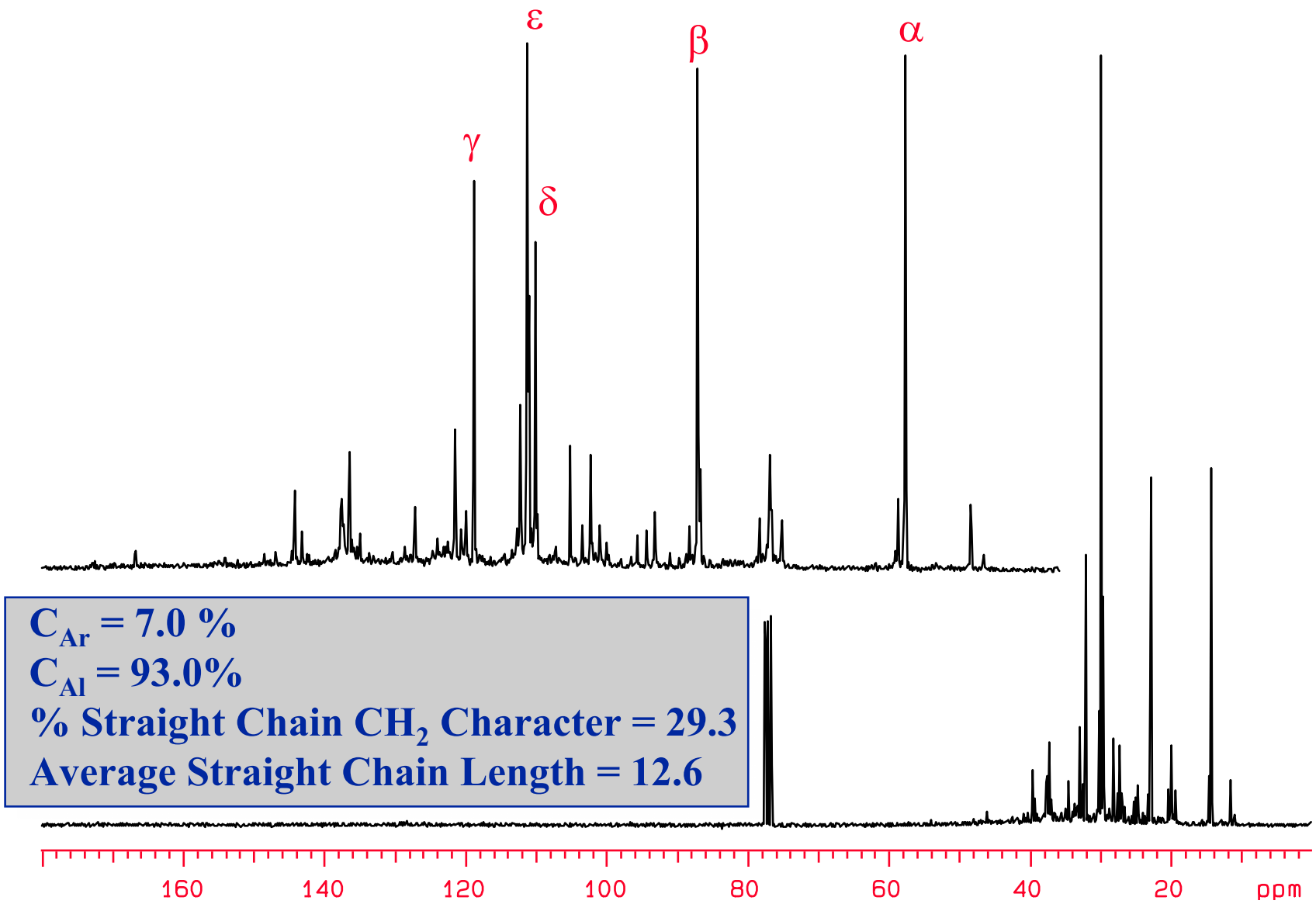
	Oil A	Oil B
API Gravity	32.16	32.7
Flash COC, F	395	505
Kin Vis 40C	19.87	22.67
Kin Vis 100C	4.05	4.34
VI	101	96
Pour Point, C	-15	-18
Color, ASTM	< 1.0	< 0.5
CCS Vis -20C	780	1080
CCS Vis -25C	1520	2140
Noack, %Loss	30.8	27.5
Sim Dist	16.98	6.2
Aniline Point,F	206.3	215.2
Nitrogen, %	0.004	0.007
Sulfur, %	0.334	0.336
PNA, %	0.62	0.4
Saturates, %	73.4	83.9
Aromatics, %	26.6	16.1

The properties of the oils are quite similar except for differences in aromatic content and viscosity index. In order to further characterize the oils ^{1}H and ^{13}C NMR was performed (Spectra shown). Oil B contains higher methyl character and contains a higher concentration of isoprenoid type molecules all of which is counter-intuitive to the sample having poorer low temperature performance properties than Oil A. The aromatic content difference may be significant. Analysis of the normal paraffin (wax) content of the two samples did not yield statistically significant differences.

