DETERMINATION OF SOLID-LIQUID EQUILIBRIA DATA FOR MIXTURES OF HEAVY HYDROCARBONS IN A LIGHT SOLVENT

Final Report

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ABSTRACT

A methodology was developed using an FT-IR spectroscopic technique to obtain solid-liquid equilibria (SLE) data for mixtures of heavy hydrocarbons in significantly lighter hydrocarbon diluents. SLE was examined in multiple Model Oils that were assembled to simulate waxes. The various Model oils were comprised of C-30 to C-44 hydrocarbons in decane. The FT-IR technique was used to identify the wax precipitation temperature (WPT). The DSC technique was also used in the identification of the onset of the two-phase equilibrium in this work. An additional Model oil made up of C-20 to C-30 hydrocarbons in decane was studied using the DSC experiment. The weight percent solid below the WPT was calculated using the FT-IR experimental results. The WPT and the weight percent solid below the WPT were predicted using an activity coefficient based thermodynamic model. The FT-IR spectroscopy method is found to successfully provide SLE data and also has several advantages over other laboratory-based methods.

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INTRODUCTION

During transportation of crude oils and other condensates in pipelines, heat losses to the environment will lead to the formation of a solid phase in the oil due to lowering of the temperature. The operating problems arising due to the formation of the solid phase in the pipeline could be minimized by investigating the variables that determine the amount of solids precipitated during the transportation. The capability to predict the wax appearance temperature and the amount of solid phase in the oil are vital to estimate the deposition of the solid in the pipeline. A thermodynamic model capable of predicting solid-liquid equilibria is required to handle deposition problems. The experimental data applicable to modeling solid-liquid equilibria for crude oils and for oils mixed with Fischer-Tropsch (F-T) liquids can be expanded using newer techniques. There are many conventional methods presently available for measurement of crude oil wax precipitation temperature (WPT). This work uses the Fourier Transform Infrared (FT-IR) spectroscopy method to simplify the methodology for making compositional measurements of mixtures of hydrocarbons.

Future online process monitoring of Fischer-Tropsch reactants, and reforming of F-T products for hydrogen production will require improved measurement technology of high molecular weight hydrocarbons, not only for process control, but also for monitoring of pipelines mixtures. The FT-IR spectroscopic technique can be used to study the SLE behavior of these F-T mixtures. The FT-IR technology could be combined with Near-IR (NIR) spectroscopy and UV spectrophotometry, which offers unique advantages for both laboratory and on-line process measurements of hydrocarbon mixtures. Knowledge of the nature of precipitation of waxes from mixtures of C-30 to C-50 in decane at the wax precipitation temperature and below is of interest to pipeline operators and is applicable to the development of a solid-liquid equilibrium model for complex heavy crude oils diluted with lighter hydrocarbons.

EXECUTIVE SUMMARY

The application of new approaches in modeling solid-liquid equilibria for crude oils and for oils mixed with Fischer-Tropsch (F-T) liquids requires more experimental data. The two important factors in the study of solid- liquid equilibria for hydrocarbon systems are specified as the following:

- Determination of the wax precipitation temperature (WPT)

- Determination of the amount of wax formed below the WPT at various temperatures

Experimental work using FT-IR spectroscopy to make solid-liquid equilibria (SLE) measurements at atmospheric pressure for model F-T oil systems was carried out in this study. These Model Oil systems were composed of long chain alkanes ranging from C-30 to C-44 in a decane solvent. These Model Oil systems were prepared in our laboratory from pure compounds. Our studies also used another Model Oil system of known solid-liquid equilibria comprised of normal alkanes from C-20 to C-30 in decane. The FT-IR spectroscopic technique was used to identify the wax precipitation temperature and the weight percent solid wax below the WPT.

The Model Oils were also studied using a Differential Scanning Calorimetry (DSC) system. The WPT and the wax dissolution temperature (WDT) of the Model Oils were determined during the cooling and heating cycles respectively. The WPT obtained from the DSC experiments were comparative to the values obtained from the FT-IR experiments. The DSC technique hence was successfully used as a secondary method for the determination of the WPT. One Model oil, which was representative of the C-30+ composition of the F-T liquids, gave rise to a different pattern in the DSC experiment. The anomalous behavior this Model Oil was explained with regard to its composition in comparison with the other Model Oils.

A solid-liquid equilibria thermodynamic model was used to predict the WPT and the amount of wax precipitated as a function of temperature. An activity coefficient model was applied with a modified regular solution model being used to describe the nonideality of the solid and liquid phases. The values of the WPT predicted by the thermodynamic model are comparable to the values of WPT obtained from the FT-IR experiment. The thermodynamic model predicts a slightly different wax content at various temperatures below the WPT when compared to the FT-IR experiment. This thermodynamic model can also be used to predict the composition of the wax precipitated at various individual temperatures below the WPT.

This work hence sets the stage for the extension of the FT-IR based study of F-T mixtures by the further inclusion of napthenic and aromatic components and also other conditions such as higher pressure and temperature.

COMPOSITION OF SAMPLE OILS AND MODEL OILS

Several samples were investigated in this work using the FT-IR and the DSC techniques. These have been broadly classified here as Sample Oils and Model Oils. The Sample/Model Oils were made up of n-alkanes and were purchased from Aldrich individually. Several Sample/Model Oils were prepared in our laboratory by mixing weighed amounts of the n-paraffins and followed by dissolution in decane. All the Sample/Model Oils had an approximately 35-weight % distribution of n-alkanes in 65-weight % of the decane solvent. The solvent decane was 99% pure with the other n-alkanes (97-99% purity) distributed in decane in varying proportions. The purity of the various n-paraffins used in the preparation of the Sample/Model Oils is indicated in Table 1.

Table 1. Purity of the n-Alkanes

n-alkanes	Purity
n-C30	99%
n-C32	97%
n-C34	98%
n-C36	98%
n-C40	98%
n-C44	99%
n-C10	99+%

The compositions of the Sample/Model Oils are discussed in the following sections. The detailed compositions of the various Model Oils and the Sample Oils are presented in *Appendix A* (Sample Oil and Model Oil Compositional Data).

Sample Oils A, B, C

The Sample Oils A, B and C were used in initial studies using the FT-IR spectroscopy experiment to determine the WPT and the weight percent solid below the WPT. Sample Oil A consisted of dotriacontane and hexatriacontane amounting to approximately 35- weight percent dissolved in decane. Sample Oil B and Sample Oil C were made up with 35-weight percent dotriacontane and hexatriacontane respectively in 65-weight percent decane. The compositions of the Sample Oils are presented in Figure 1. These Sample Oils were used primarily to demonstrate the capability of the analyst using the FT-IR instrument in collecting solid-liquid equilibria data. The data obtained from the FT-IR experiments were found to be reproducible and repeatable. The FT-IR analysis of the Sample Oils also helped in studying the precipitation characteristics of the individual n-alkane, dotriacontane in the case of Sample Oil B and hexatriacontane in the case of Sample Oil C.

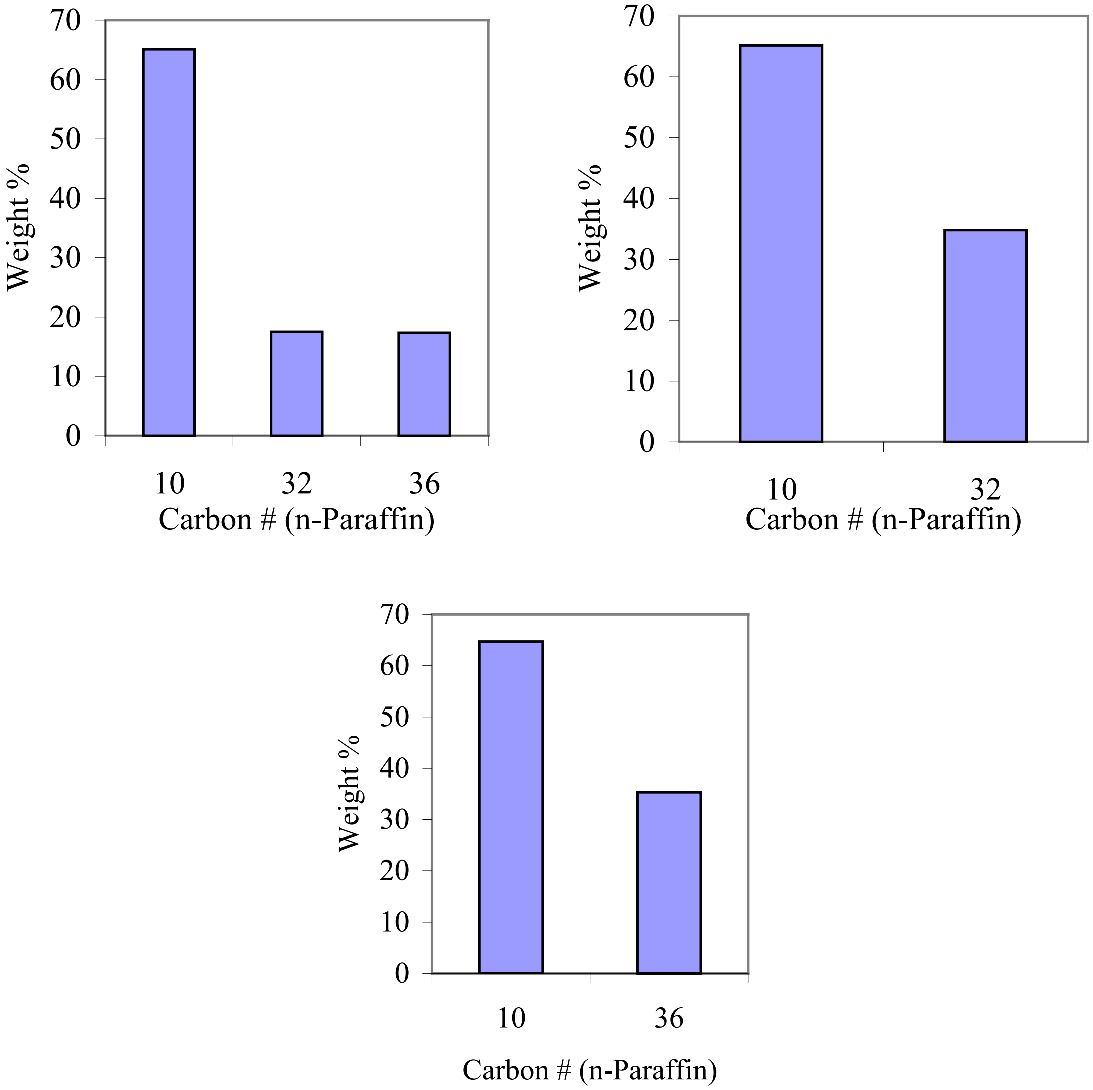

Figure 1. Carbon Number of the n-Paraffins in the Sample versus their Weight % in the Sample for (a) Sample Oil A (b) Sample Oil B and (c) Sample Oil C.

Model Oils

Model Oil A

Model Oil A was made with six approximately equal molar alkanes (35 wt%) in decane. The six n-alkanes were triacontane, dotriacontane, tetracontane, hexatriacontane, tetracontane and tetratetracontane. These six n-alkanes were chosen due to ease of their availability and the distribution of the carbon numbers from C-30 to C-50.

Model Oil B

Model Oil B was made with the same components as that of Model Oil A but the composition was altered based on data obtained from the literature. The composition was based on data obtained from the work done by J.C.W. Kuo ["Slurry Fischer-Tropsch/Mobil Two Stage Process of Converting Syngas to High Octane Gasoline"; Final Report – June 1983; Figure 9; DOE Contract No. AC22-80PC30022]. The composition was based on a plot of the weight fraction/carbon number versus the carbon number. In the above-mentioned work the carbon number distribution of the F-T products was described by the Schulz-Flory distribution (based on the material balance).

The weight percent data of the individual alkanes in Model Oil B as a function of their carbon number is presented in Figure 2. Model Oil B is not a simulant of the Fischer-Tropsch wax but is just modeled on the F-T wax composition representatively. The difference between the equimolar distribution of the n-alkanes in Model Oil A and the representative distribution in Model Oil B would give more information on the precipitation behavior of these n-alkanes.

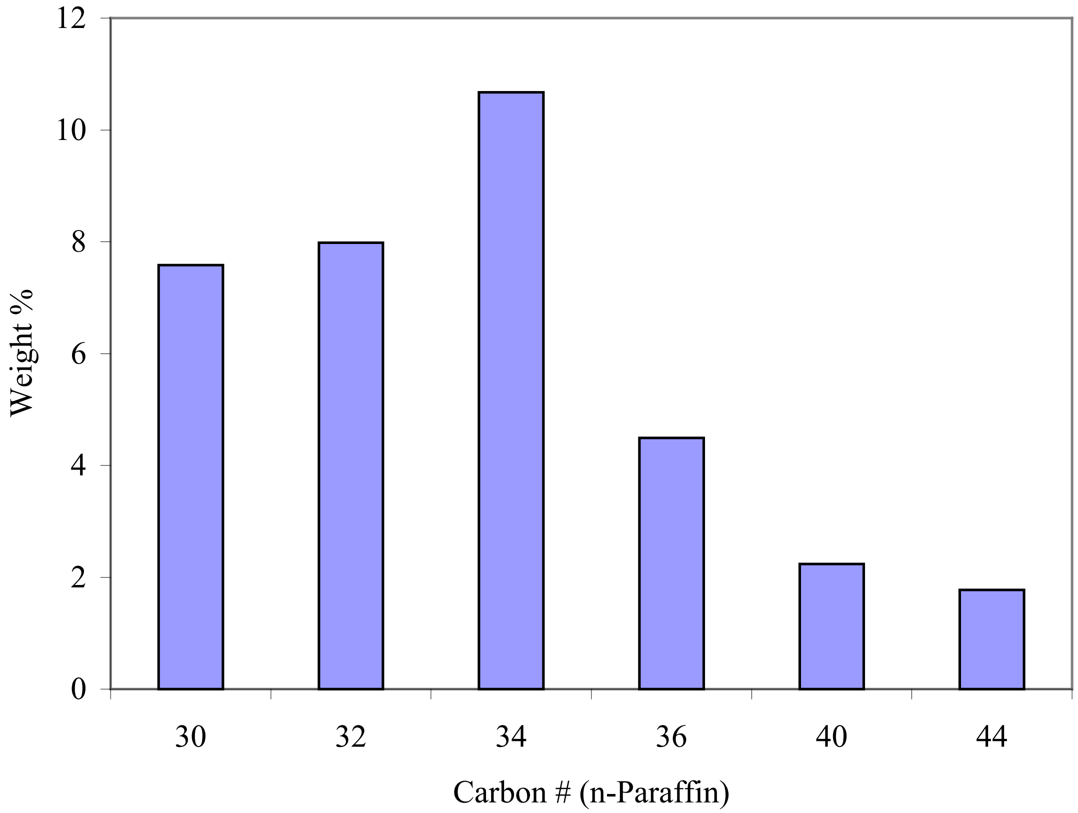

Figure 2. Model Oil B – Carbon Number of the n-Paraffins in the Sample versus their Weight % in the Sample.