Comparison of ^{1}H Data for Contrasting Oils

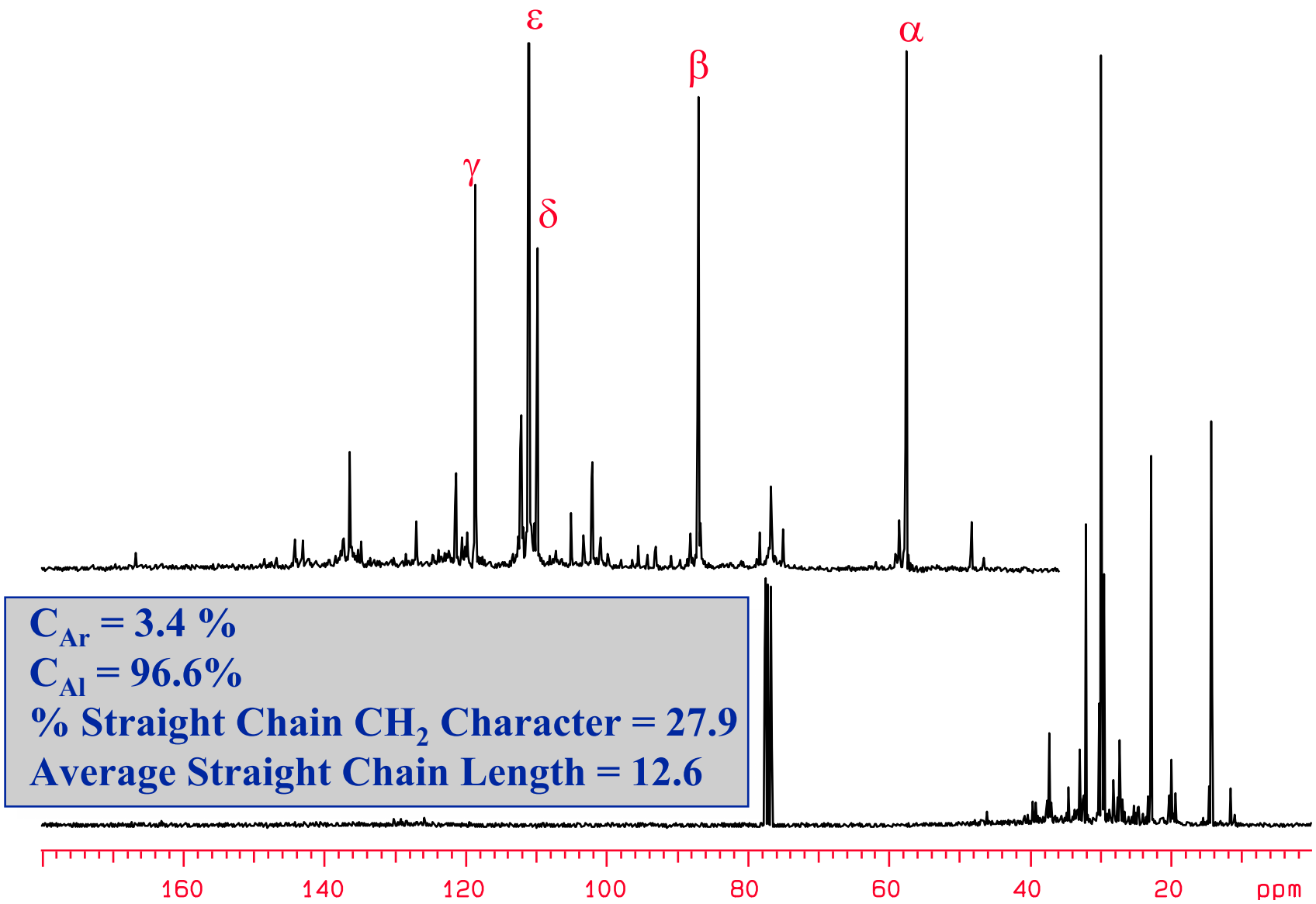


^{13}C NMR of Oil B - MRV Test Passing Oil



C_{Ar} = 7.0 %
C_{Al} = 93.0%
% Straight Chain CH_2 Character = 29.3
Average Straight Chain Length = 12.6

^{13}C NMR of Oil A - MRV Test Failing Oil



C_{Ar} = 3.4 %
C_{Al} = 96.6%
% Straight Chain CH_2 Character = 27.9
Average Straight Chain Length = 12.6

Solid-State ^2H NMR Studies of Low Temperature Crystallinity Problems Utilizing a Perdeuterated Probe Molecule

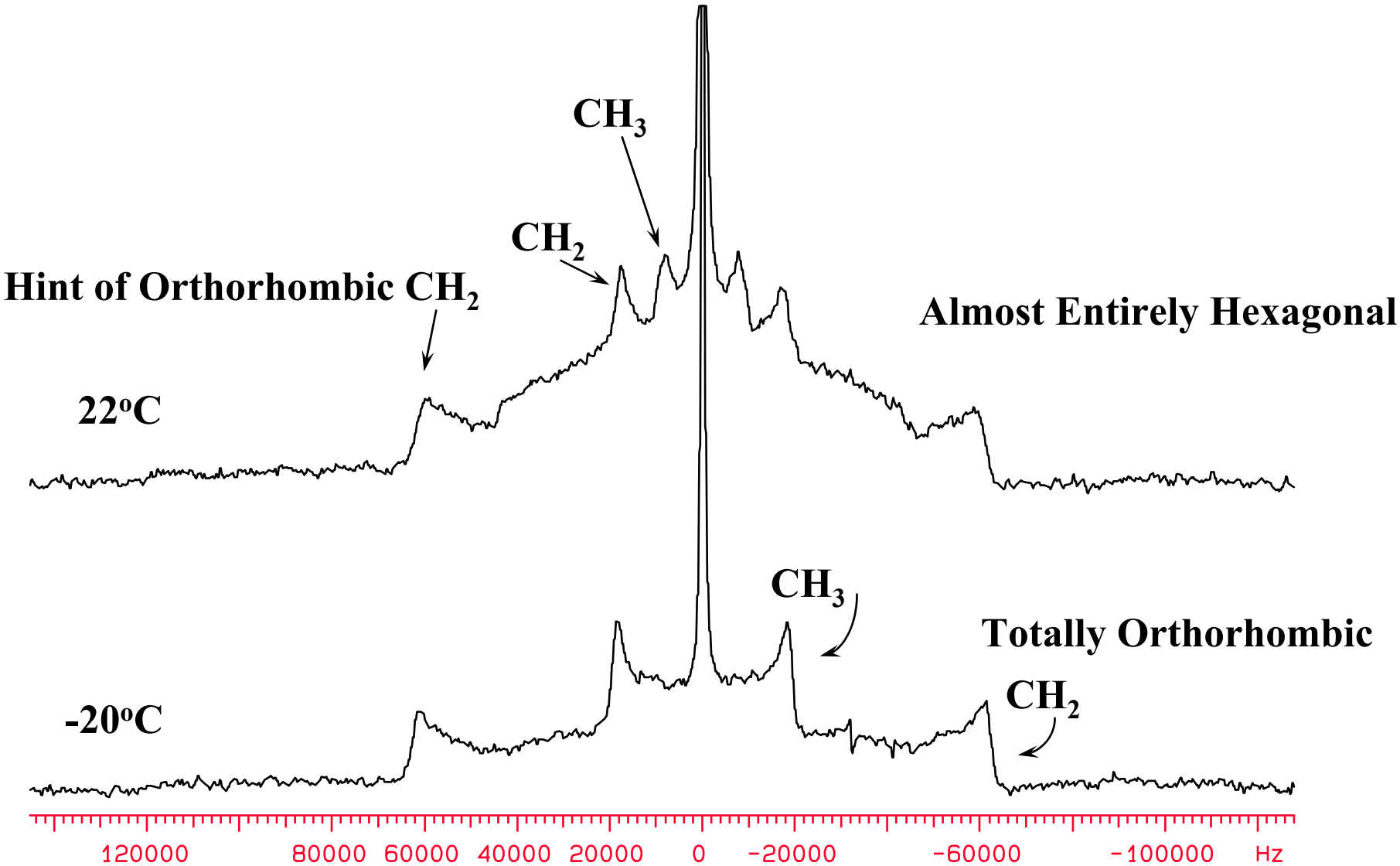
As the wide array of physical and chemical testing did not identify the differences that might explain the low temperature differences in the base oils a crystallinity investigation utilizing a perdeuterated n-paraffin molecule ($C_{19}D_{40}$) was undertaken. The nonadecane-d40 molecule has been studied in the past (1) and revealed an interesting difference in the crystal structures that were formed at low (< 22°C) and high temperatures (>22 and < 32°C). The low temperature form which has an orthorhombic unit cell consists of layers of molecules oriented in the trans conformation. The high temperature crystal structure is called 'hexagonal' and consists of less tightly packed layers in which hindered rotation of the alkane backbone can occur. This hexagonal phase may be associated with the wax gel networks associated with low temperature pumpability problems in base oils.