Model Oil C

Roehner [1, 2] has previously analyzed a Model Oil made up of n-alkanes from C-20 to C-30 (35 weight %) in 65 weight % decane. This Model Oil was purchased from Supelco as a custom mix and is referred to as Model Oil C in this work. This Model Oil was made to match a system previously analyzed by Pauly et al. [3]. The n-alkanes used to make up Model Oil C were of 98-99% purity. Roehner has already studied Model Oil C using the FT-IR spectroscopy method to determine the WPT and the weight percent solids (as a function of temperature) below the WPT. This Model Oil however, has not been analyzed by using the DSC experiment. In this work, additional FT-IR analyses were done and the sample was also analyzed using DSC. A bar chart of the weight percent of the n-paraffins versus their corresponding carbon number is presented in Figure 3.

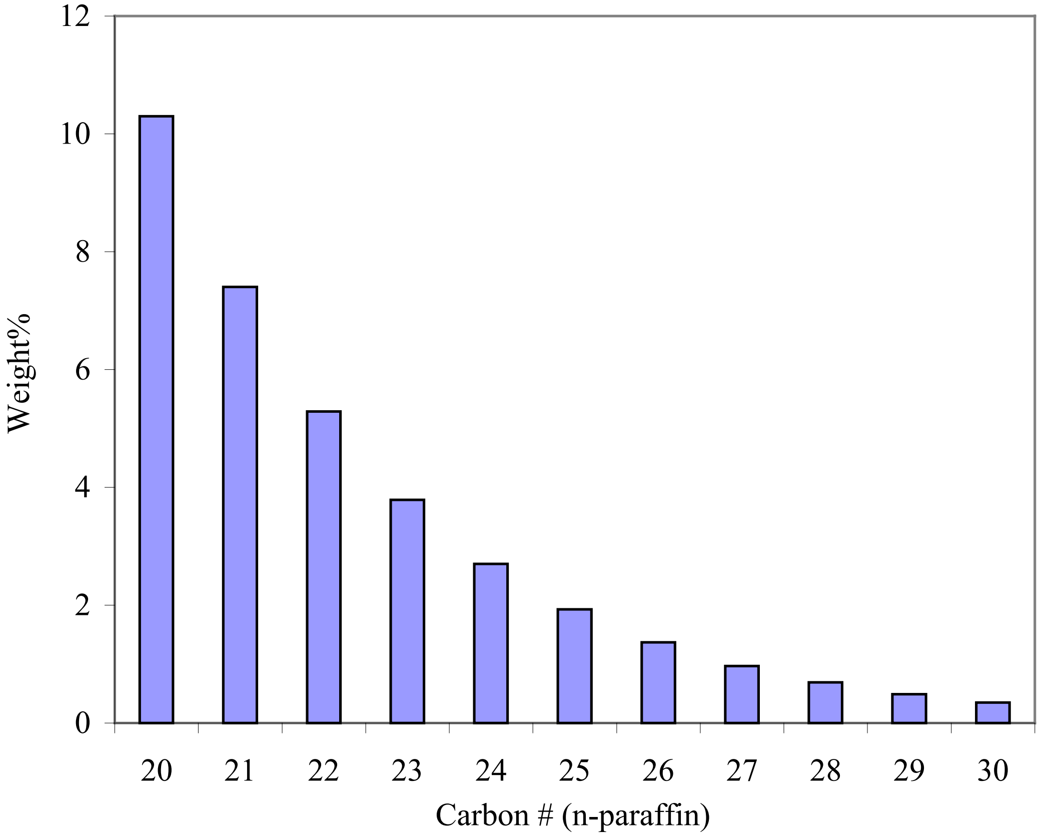

Figure 3. Model Oil C – Carbon Number of the n-Paraffins in the Sample versus their Weight % in the Sample.

SOLID – LIQUID EQUILIBRIA MEASUREMENT

The study of solid-liquid equilibria is divided into two different sections in this work. The first deals with the measurement of the wax precipitation temperature. The second part involves the calculation of the amount of solid wax precipitated as a function of the temperature below the WPT.

MEASUREMENT OF WAX PRECIPITATION TEMPERATURE

The wax precipitation temperature (WPT) is defined as the temperature at which wax crystallization begins. Modeling of solid-liquid equilibria for crude oils and for oils mixed with Fischer-Tropsch liquids requires accurate identification of the WPT.

Summary of WPT measurement methods

Crude oil WPT has been measured using conventional experimental methods such as differential scanning calorimetry (DSC) [4-8], viscometry [5-10], near-IR spectroscopy (NIR) [11] and cross-polarized microscopy (CPM) [5, 7, 12-15]. The measurement of WPT by DSC is explained in detail in a later section in this report. The WPT is identified by the change in viscosity with temperature in the viscometric method. Polarized light is used to observe the sample in the CPM method. The wax crystals in the solid phase rotate the polarized light, the onset of which is determined as the WPT.

The FT-IR spectroscopy method has been used by Roehner [1, 2] to determine the WPT of crude oils. Roehner has compared the WPT's obtained for two crude oils (from different sources) using the FT-IR technique with the WPT's obtained from other methods such as viscometry, cross-polarized microscopy and differential scanning calorimetry. The FT-IR spectroscopy technique was shown to compare well with the other conventional methods in the measurement of WPT. In this work the FT-IR spectroscopic method and the DSC technique have been used for the determination of the WPT of the Model Oils. The methods used and the results obtained are discussed in the following sections.

FOURIER TRANSFORM – INFRA RED SPECTROSCOPY

The FT-IR spectroscopic method as described by Roehner [1, 2] was used in the identification of the WPT's of the various Model Oils. The theoretical background of the method, the identification of the WPT and the calculations used are explained in detail in the following sections.

The summary of the experimental method, details of equipment used, calibration and the procedure along with other details of the FT-IR method used are documented comprehensively in *Appendix B* (FT-IR Spectroscopy of Crude Oils/Model Oils).

Theoretical background

FT-IR spectroscopy is used to measure the absorbance associated with the molecular vibrations present in the sample. The Beer-Lambert law is used to calculate the absorbance of a component as follows:

$$A = abc \qquad (2.1)$$

where a is the absortivity, b is the path length and c is the concentration of the component which is being analyzed. The band at 720 cm^{-1} in the IR spectra is due to the presence of long chain methylene carbon (LCM) in hydrocarbons. The LCM carbon has more than four methylene groups in a single row [16]. The 720 cm^{-1} band in the IR spectra is associated specifically with the CH_2 rocking vibrations [16, 17]. The LCM carbon has been found to be the primary functional group responsible for the formation of solid wax.

Snyder et al. [18] have defined the intensity of a band in the IR spectra as,

$$I = \frac{1}{b\rho}\int A_{\nu}\,d\nu \qquad (2.2)$$

where b is the sample path length, ρ is the density of the sample, and A_{ν} is the absorbance at wavenumber ν (720 cm^{-1} in this case)

The intensity of the 720 cm^{-1} band in the IR spectra is found to increase with decrease in temperature of the sample. This is due to the density change with temperature and also due to the formation of a solid phase. The WPT of the sample can be calculated by studying the changes in the intensity of this particular band. The FT-IR experiment involves gradually decreasing the temperature of the sample and measuring the absorbance at various temperatures after equilibration. When the sample is cooled below the WPT, it should cross a solid-solid transition temperature (hexagonal to orthorhombic). This results in the splitting of the 720 cm^{-1} peak into a doublet [16]. This can be observed in the spectra obtained for the Model Oils in this work.

WPT measurement

Above the WPT, the total absorbance ($A_{720} = A_{tot}$) can be attributed to the rocking of the liquid phase LCM carbons. Below the WPT, the total absorbance will be the sum of the rocking of liquid and solid phase LCM carbons.

$$A_{720} = a_l b c_l \quad \rightarrow \text{Above the WPT} \qquad (2.3)$$

$$A_{720} = a_l b c_l + a_s b c_s \quad \rightarrow \text{Below the WPT} \qquad (2.4)$$

where a_l and a_s are the absortivities of the liquid and solid phase LCM carbons, and c_l and c_s are the concentrations of the liquid and solid phase LCM carbons. The total absorbance decreases in the liquid phase with reduction in temperature initially during the course of the experiment. This is due to the change in the total LCM carbon concentration due to the change in the sample density with temperature. Below the WPT, the creation of the solid phase would also contribute to the total absorbance. This gives rise to a distinct change in slope in a plot of A_{tot} as a function of temperature. This can be attributed to the higher absorptivity of the solid phase made up of LCM carbon. The temperature where the change in slope occurs is recorded as the WPT.

Identification of WPT

The peak areas between 735 and 715 cm^{-1} were calculated for all the spectra using the Spectrum 2.0 software [19]. This gave the total absorbance for each spectrum associated with the LCM rocking vibrations. Any effect of baseline shifts during the course of temperature reduction was resolved according to the following method. The base area (A_B) of the peak in consideration (735 and 715 cm^{-1}) was calculated for the first test temperature. This was obtained as the difference between the uncorrected peak area (A_{UP}) and the corrected peak area (A_{CP}) obtained from the peak area/height routine in the software used.

$$A_{B1} = A_{UP1} - A_{CP1} \quad \text{(1- first test temperature)} \qquad (2.5)$$

This base area was then added to the corrected peak area obtained for each test temperature to calculate the total absorbance at each test temperature.

$$A_{tot} = A_{B1} + A_{CPx} \quad \text{(x - other test temperatures)} \qquad (2.6)$$

The total absorbance obtained in this method was plotted against the corresponding temperatures. Two different lines were fitted (linear best-fit) from the two ends of the temperature range investigated. The WPT was the identified as the intersection of these two lines.

Results and Discussion

The results obtained from the FT-IR analysis of the various Model Oils are discussed individually in the following sections.

Model Oil A

The spectra obtained from the IR at 720 cm^{-1} for Model Oil A (Test Run 4) at various test temperatures are presented in Figure 4. The doublet that is seen at lower temperatures indicates the presence of orthorhombic crystals. A plot of the peak area (735-715 cm^{-1}) for the spectra presented in Figure 4 versus temperature is presented in Figure 5. The WPT is found to be 61°C for Test Run 4. The average WPT observed for the various runs on Model Oil A was 61ºC. The calculate standard deviation was 0.52. The summary of the wax precipitation data obtained for Model Oil A is presented in Table 2.

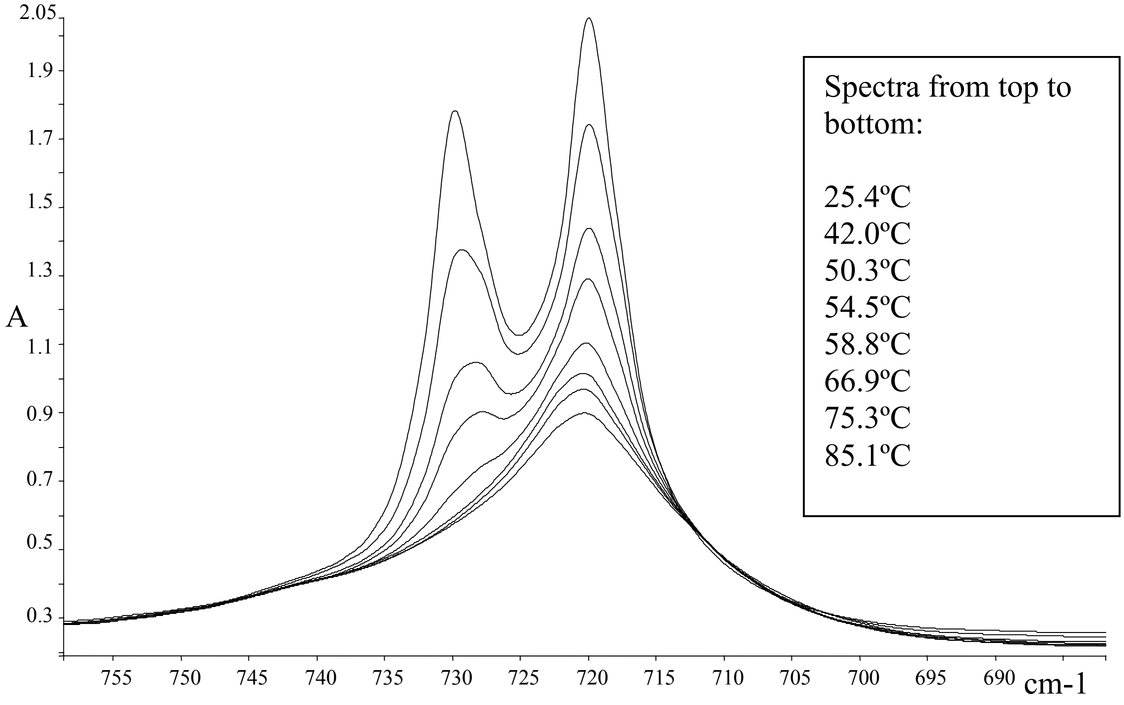

Figure 4. Model Oil A, Spectra at 720 cm^{-1} for Various Temperatures.