Experimental

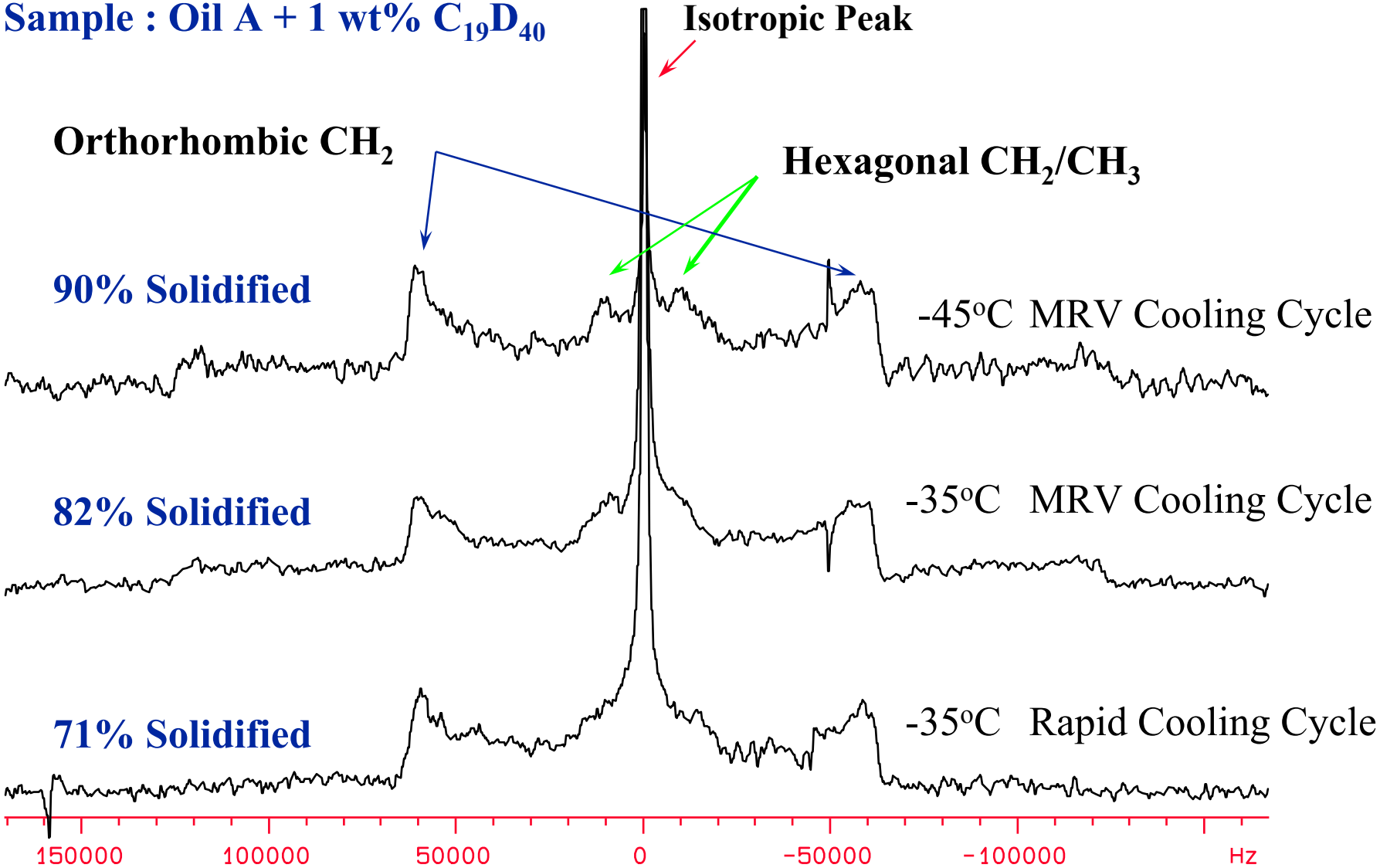
^2H NMR experiments were performed on a Unity-300 spectrometer equipped with high power solids amplifiers operating at 46.04 MHz. The probe was a Varian wideline probe operating with a spin echo sequence, a 1.5 μs π/2 pulse, a 10 s relaxation delay, a 0.75 MHz spectral width, and a 80 μs echo delay. Line broadening of 500 Hz was used. An extended VT dewar was used to maintain low temperature operation for 51 hours. The MRV test cooling cycle was followed as closely as possible acquiring spectra during pauses at descending temperature plateaus. A rapid cooling cycle was also applied which comprised of rapid cooling from 30°C to -35°C in a 15 minute period.

1. M.G. Taylor et al., J. Chem. Phys. 78(8), 5108 (1983).

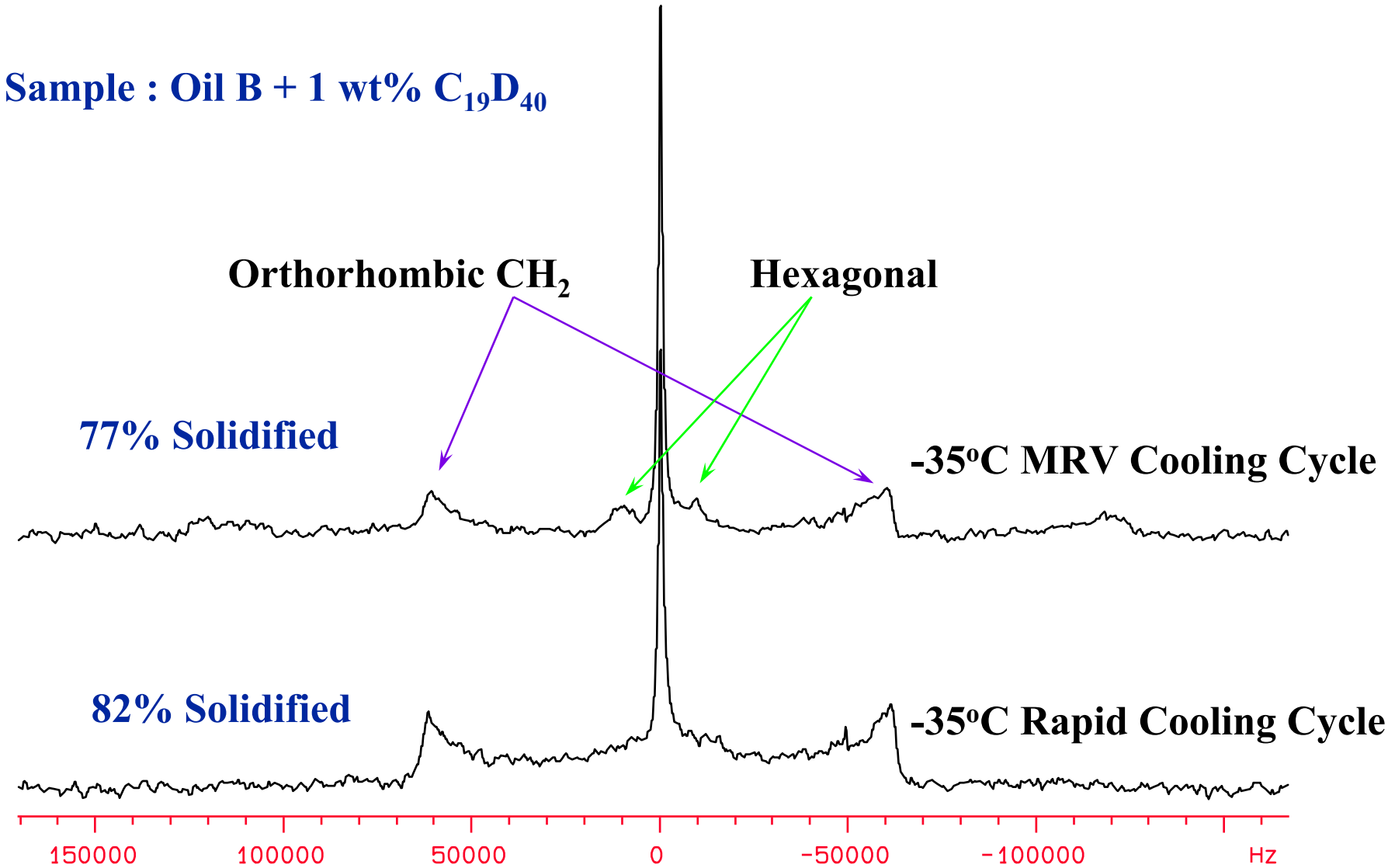
^2H Lineshape Behavior of Pure n-$C_{19}D_{40}$