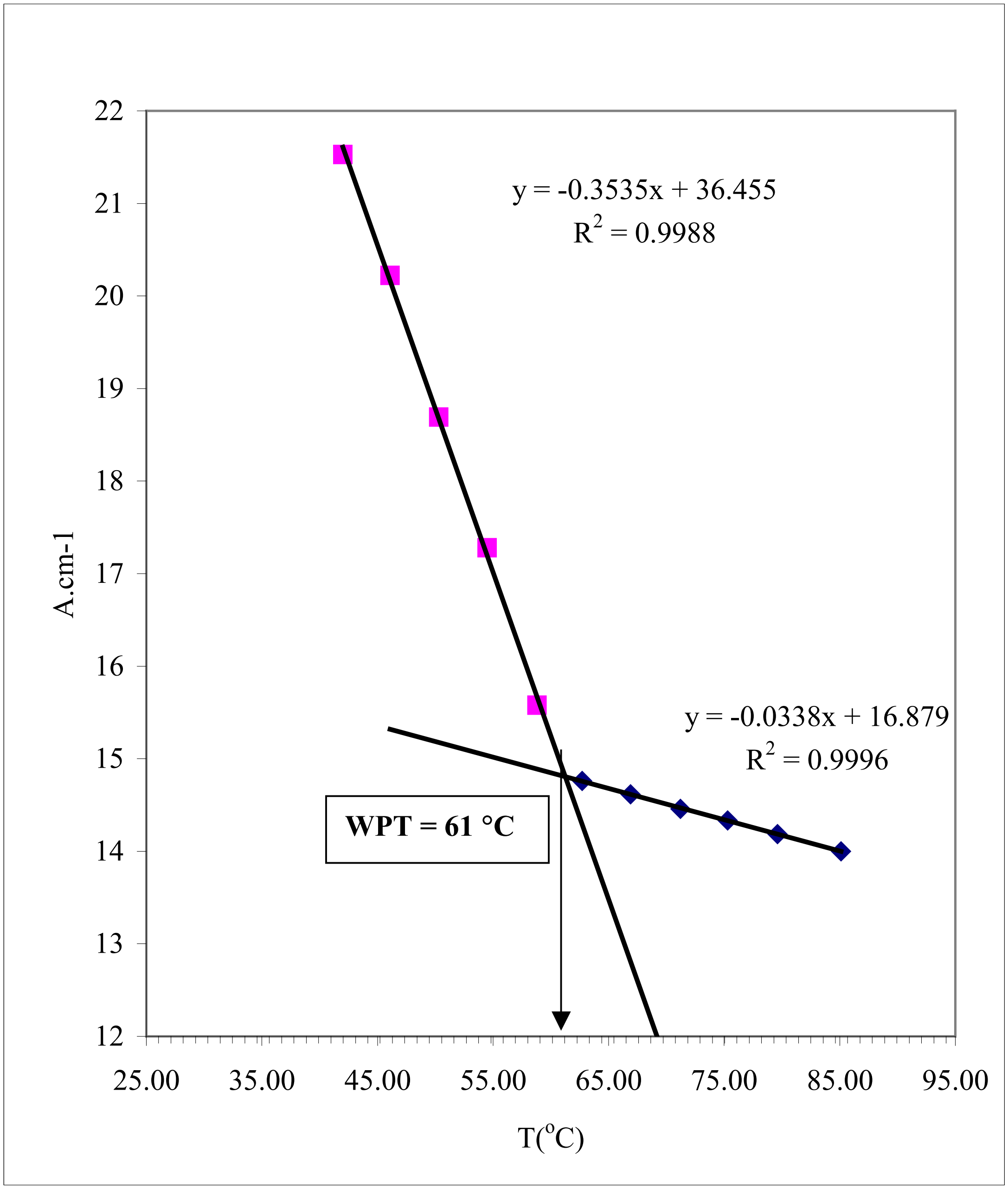

Figure 5. Model Oil A, Test Run 4, Peak Area (735-715 cm^{-1}) versus Temperature

Table 2. WPT Data Obtained by FT-IR Experiments for Model Oil A

Test Run	1	2	3	4	5	Avg.	SD
Measured WPT (°C)	60	61	61	61	60	61	0.52

Avg. – mean, SD – standard deviation

Model Oil B

The spectra at at 720 cm^{-1} from the IR for Model Oil B (Test Run 4) at various temperatures are presented in Figure 6. The spectra show two peaks due to the formation of orthorhombic crystals at lower temperatures. The peak area from 735-715 cm^{-1} in the spectra was integrated and plotted as a function of the temperature. This is presented in Figure 7. As seen from Figure 7, the change in slope of the peak area versus temperature is not significant at the liquid-solid phase transition. This can be explained based on the composition of Model Oil B. Both Model Oil A and Model Oil B have the same components as can be seen from Table A.4 and Table A.5 in *Appendix* A (Sample Oil and Model Oil Compositional Data). However the weight percent of each component differs in both of these Model Oils. Model Oil B has a lower weight percent of the higher molecular weight paraffins (n-C_{44}). The higher molecular weight paraffins precipitate first as the temperature of the sample is lowered. In Model Oil A, the weight % of the high molecular weight paraffin (n-C_{44}) is about 7 whereas in Model Oil B the weight % is 1.7. Hence due to the lower weight percent of the higher molecular weight paraffin (n-C_{44}), the change in slope is not significant as in Model Oil A. The WPT for Model Oil B is determined by focusing on the temperature region close to the WPT as presented in Figure 8. The WPT is indicated as 61ºC in Figure 8. The average WPT observed for the test runs was 61ºC with a calculated standard deviation of 0.55. The summary of the wax precipitation data obtained for Model Oil B is presented in Table 3.

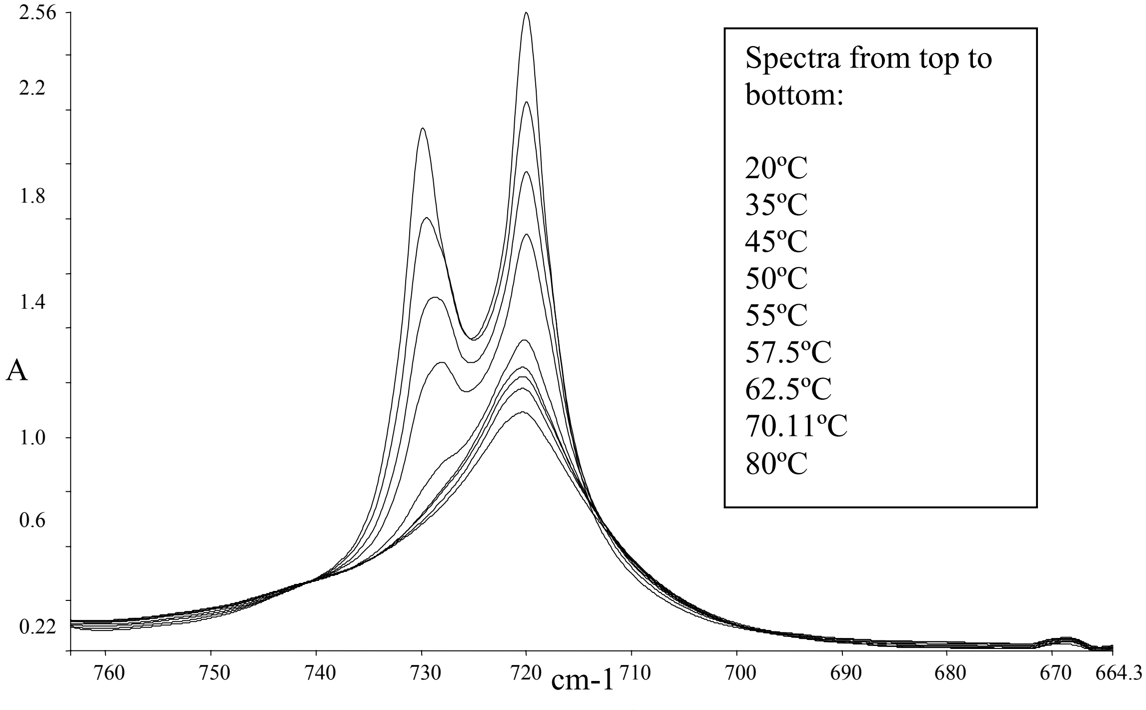

Figure 6. Model Oil B, Spectra at 720 cm^{-1} for Various Temperatures.

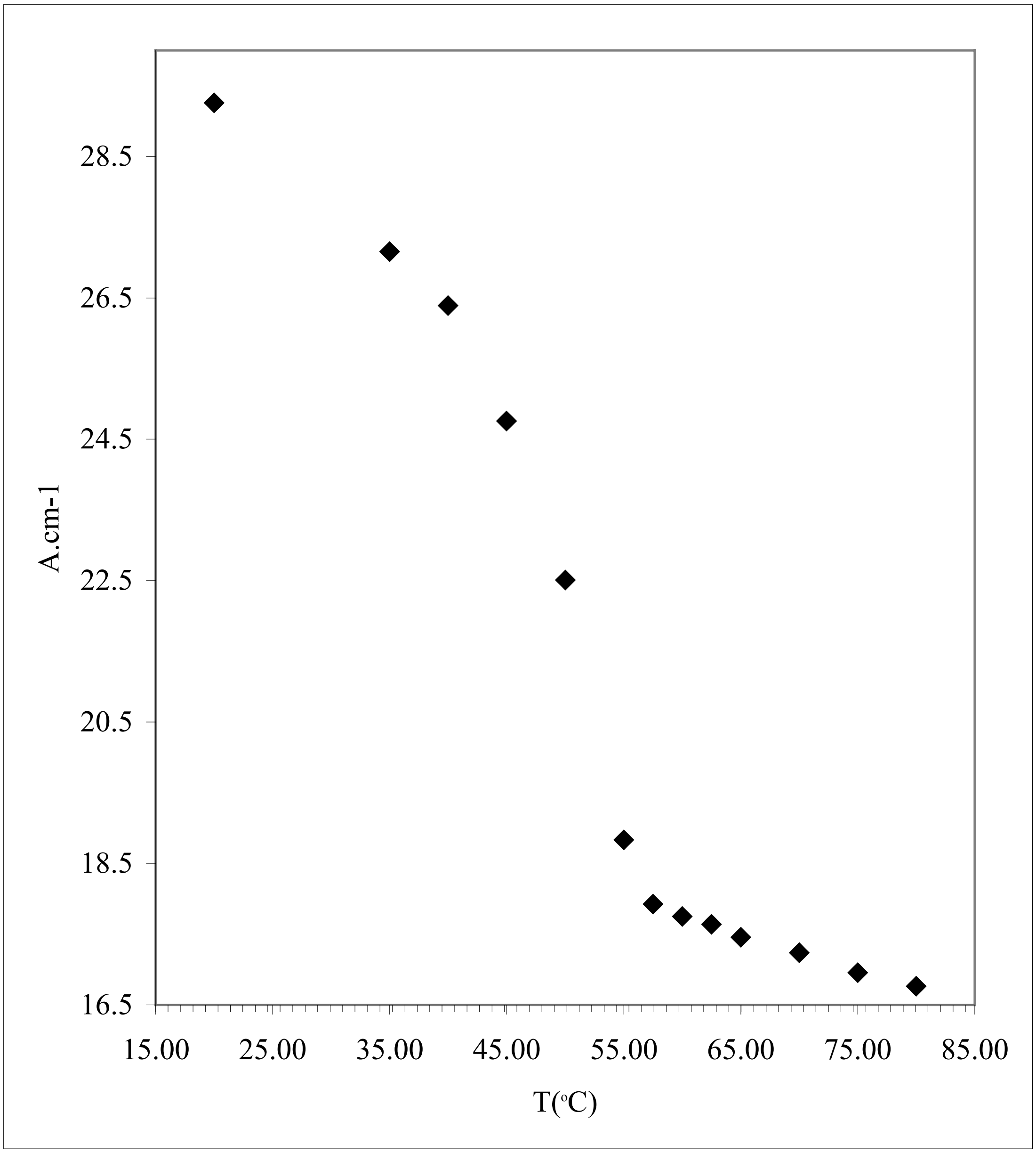

Figure 7. Model Oil B, Test Run 4, Peak Area (735-715 cm^{-1}) versus Temperature

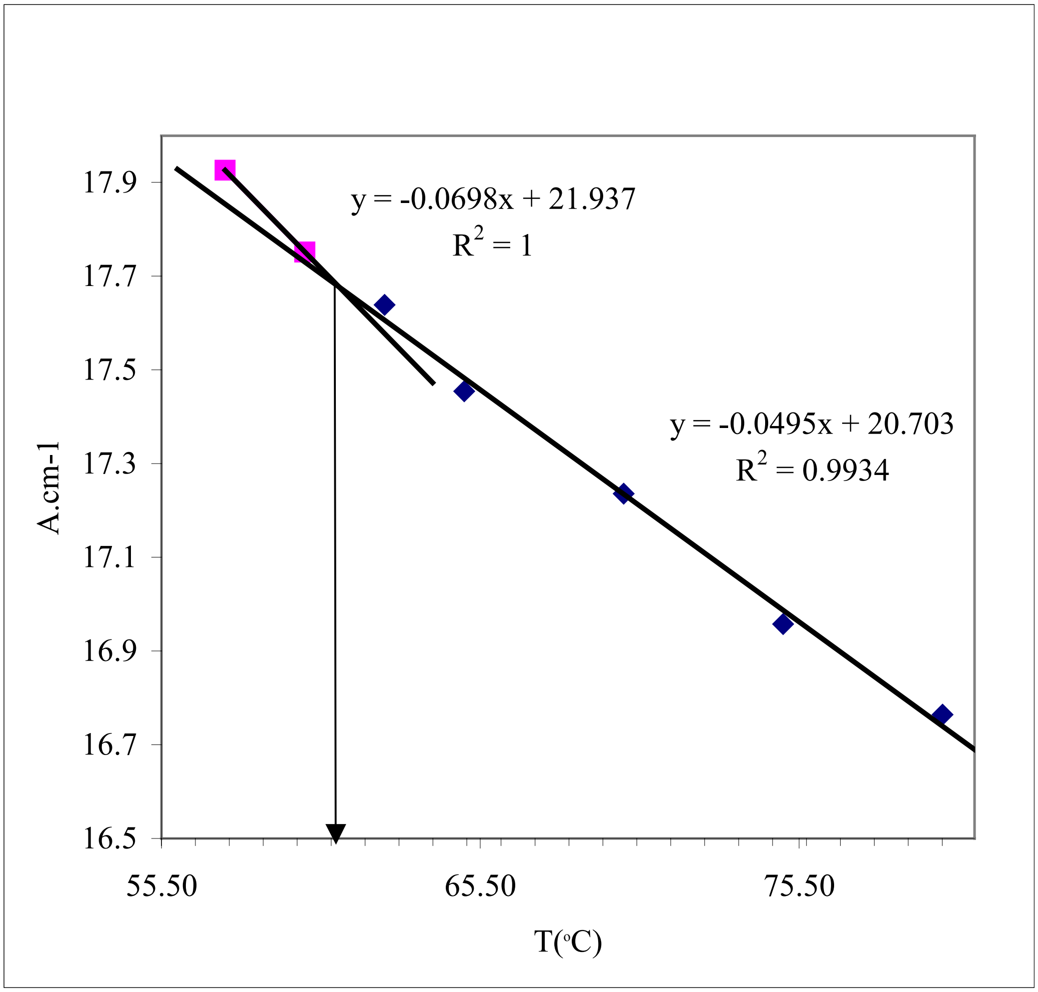

Figure 8. Model Oil B, Test Run 4, Peak Area (735-715 cm^{-1}) versus the Temperature Region Close to the Change in Slope of the Absorbance; WPT = 61°C

Table 3. WPT data obtained by FT-IR experiments for Model Oil B

Test Run	1	2	3	4	5	Avg.	SD
Measured WPT (°C)	60	61	61	61	60	61	0.55

Avg. – mean, SD – standard deviation

Model Oil C

Two test runs were carried out on Model Oil C using the FT-IR technique. The WPT data obtained from these test runs are shown in comparison with previously published data [2] in Table 4 below. The WPT obtained in these two test runs match very well with the previously published data.

Table 4. WPT Data Obtained by FT-IR Experiments for Model Oil C

Test Run	1	2	Published Values [2] - Avg.
Measured WPT (°C)	20.7	20.6	20

Avg. – mean

The spectra at 720 cm^{-1} obtained from test run 1 for Model Oil C at various temperatures is presented in Figure 9. The doublet observed in Figure 9 at lower temperatures is due to the presence of orthorhombic crystals. The peak areas (735-715 cm^{-1}) for these spectra have been integrated and plotted as a function of the temperature in Figure 10. The WPT has been identified as 20.7°C from Figure 10. The average WPT found in the literature was 20°C [1, 2] with the calculated RSD of 3.92%.

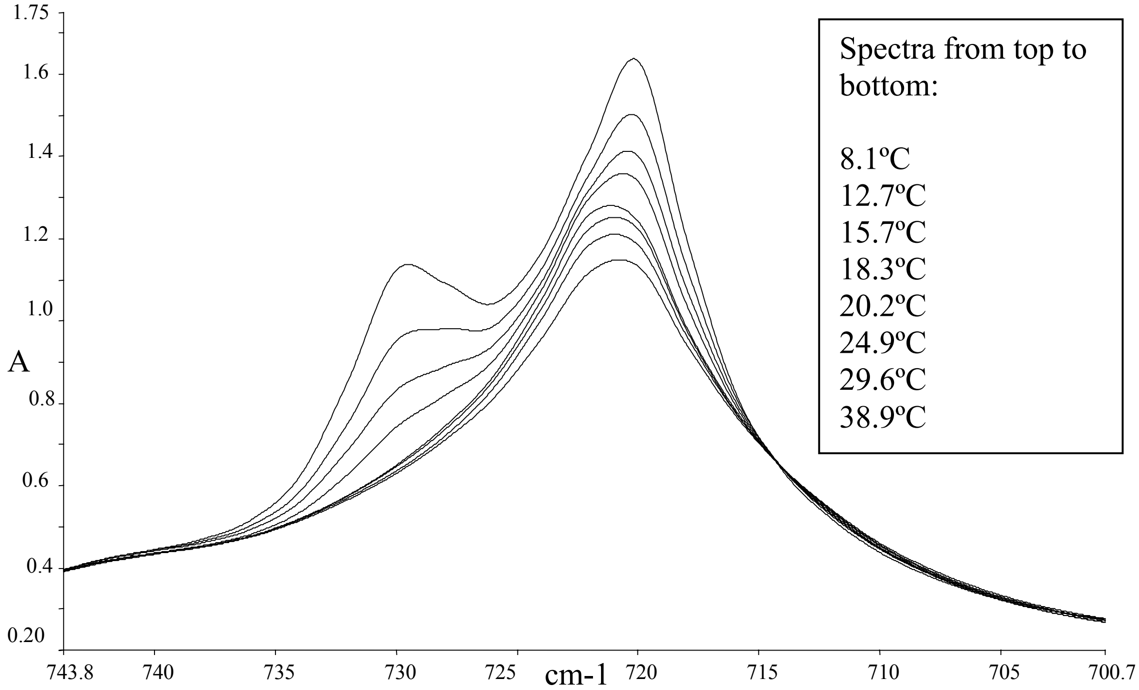

Figure 9. Model Oil C, Spectra at 720 cm^{-1} for Various Temperatures.

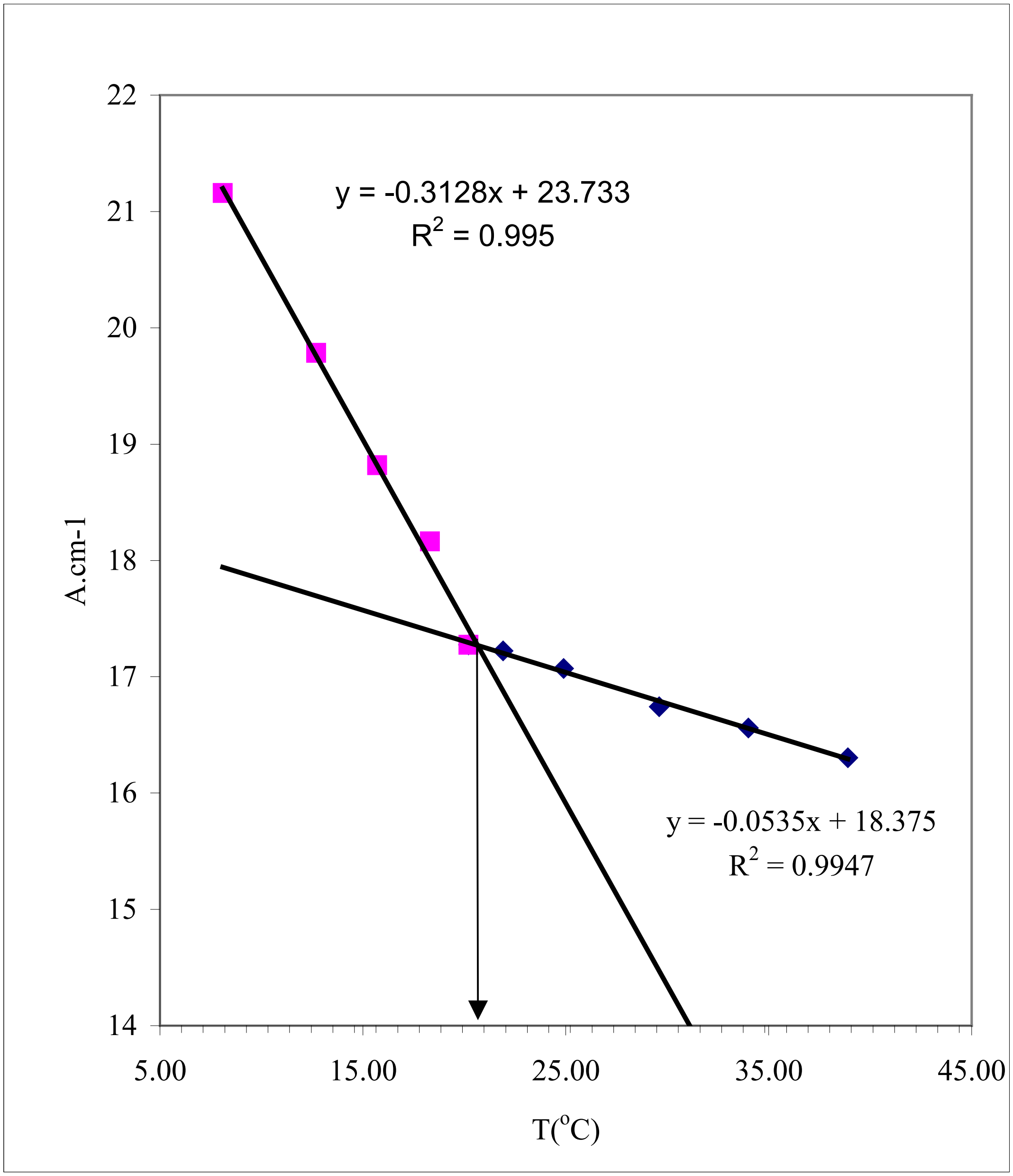

Figure 10. Model Oil C, Test Run 1, Peak Area (735-715 cm^{-1}) versus Temperature; WPT= 20.7°C

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Background

The onset of wax crystallization is found using the DSC by measuring the latent heat of the samples. Precipitation and dissolution of the wax in the samples will give out and absorb heat respectively. On cooling the sample, an exothermic change is observed which is related to the wax crystallization. The onset temperature of this effect is defined as the wax precipitation temperature.

Experiments

DSC analysis of the Model Oils showed distinct exothermic peaks during the cooling cycle the onset of which was interpreted as the WPT. WPT values obtained from the DSC analysis of the Model Oils were used for comparison with the respective values obtained from by the FT-IR spectroscopic technique. The precision and sensitivity of the instrument depends upon the cooling rates used during the experiments. The sensitivity of the DSC decreases with a lower cooling rate while the precision is affected in the case of higher cooling rates. Sample cooling rates of 1,5 and 10ºC per minute were used for various samples contained in hermetically sealed sample pans. The DSC calibration and procedure along with other details of the method used is given in *Appendix C* (Differential Scanning Calorimetry(DSC) of Crude Oil Solids/Model Oils).

Results and Discussion

Model Oil C

Five test runs were carried out on Model Oil C using the DSC technique. The different WPT's obtained from the test runs are tabulated in Table 5. The average WPT were determined to be 20°C with a standard deviation of 0.55. This average WPT obtained from the DSC experiment is the same as the average WPT obtained from the FT-IR experiments (20°C). The thermogram obtained from test run 2 is presented in Figure 11. The cooling rate in this test run was 5ºC/min. The temperature range analyzed ranged from 100°C to -30°C. A single peak is seen during the cooling and heating cycles in the experiment. The temperature corresponding to the onset of the peak during the cooling cycle is 20°C (rounded off), which is the WPT. The dissolution temperature of Model Oil C at 26°C is also marked in the heating cycle curve.