^{2}H Lineshape of Oil A Under Different Cooling Cycles



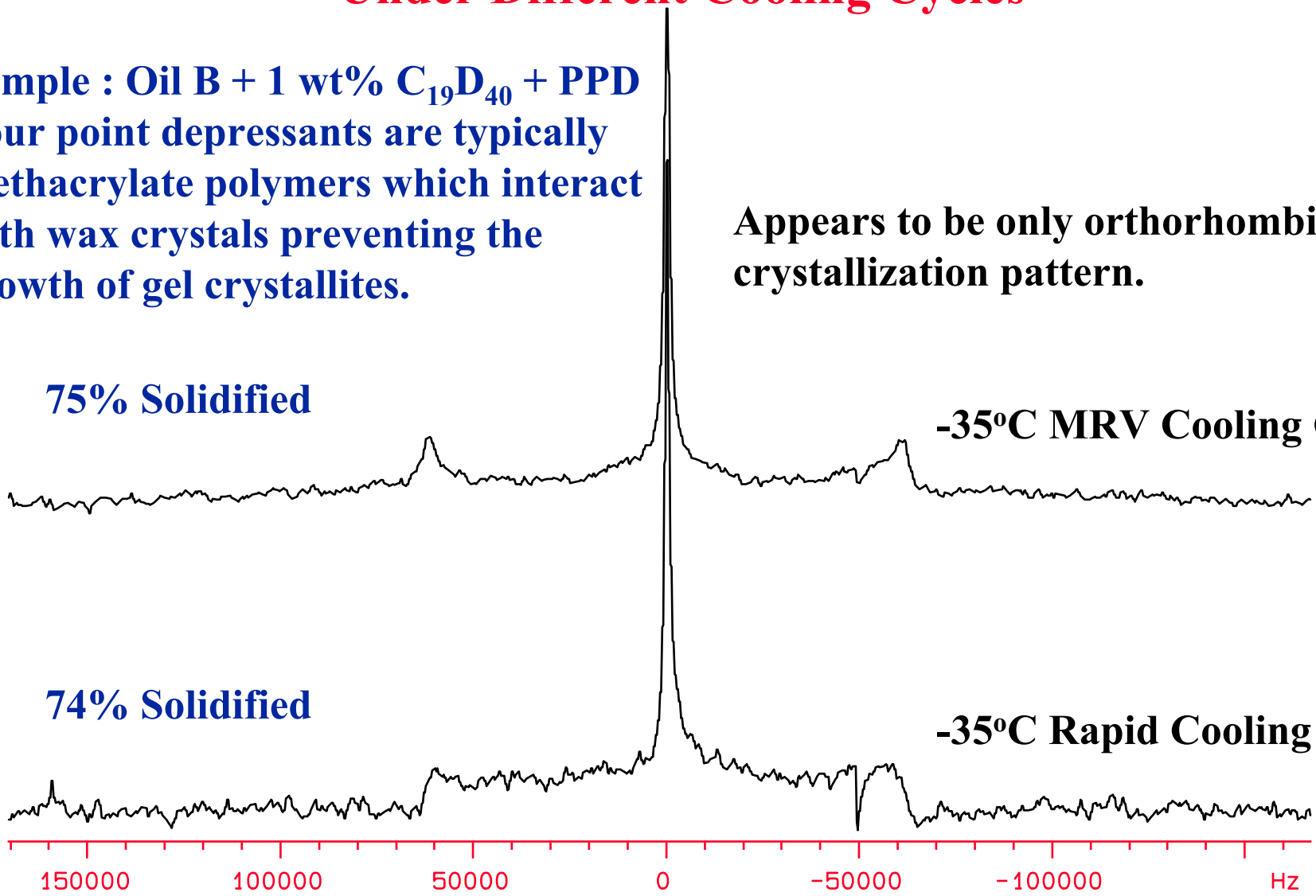
^{2}H Lineshape of Oil B Under Different Cooling Cycles