Table 5. WPT Data Obtained by DSC Experiments for Model Oil C

Test Run	1	2	3	4	5	Avg.	SD
Measured WPT (°C)	20	20	19	19	20	20	0.55

Avg. – mean, SD – standard deviation

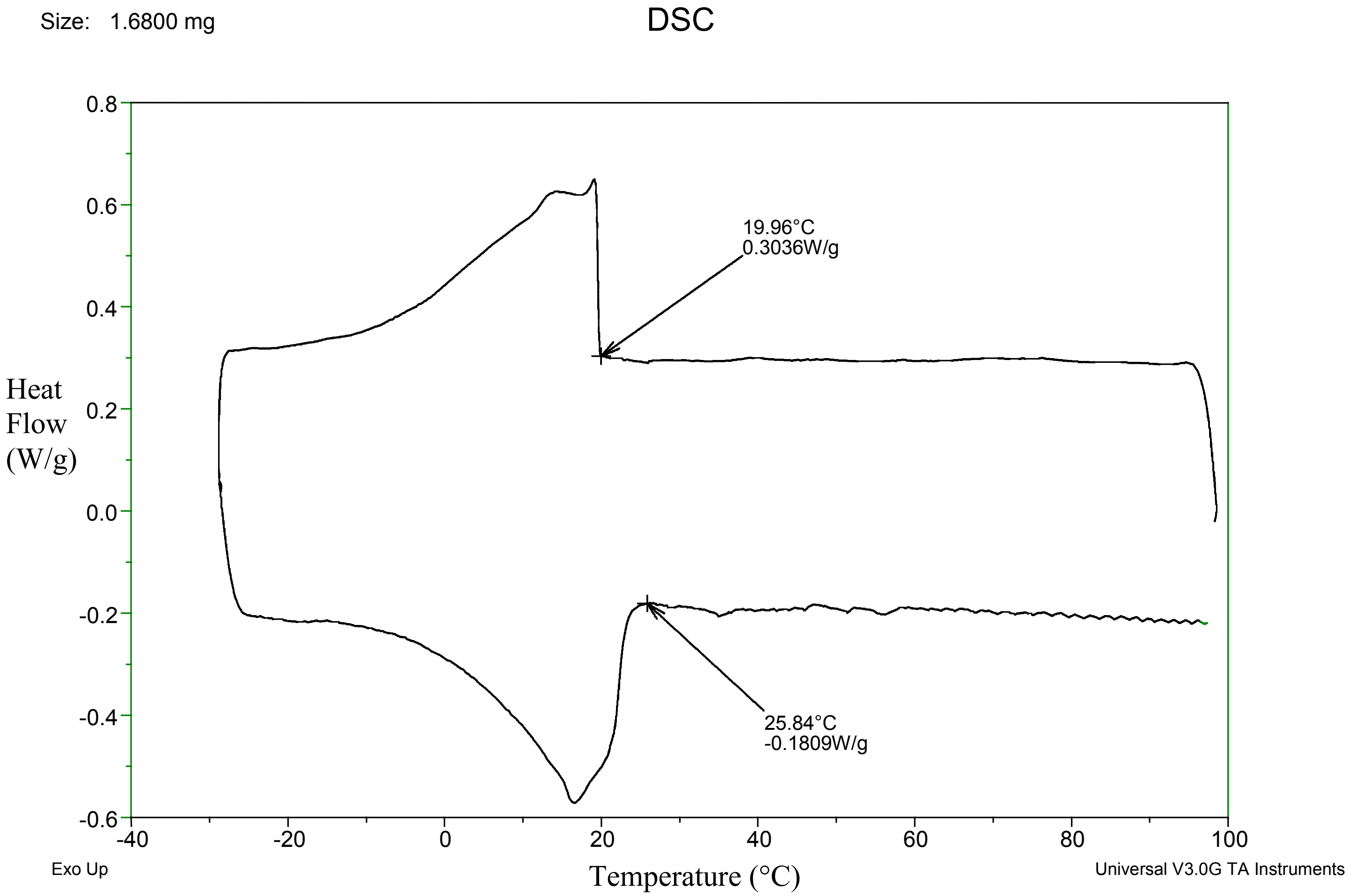

Figure 11. DSC Thermogram of Model Oil C with a Cooling Rate of 5°C/min.

Model Oil A

Multiple experimental runs were conducted for Model Oil A with various cooling rates. A thermogram (test run 1) from the DSC experiment for Model Oil A at a cooling rate of 1ºC/min is presented in Figure 12. Once again as in Model Oil C, a single peak is seen during the heating and cooling cycles. The range of temperatures investigated was from 90°C to 20°C. The onset of the peak (cooling cycle) is 58°C (WPT) and the WDT was determined to be 61°C. The average WPT from the FT-IR experiments for Model Oil A was 61°C.

Model Oil B

The DSC thermograms of Model oil B, unlike Model Oil C and Model Oil A, showed three distinct peaks during the cooling cycle. The cooling cycle typically ranged from 100ºC to 10ºC. A typical thermogram obtained for Model Oil B is presented in Figure 13. The cooling rate used for this experimental run was 1ºC/min. It can be observed from Figure 13 that the onset of the first peak is at a higher temperature than the WPT obtained from the FT-IR experiments. The average WPT for Model Oil B from the FT-IR technique was 61ºC. The first peak is observed at 68ºC. The temperature corresponding to the onset of the second peak in Figure 13 is 61ºC. This is close to the WPT from the FT-IR experiments. A separate third peak is found at 53ºC. The heating cycle curve seen below the cooling cycle curve also has three peaks corresponding to three dissolution temperatures. The WPT and the WDT hence was not determined from the DSC for Model Oil B. The reason for the anomalous behavior of Model Oil B can be explained based on comparison of compositions with the other Model Oils (C and A).

Model Oil C has a continuous distribution of its components (n-alkanes) from C-20 to C-30 in decane. Hence there is a continuous precipitation pattern of the n-alkanes below the WPT. Similarly a single peak is seen in the DSC thermogram for Model A due to its equimolar distribution of components. However in the case of Model Oil B, there is wide gap in the weight percent of its components (Appendix A - Table A.5). The n-alkane with the highest carbon number (C-44) possibly precipitates completely before the others (say C-34) starts to precipitate. This is a probable cause for the presence of multiple peaks in both the cooling and heating cycles. This can be studied by conducting DSC experiments on individual n-alkanes and determining their WPT's and WDT's. The effect of cooling rates on these properties should also be investigated in the future.

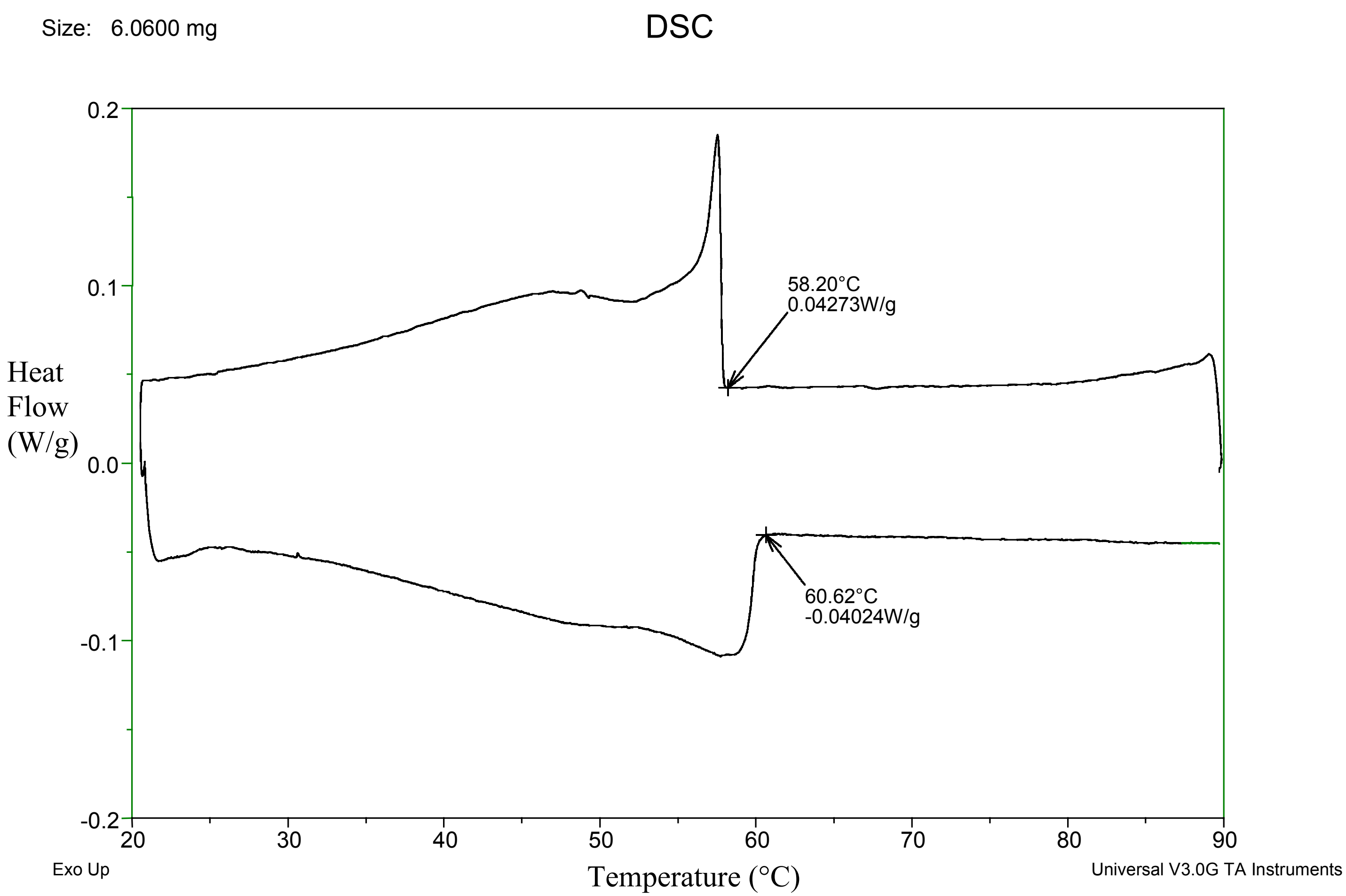

Figure 12. Model Oil A, Thermogram with Cooling Rate of 1ºC/min.

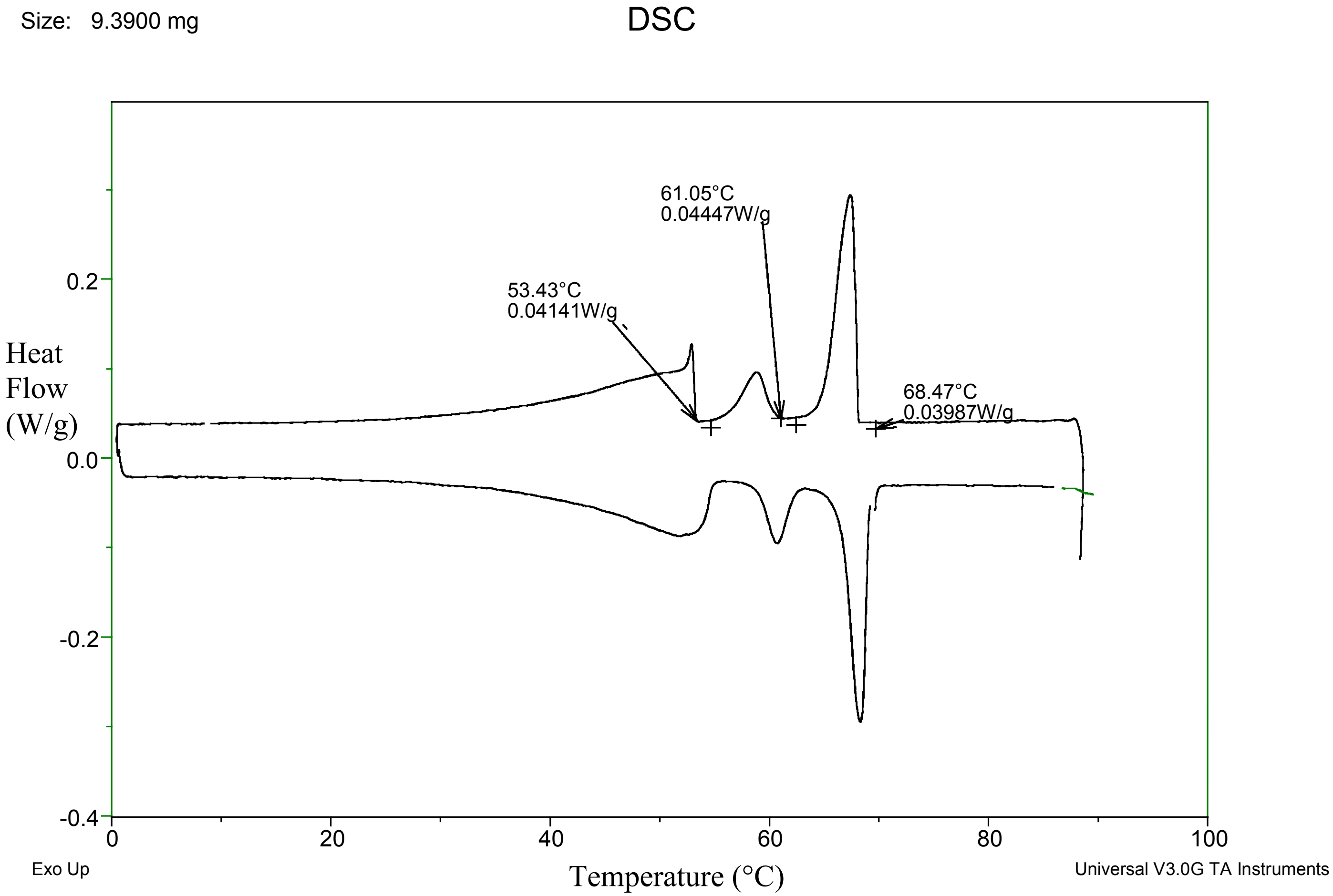

Figure 13. Model Oil B, DSC Thermogram with a Cooling Rate of 1ºC/min.

MEASUREMENT OF WEIGHT PERCENT SOLID BELOW THE WPT

Roehner has used the FT-IR spectroscopic technique previously to identify the weight percent solid versus temperature for crude oils [1, 2] and model oils. The results from the FT-IR analysis were found to match the estimation of the weight percent solid wax obtained from centrifuge data. The methodology (background and associated calculations) used to calculate the weight percent solid wax with decreasing sample temperature is explained briefly in the following sections.

FT-IR Spectroscopic Method - Background

The precipitated solid usually consisted of alkanes with a carbon number greater than 25 for crude oils. The amount of solid phase LCM carbon present would be equal to the amount of the solid in the sample analysed. Roehner [1, 2] used the following equation [2] to estimate the weight percent solids for crude oil systems.

$$\text{Wt \% solid} = [(c_s/c_{total})\,(f_{LCM\ carbon})\,(f_{carbon})\,(M)] * 100\% \qquad (2.7)$$

where c_s -- concentration of the LCM carbon in the solid phase

c_{total} -- total concentration of LCM carbon in the solid and liquid phases

$f_{LCM\ carbon}$ -- LCM fraction of carbon in the sample

f_{carbon} -- fraction of total sample comprised of carbon

M -- multiplier to account for additional material other than LCM carbon in the solid phase

The fractional and multiplier factors were assumed to be independent of temperature and hence summed into one factor C.

$$\text{Wt \% solid} = (c_s/c_{total})\,(C) * 100\% \qquad (2.8)$$

C is assumed to to be equal to 1 in the original work [2] and is followed in the calculations followed here.

As described in the earlier parts of this chapter, the absorbance at 720 cm^{-1} can be determined from the following equation:

$$A_{720} = a_l b c_l \quad \rightarrow \text{Above the WPT} \qquad (2.9)$$

$$A_{720} = a_l b c_l + a_s b c_s \quad \rightarrow \text{Below the WPT} \qquad (2.10)$$

The first term on the right hand side of equation 2.10 can be written as A_l, which is the liquid absorbance. The equation can be simplified to calculate the concentration of the solid phase.

$$c_s = (A_{720} - A_l)/\, a_s b \qquad (2.11)$$

Substituting into equation 2.8 we obtain,

$$\text{Wt \% solid} = [(A_{720} - A_l)/\, a_s b c_{total}] * 100\% \qquad (2.12)$$

The average sample absorptivity for the LCM carbon is a fraction of the solid LCM carbon absorptivity.

$$a_{av} = f\,a_s \tag{2.13}$$

Also,

$$A_{total} = a_{av} b c_{total} \tag{2.14}$$

Combining 2.13 and 2.14 and inserting the result in 2.12, the following expression for the weight % solid as obtained.

$$\text{Wt\% solid} = [(A_{total} - A_l)/\, A_{total}] * 100\% \tag{2.15}$$

Calculations

The A_l and A_{total} were determined from integrating the peak area from 735 – 715 cm^{-1} for various temperatures. The A_l (below the WPT) was determined by using a linear regression fit to the experimental peak area above the WPT and extrapolating it below the WPT. Equation 2.15 was then applied to calculate the weight % solid wax at various temperatures below the WPT. A sample plot is shown in Figure 14.

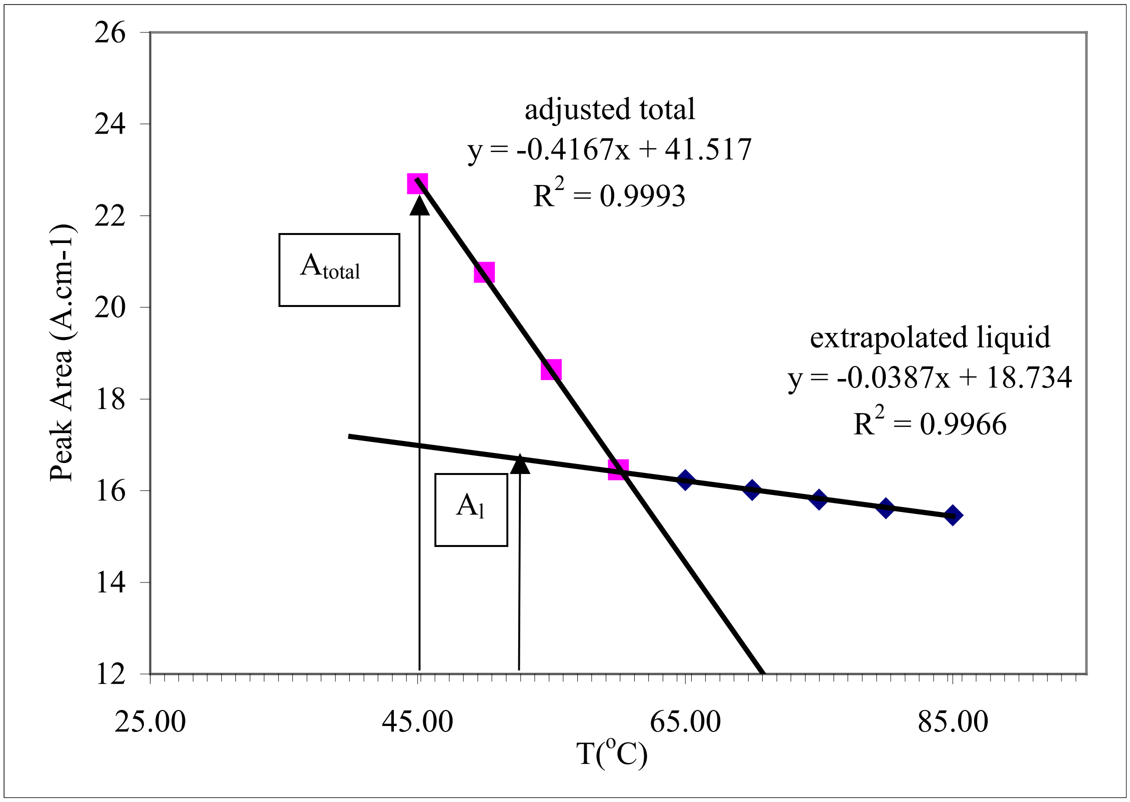

Figure 14. Model Oil A, Test run 5, Peak Area (735-715 cm^{-1}) versus Temperature

Results and Discussion

Model Oils A, B and C

The amount of solid wax formed was calculated using the methodology described previously for the three Model Oils. The weight % solid versus temperature for Model Oil A is presented in Figure 15. Similarly, the weight percent solid wax data for Model Oils B is presented in Figure 16. For all these Model Oils, it can be noted that the weight % solid goes to a value of around 35 weight % at the lowest temperatures analyzed. All the Model Oils were made up of approximately 35-weight % of the n-alkanes in the decane solvent. This provides additional validation for the use of the FT-

IR spectroscopic technique as a method for estimating the weight % percent solid data below the WPT. The weight percent solid data obtained from the FT-IR experiment is compared to the predicted weight percent data from thermodynamic modeling in the next chapter.

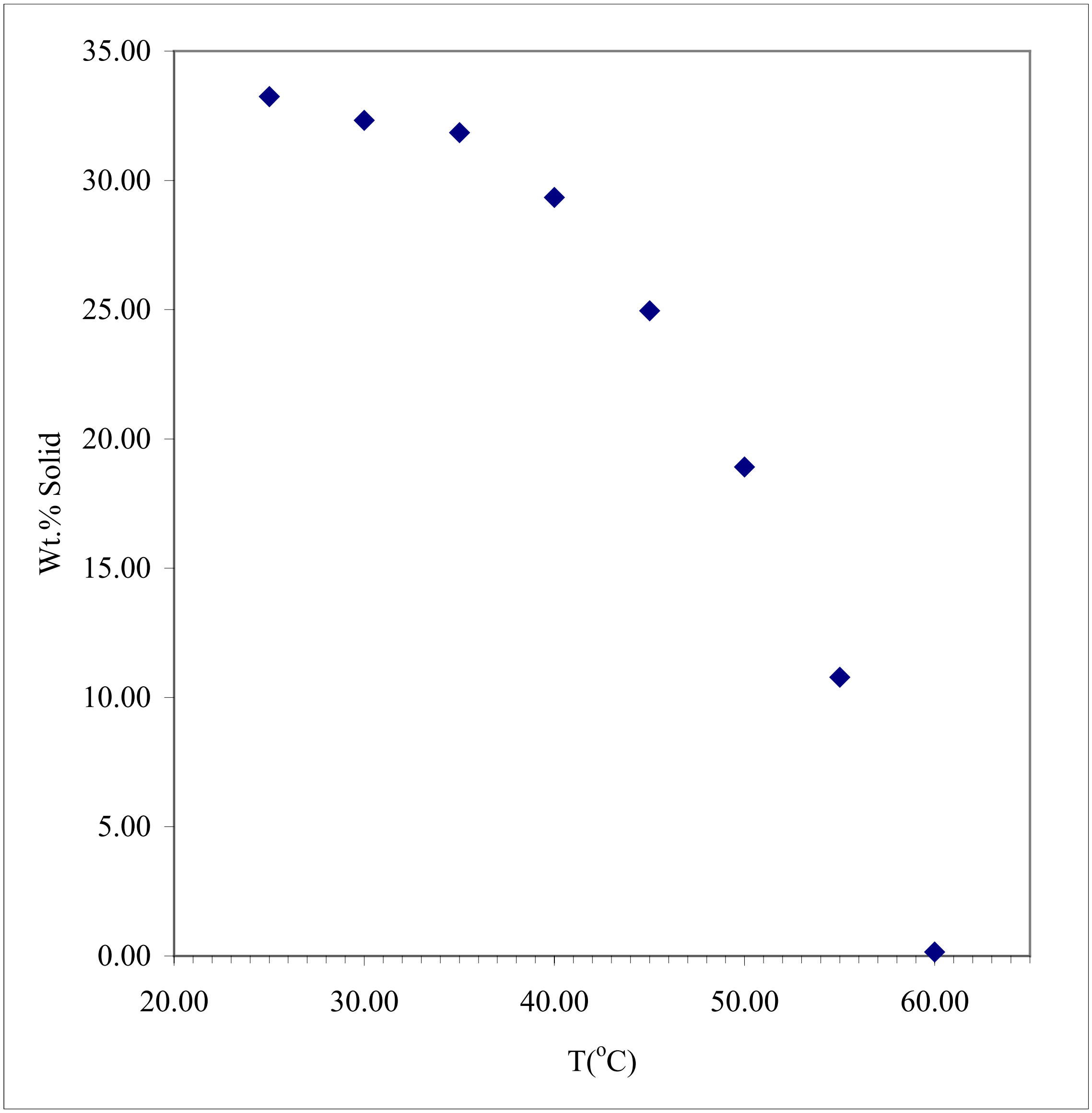

Figure 15. Model Oil A, Test run 5, Weight % Solid versus Temperature

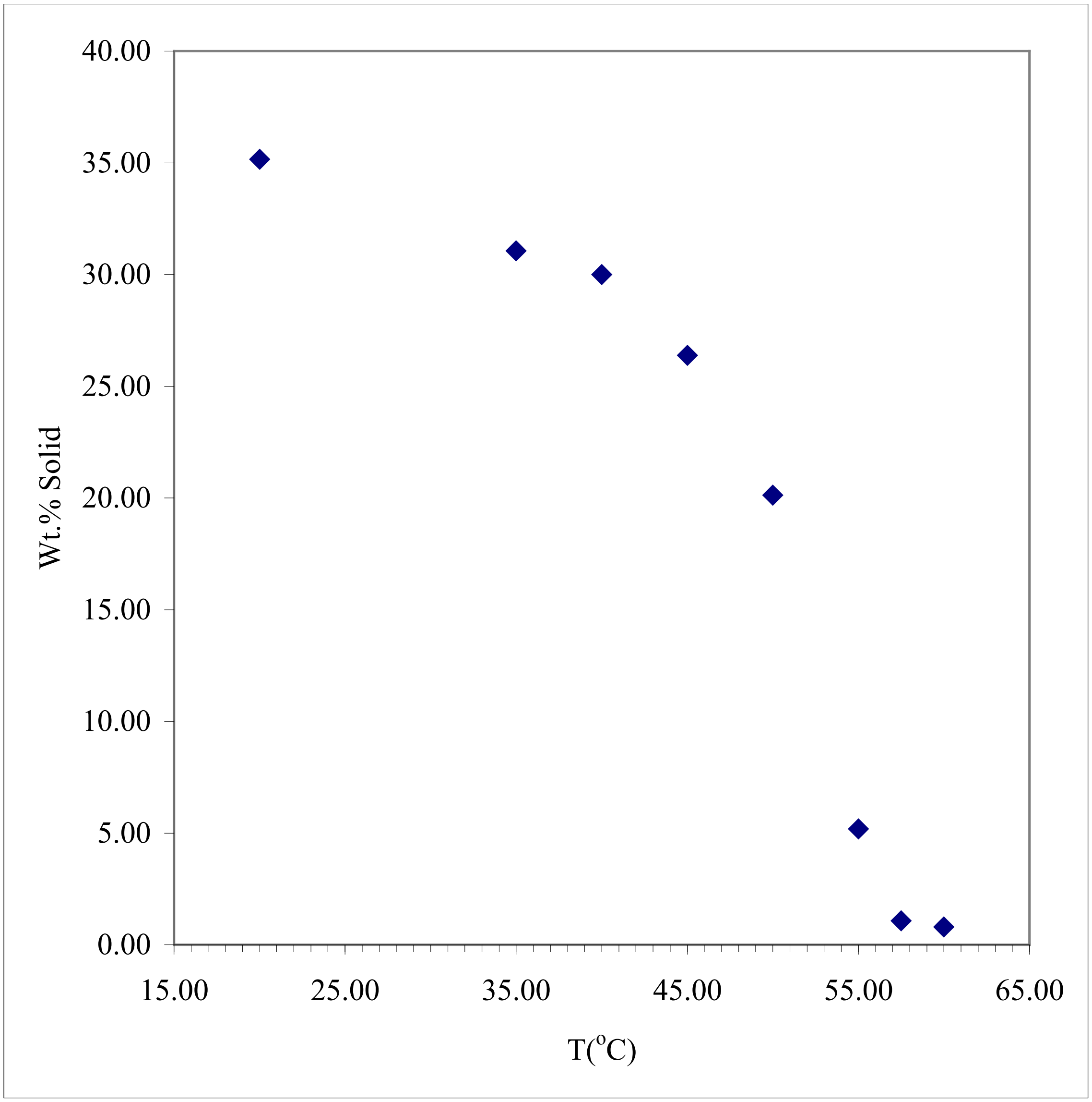

Figure 16. Model Oil B, Test run 4, Weight % Solid versus Temperature

THERMODYNAMIC MODELING

The solid-liquid equilibrium for the Model Oils studied in this work has been modeled using a model developed by Leelavanichkul [20] at the University of Utah. An activity coefficient based thermodynamic model was used in the modeling study. This model predicts the wax precipitation temperature and the weight percent solid and the precipitated solid composition below the WPT for various temperatures. The theoretical background and the model itself are discussed here.