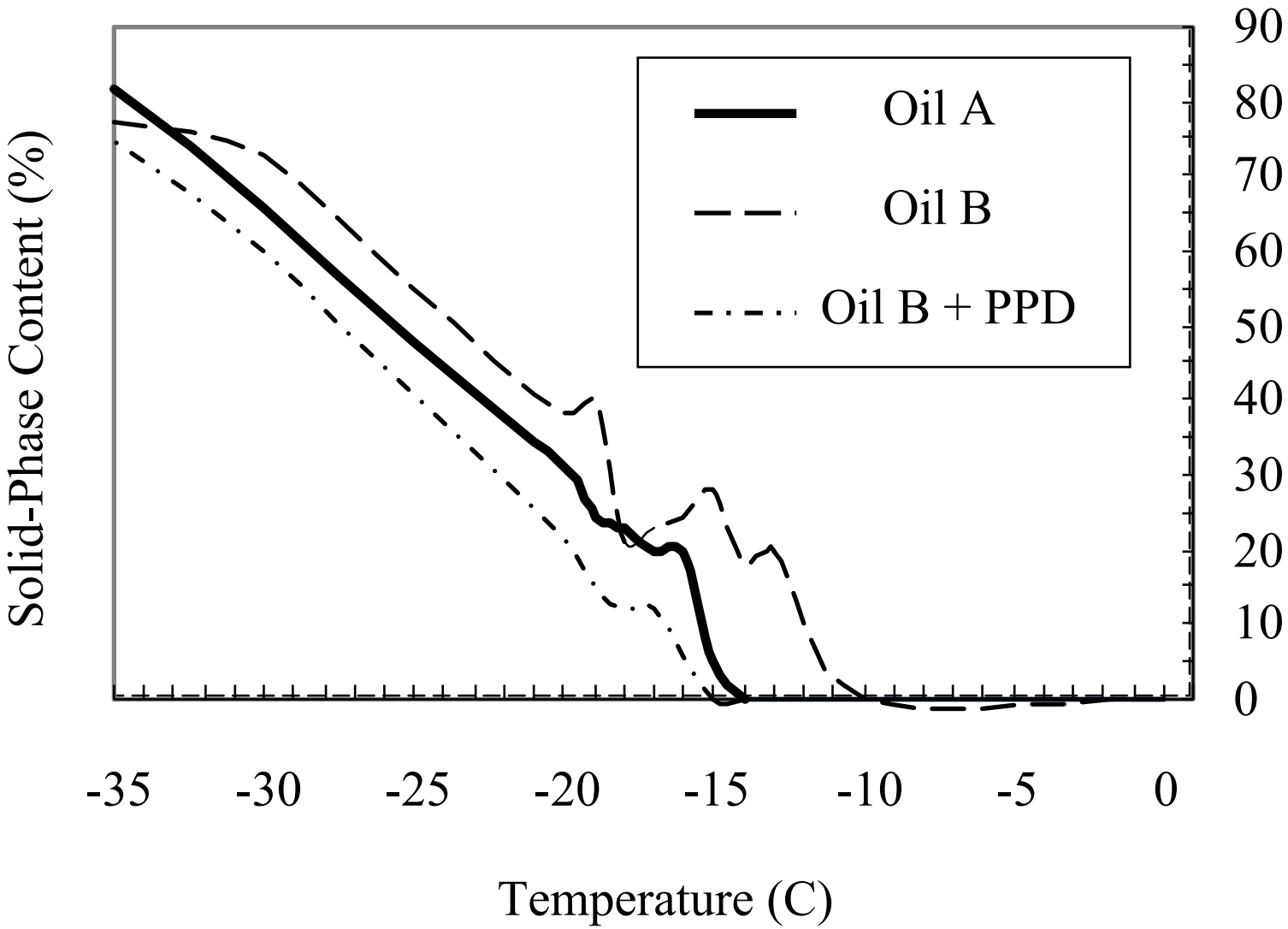


^{2}H Lineshape of Oil B With Pour Point Depressant Additive Under Different Cooling Cycles