Theoretical Background [21-26]

Solid-liquid phase equilibrium was used to study wax precipitation and amount of solid precipitation. The fugacity of the various components in the solid phase is equivalent to their corresponding fugacity in the liquid phase at thermodynamic equilibrium. This basic equivalence was used to develop a system of equations relating various thermodynamic properties. The solid-liquid equilibrium constant, K_i^{SL}, was obtained as,

$$K_i^{SL} = \frac{x_i^S}{x_i^L} = \frac{\gamma_i^L}{\gamma_i^S} \frac{f_i^{oL}}{f_i^{oS}} \exp\left[\int \frac{V_i^L - V_i^S}{RT} dP \right] \qquad (3.1)$$

where f_i^S is the fugacity of the component i in the solid phase, γ_i^S is the activity coefficient of component i in the solid phase, f_i^{oS} is the standard state fugacity of component i in the solid phase, x_i^S is the mole fractions of component i in the solid phase, V_i^S is the molar solid volume of component i, P is the pressure, R is the universal gas constant and T is the temperature. The terms in the equation relating to the liquid phase have the superscript *L*.

The standard state fugacity was derived as:

$$\frac{f_i^{oL}}{f_i^{oS}} = \exp\left[\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right)-\frac{1}{RT}\int_T^{T_i^f}(C_P^L - C_P^S)dT + \frac{1}{R}\int_T^{T_i^f}\frac{C_P^L - C_P^S}{T}dT\right] \tag{3.2}$$

where T_f is the normal melting temperature for a pure component, ΔH^f is the enthalpy change associated with a liquid-solid transition at a temperature lower than T_f, C_p^L and C_p^S are the liquid-phase and solid-phase heat capacities respectively.

The solid-liquid equilibrium constant was then modified and expressed as follows:

$$\frac{x_i^S}{x_i^L} = \frac{\gamma_i^L}{\gamma_i^S}\exp\left[\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right)-\frac{1}{RT}\int_T^{T_i^f}(C_P^L - C_P^S)dT + \frac{1}{R}\int_T^{T_i^f}\frac{C_P^L - C_P^S}{T}dT\right]\exp\left[\frac{P}{RT}(V_i^L - V_i^S)\right] \tag{3.3}$$

The above equation for the equilibrium constant was used as the basis for the modeling work carried out. The three terms indicated in the equation represents the effect of composition, temperature and pressure respectively in both the solid and liquid phases.

Model Description

It was assumed that the solid hydrocarbon content was a single homogeneous solid phase in equilibrium with the liquid phase. From previous work [25], the volume difference between the liquid oil and the solid wax that it forms does not seem to have an effect on the results obtained. When the volume change is small, the second exponential term in Equation 3.3 will be close to unity. Also the effect of pressure was found to be negligible on each phase [25].

The modified regular solution theory was used to describe the non-ideality of the solid and liquid phases. The regular solution theory has been used extensively for studying wax precipitation in crude oils [25, 27]. The activity coefficient ratio in Equation 3.3 was obtained by using a modified regular solution theory method [28] and the activity coefficients were calculated using the Scatchard-Hildebrand regular solution theory [29-33]. Including the activity coefficient ratio in Equation 3.3, the following expression for the equilibrium constant was derived.

$$\frac{x_i^S}{x_i^L} = \exp\left[\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right)-\frac{1}{RT}\int_T^{T_i^f}(\Delta C_{Pi})dT+\frac{1}{R}\int_T^{T_i^f}\frac{\Delta C_{Pi}}{T}dT+\frac{\nu_i}{RT}\left[(\bar{\delta}-\delta_i)_L^2-(\bar{\delta}-\delta_i)_S^2\right]\right] \tag{3.4}$$

where δ is the average solubility parameter of each phase and δ_i is the solubility parameter of component i in the mixture. Applying another substitution for the change in the heat capacity, the solid-liquid equilibrium equation was obtained.

$$\frac{x_i^S}{x_i^L} = \exp\left[\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right)-\frac{aMW_i}{RT}\left(\frac{T_i^f}{T}-1-\ln\frac{T_i^f}{T}\right)-\frac{bMW_i}{RT}\left(\frac{(T_i^f)^2}{T}+T-2T_i^f\right)+\frac{\nu_i}{RT}\left[(\bar{\delta}-\delta_i)_L^2-(\bar{\delta}-\delta_i)_S^2\right]\right] \tag{3.5}$$

Equation 3.5 was then numerically solved using the Newtons method [34] and the WPT and weight percent data were obtained.

Results and Discussion

The composition of the Model Oils was used in the thermodynamic model to calculate the WPT and the weight percent solid below the WPT. The WPT's obtained for the various Model Oils by thermodynamic modeling is shown in comparison with the average values obtained from the FT-IR spectroscopic technique in Table 6 below.

Table 6. Comparison of WPT's for Various Model Oils from Different Methods

	FT-IR – Avg. WPT	Modeling - WPT
Model Oil A	61ºC	62ºC
Model Oil B	61ºC	60ºC

The WPT's from the thermodynamic modeling are found to match the WPT's from the FT-IR experiment closely. The weight percent solid wax at different temperatures below the WPT for Model Oil A obtained from the modeling study was compared to the weight solid wax content obtained from the FT-IR experiments as described previously. This is presented graphically in Figure 17. Similarly the comparison plots for Model Oil B is presented in Figure 18. The predicted values of the amount of wax below the WPT are higher for Model Oil A than the experimentally observed values.

The thermodynamic model used in this work can be developed further. More detailed information on the Model Oils will be required for the development of the wax precipitation model. The Model oils used in this work may consist of some amount of isoparaffins. This has been observed in HTGC studies of the Model Oils used in this work. Complete characterization of the Model Oils using the HTGC technique will enable the thermodynamic model to predict solid-liquid equilibria data closer to experimental values.

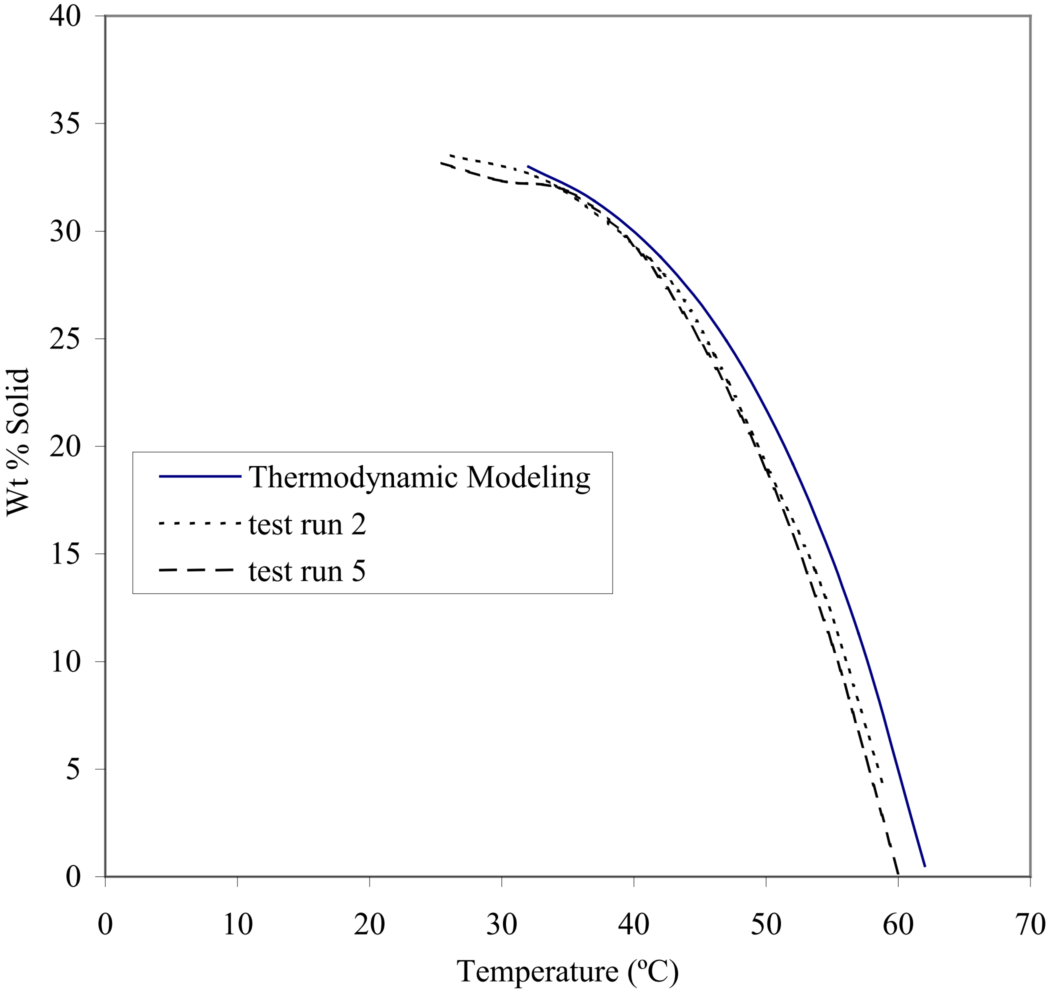

Figure 17. Model Oil A, Comparison of Weight % Solids below the WPT from Different Experimental Runs and Modeling.

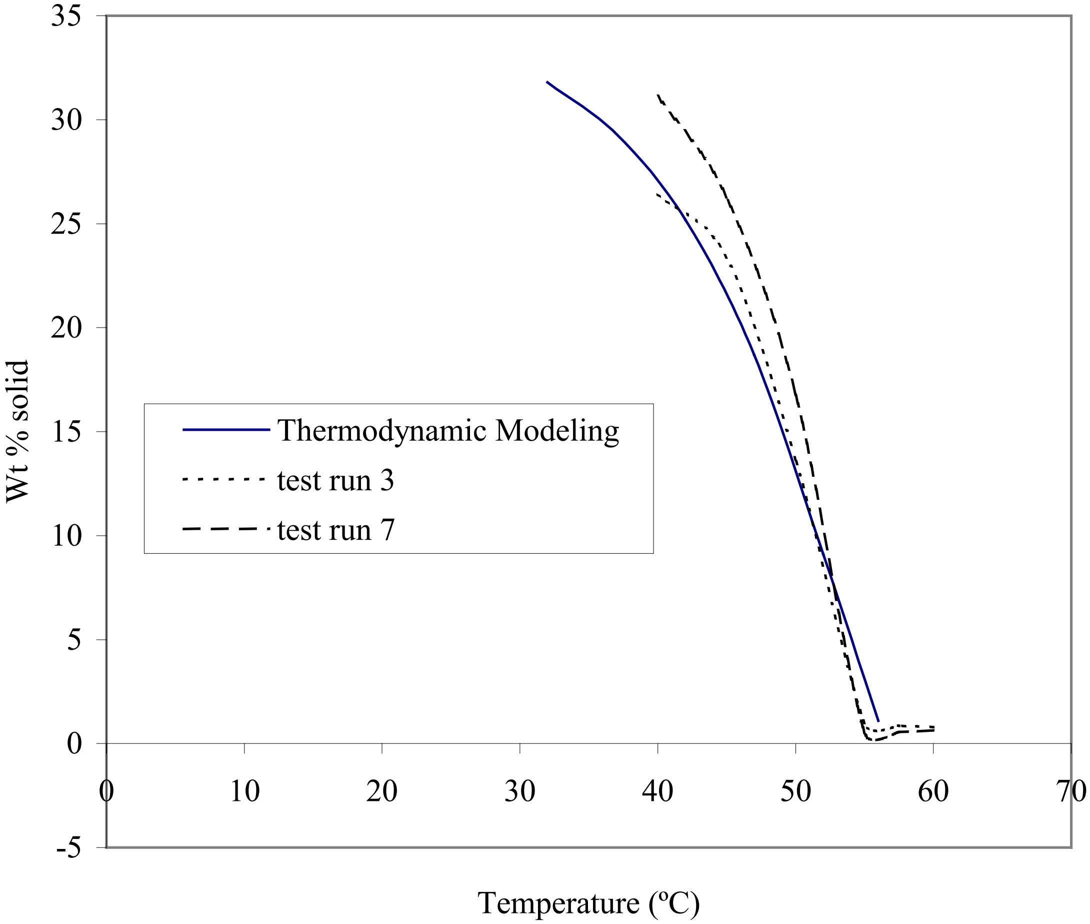

Figure 18. Model oil B, Comparison of Weight % Solids below the WPT from Different Experimental Runs and Modeling.

CONCLUSIONS

Model Oils of heavy alkane hydrocarbons in significantly lighter hydrocarbon diluents were prepared and analyzed. These Model oils provided initial representative behavior of the solid-liquid equilibria of the F-T products.

The FT-IR spectroscopic technique was successfully used to obtain solid-liquid equilibria data. It was found to accurately identify the wax appearance temperature for the various mixtures. The DSC method was used as a secondary method of determining the WPT.

The FT-IR method was also used to calculate the amount of solid wax below the WPT as a function of temperature. The wax precipitated below the WPT can be separated by conventional methods such as filteration and analyzed using the high temperature gas chromatography. The correction for trapped liquids in the filtered solid phase can be made by HTGC. This can then be compared with the predicted compositions of the precipitated wax using the activity coefficient based thermodynamic model. The characterization of the solid and liquid equilibrium compositions for Model Oils at and below the WPT will provide data usable in the advancement of SLE modeling and understanding the nature of hydrocarbon solid-liquid equilibria at temperatures at and below the WPT.