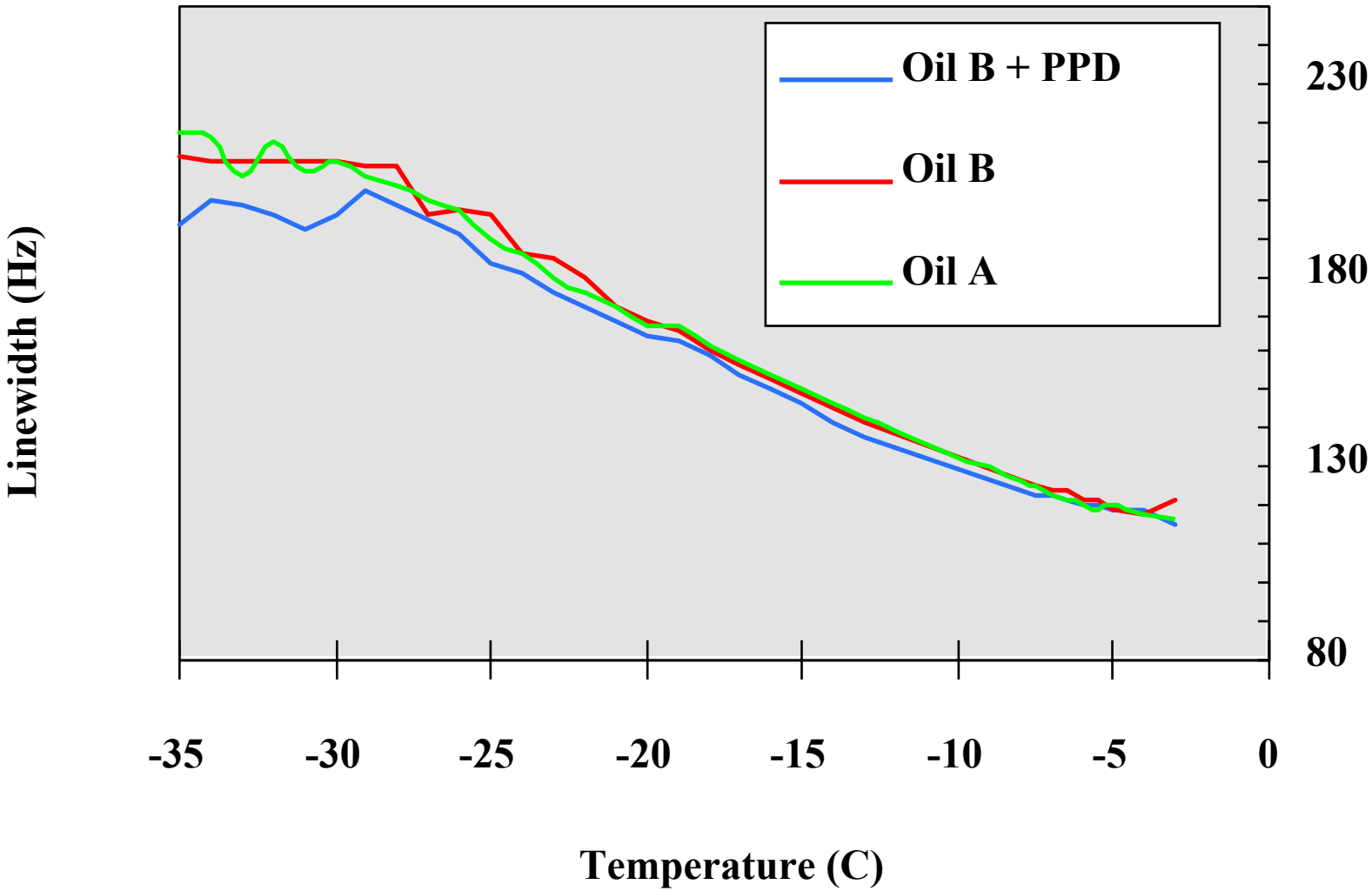
Sample : Oil B + 1 wt% $C_{19}D_{40}$ + PPD
Pour point depressants are typically methacrylate polymers which interact with wax crystals preventing the growth of gel crystallites.

Appears to be only orthorhombic crystallization pattern.




Solid-Phase Content (%)
90
80
70
60
50
40
30
20
10
0
Oil A
Oil B
Oil B + PPD
-35
-30
-25
-20
-15
-10
-5
0
Temperature (C)

Isotropic Peak Linewidth Increase With Decreasing Temperature



Summary

^{2}H NMR can be readily utilized to study the low temperature crystallinity behavior of base oils.

Use of perdeuterated n-$C_{19}D_{40}$ allows for ready observation of hexagonal and orthorhombic crystallite formation. Degree of solidification as well as motional restriction can also be discerned from the ^{2}H data.

The amount of total degree of solid-phase formation and crystallite form are highly dependent on the temperature cycle to which the oil is exposed. The MRV cooling cycle appears to enhance the formation of hexagonal crystallites which may be the crystal form of the paraffinic gel matrix.

Addition of pour point depressant suppresses the formation of hexagonal crystallites.

Future work in this area will involve investigation of a wider range of MRV test failing oils. More repeat runs need to be performed and the optimum level of n-$C_{19}D_{40}$ addition should be ascertained. The interaction of perdeuterated methacrylate additives with the wax crystallites could be readily observed utilizing both ^{2}H wideline and ^{1}H-^{2}H CP/MAS experiments.