The Model Oils considered in this work were comprised only of normal alkanes. The FT-IR method applied in this study can be now used to investigate Model Oils with the inclusion of naphthenic, olefinic and aromatic compounds potentially present in the F-T mixtures and processed (reformed) F-T mixtures. Also the experiments can be carried out at conditions of higher pressure and temperature. The SLE data thus obtained from the FT-IR experiments could be combined with data from Near-IR (NIR) and UV spectra for measuring solid-liquid-vapor equilibria for F-T mixtures.

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LIST OF ACRONYMS AND ABBREVIATIONS

C #	Carbon Number
CH_2	Methylene
CPM	Cross-Polarized Microscopy
DSC	Differential Scanning Calorimetry
F-T	Fischer-Tropsch
FT-IR	Fourier Transform-Infrared Spectroscopy
HTGC	High Temperature Gas Chromatography
IR	Infrared
LCM	Long Chain Methylene
NIR	Near Infrared
SLE	Solid Liquid Equilibria
UV	Ultra Violet
WPT	Wax Precipitation Temperature

APPENDIX A

SAMPLE OIL AND MODEL OIL COMPOSITIONAL DATA

TABLE A.1. SAMPLE OIL A

Component	Wt %
nC10	65.1
nC32	17.5
nC36	17.4
total	100.0

TABLE A.2. SAMPLE OIL B

Component	Wt %
nC10	65.17
nC32	34.83
total	100.00

TABLE A.3. SAMPLE OIL C

Component	Wt %
nC10	65.71
nC36	35.29
total	100.00

TABLE A.4. MODEL OIL A

Component	Wt %
nC10	65.036
n-alkanes	34.964
total	100.00

Individual n-alkanes	Mole %
nC30	16.6356
nC32	16.5842
nC34	16.6613
nC36	16.6420
nC40	16.7770
nC44	16.6999
total	100.0000

TABLE A.5. MODEL OIL B

Component	Wt %
nC10	65.26
nC30	7.583
nC32	7.98
nC34	10.673
nC36	4.494
nC40	2.236
nC44	1.772

TABLE A.6. MODEL OIL C

Component	Wt %
n-C10	64.73
n-C20	10.30
n-C21	7.40
n-C22	5.29
n-C23	3.79
n-C24	2.70
n-C25	1.93
n-C26	1.37
n-C27	0.97
n-C28	0.69
n-C29	0.49
n-C30	0.35
total	100.00

APPENDIX B

FT-IR SPECTROSCOPY OF CRUDE OILS/MODEL OILS

Prepared by:	R. Roehner / D. Reese/ R. Karthik
Applicable to:	**FT-IR Spectroscopy of Crude Oils/Model Oils**

Technical Review:	N. F. Dahdah	Date:
Safety Review:	N. F. Dahdah	Date:
Quality Assurance Review:	J. V. Fletcher	Date:
Management Review:	F. V. Hanson	Date:

SCOPE: This procedure addresses the generation of infrared (IR) spectra for crude oil/model oil samples, and the interpretation of the spectra to obtain wax precipitation temperature (WPT) and estimation of weight percent precipitated solid wax versus temperature. Specifically this method covers the measurement of IR absorbtion at wave numbers in the region from 4000 cm^{-1} to 650 cm^{-1}, at temperatures ranging from 60°C to -5.0°C using a temperature controlled liquid sample cell of known path length.

SUMMARY OF THE METHOD: The crude oil/model oil IR spectra (from 4000 cm^{-1} to 600 cm^{-1}) are obtained over a temperature range (60°C to -5.0°C) by measuring IR absorbance of a neat sample held in a temperature controlled liquid cell between NaCl windows using a Fourier Transform-Infrared (FT-IR) Spectrometer. Peak areas attributed to rocking vibrations of long chain methylene groups for each temperature are obtained by integration of the spectral data from 735 cm^{-1} to 715 cm^{-1}. A plot of these peak areas versus temperature is generated using an electronic spreadsheet and used to identify the WPT and estimate wt.% solid versus temperature. The hardcopy results produced from this procedure include: a printed IR spectra (4000 cm^{-1} to 600 cm^{-1}) collected at approximately 45-70°C (liquid state), a printed overlay of IR spectra from approximately 760 cm^{-1} to 690 cm^{-1} for all temperatures used to identify the WPT, and the printed results of spreadsheet calculations for the WPT and estimation of wt.% solid versus temperature. All spectra obtained are saved as electronic data files. A replicate analysis is performed to verify that the values obtained for the WPT and wt.% solid versus temperature are within the estimated precision for the method.

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Related Procedures:

U004 Liquid Sample Storage & Production Procedure

University of Utah Chemical Hazardous Waste Disposal Procedures (available online at www.ehs.utah.edu/enviro/dispose.htm).

SAFETY PRECAUTIONS: Crude oil, model oils, toluene, and chloroform are toxic-flammable materials. Crude oil vapors can cause a flash fire. Review and consult MSDS.

TABLE OF CONTENTS

List of Tables / Figures / Example Forms

A. Equipment and Supplies

Two FT-IR spectroscopic systems are used. The sketches of the FT-IR spectroscopy systems used are given in Figure 4 and Figure 5.

1. Perkin Elmer 1600 FT-IR Spectrometer or 16-PC Spectrometer, with Spectrum v2.00 Software running on a PC with plotting capability, or equivalent.
2. IBM Formatted 1.44 MB, 3.5" Disc.
3. SpectraTech HC-32 Temperature Controlled Liquid FT-IR Cell (modified by replacement of stainless steel coolant loop with ¼" copper tubing loop for increased coolant flow) with 32mm NaCl windows (Special Care Note 1), and a 0.100 mm lead spacer. Two FT-IR cells are used, one with a K-Type thermocouple and the other with a J-Type thermocouple.
4. Brookfield TC-500 Bath or equivalent.
5. Brookfield HT-105 Controller or equivalent.
6. Omega HH-22 Digital Thermometer or equivalent.
7. Julabo F-25 Bath with a Julabo TCCB RTD converter.
8. Syringe, 3 cc, Luer - Lock Tip.
9. Syringe, 10 cc, Luer - Lock Tip.
10. Gloves, nitrile
11. Beaker (3), 50 ml , Pyrex or equivalent.
12. Kimwipes
13. 50 ml sample bottle, screw lid with teflon coating
14. Sorbent pad(s)
15. Dry nitrogen supply via small diameter teflon tubing.
16. 250 ml Erlenmeyer Flask, with side connection.
17. Form 201-2 FT-IR LCS Data Sheet
18. Form 201-3 FT-IR Testing Experiment Data Sheet

SPECIAL CARE NOTE (1): NaCl liquid cell windows must be stored in a dessicator, and never allowed to come in contact with water.

B. Reagents and Standards

1. Chloroform, HPLC grade.
2. Toluene cleaning solvent.
3. 3M Quantitative IR Card 61 (polyethylene), Part No. 0020-104.

C. Quality Control

1. Sample Batches. A sample batch is to be comprised only of a single aliquot taken from a single source of crude oil (parent sample)/model oil, and must be analyzed (same test period) immediately after successful production of an IR spectra for an LCS per section D of this procedure.

2. Instrumentation. The FT-IR Spectrometer to be used must be able to repeat wavenumber absorbance measurements within +/- 1.0%, and with 4 cm^{-1} resolution. Perkin Elemer 1600 FTIR, or 16-PC FT-IR Spectrometers must pass an instrument performance verification (IPV) performed by Perkin Elmer on a yearly basis. Equivalent FT-IR Spectrometers must be certified in an equivalent manner.

3. Analysts. Analysts involved in sample testing must have met training requirements for the procedure to be used. Training for this procedure involves the performing the procedure for five samples from the same aliquot while monitored by an analyst experienced in the procedure. Training test results produced by the student analyst must meet procedure performance criteria.

4. Accuracy. Each sample and replicate analyzed must include a duplicate analysis of an LCS at the start of testing. This LCS must have been previously analyzed to obtain a known IR spectra. (Note: Bias cannot be determined for this procedure, since there are no acceptable reference standards.) This repeat analysis of the LCS must show absorbance measurements for specified peaks in the spectral region between 4000 cm^{-1} to 650 cm^{-1} to be repeatable within ± 5.0%. Temperature measurement associated with this procedure is ± 1.0°C.

5. Precision. Procedure precision will be checked through analysis of a replicate sample taken from the same sample aliquot. Values for the WPT obtained from the sample and replicate analyses should be within ± 1.0°C. Values for estimated wt.% solid obtained from the sample and replicate analyses should be within ± 10% for temperatures more than 5°C below the WPT.

D. Calibration and Standardization

1.) Any calibration required for the Perkin Elmer 1600 Series FT-IR Spectrometers (1600 or 16-PC) must be performed by a manufacturers representative as part of passing an IPV certification by Perkin Elmer. An IPV certificate must be obtained yearly. *Note: Moving the FT-IR spectrometer will necessitate re-certification.*

2.) A laboratory control standard (LCS) of polyethylene film in the form of a fabricated Quantitative IR card is to be used. Analysis of the LCS will consist of sixteen scans to generate known data. Experimental results are then summarized on Form 201-2 FT-IR LCS Data sheet for each peak absorbance in the spectral region between 4000 cm^{-1} to 650 cm^{-1}. Each subsequent analysis of the LCS as part of this general testing procedure must reproduce the peak absorbances (within 4 cm^{-1} location) of designated peaks within +/-1.0%.

3.) The HC-32 liquid cell thermocouple (TE-002) must be checked prior to each sample analysis using an Omega HH-22 Digital Thermometer (TI-000) by comparing the measured liquid cell temperature (TE-002) with the liquid cell temperature measured by the reference thermocouple (TE-001). These thermocouples should differ by no more than 0.2°C. The reference digital thermometer/thermocouple (TI-000/TE-001) must be calibrated (± 1.0°C) to NIST standards on a yearly basis.

E. Procedure

Keep all notes in a numbered project lab notebook.

Procedure for Preparation of LCS

1. Obtain Form 201-2 FT-IR LCS Data Sheet. Record the initial information requested, also start an entry in a TAPS-COS Lab Notebook to document notes relating to LCS preparation and testing.

2. Obtain and label a polyethylene IR card as LCS### (i.e. LCS001, LCS002 as required in sequence) using a ballpoint pen.

3. After switching on the FT-IR Spectrometer and allowing it to warm up for 30 minutes, obtain a sixteen scan IR spectra from 4000 cm^{-1} to 650 cm^{-1}, with 4.0 cm^{-1} resolution, using Spectrum v2.00 Software and save spectra as LCS###.sp (i.e. LCS001.sp, LCS002.sp, LCS003.sp, etc.) at room temperature.

4. Complete Form 201-2 FT-IR LCS Data Sheet to determine values and locations for specified peak absorbances.

5. Place IR card in a polyethylene storage bag, seal and place in cupboard at room temperature.

6. Place the completed Form 201-2 FT-IR LCS Data Sheet in the TAPS-COS project file, and place a copy of the completed form with the LCS-IR card stored.

Analytical Sequence:

1. Start entries on Form 201-3 FT-IR Test Experimental Data Sheet, and in the lab notebook.

2. Obtain an 8 ml aliquot of the crude oil to be tested into an 8 ml sample vial with a teflon coated lid per U004 Liquid Sample Storage & Production Procedure (this requires an initial day of work, and therefore should be undertaken prior to any FT-IR work). This is not necessary for the Model Oils.

3. Using the calibrated digital thermometer/thermocouple (TI-000/TE-001) check the HC-32 liquid cell thermocouple (TE-002). This is done by connecting TE-002 to port 1 on the HH-22 digital thermometer, and inserting the reference thermocouple (TE-001) between the metal cell body and the cell heat retention ring. Record the difference between the thermocouples after an equilibration time of approximately 10 minutes. This difference should not be greater than 0.2°C. If a greater temperature difference exists, do not collect data-troubleshoot difference to resolution with criteria of maximum 0.2°C difference. This work is not necessary when using the Spectroscopy system II which has a feedback loop back to the heater/cooler system.

4. Switch on Perkin Elmer 1600 FT-IR Spectrometer and allow to warm-up for 30 minutes, and insert a 3.5" computer disc for file storage/backup. <Notes: It is best to leave the spectrometer on at all times. For a detailed description of the following steps involving interface operation of the Perkin Elmer 1600 FT-IR Spectrometer see Running The Model 1600, Tutorials For New Users, Perkin Elmer, November 1987, Instructions - Model 1600, FT-IR Spectrometer, November 1987, and on-line documentation for Spectrum v2.00 Software.>

5. Obtain a background IR spectra using the Spectrum v2.0 software and the FT-IR spectrometer with an empty sample holder (equivalent to the air in the lab) for 4000 cm^{-1} to 650 cm^{-1}, 4.0 cm^{-1} resolution, 16 scans. Name the background file as scanbg##.sp, where ## is a sequential number for the background scans, and .sp is the spectrum file designator for the Spectrum v2.0 software. Provide the following as a file descriptor as input in the file setup window: Background, date (i.e., Background, 8/3/00) Print a copy of the background spectrum obtained for data review.

6. Obtain a replicate IR spectra for the current LCS at room temperature using the Spectrum 2.0 software. Plot the current LCS and replicate LCS spectra on the screen (previously run and saved), and using the screen cursor, verify that the measured absorbance values are within $^{+}$5.0% and that the peaks are located within 4 cm^{-1} of the previously measured / reported values for the LCS. If observed absorbances do not meet these criteria, the observed results are not "comparable", and no data collection should take place until this problem is resolved. Print a copy of the LCS replicate spectra obtained for data review. Name the replicate LCS file as LCR###.sp (i.e., LCR001.sp, LCR002.sp, etc.), where ### is a sequential number for the replicate scans, and .sp is the spectrum file designator for the Spectrum v2.0 software. Provide the following as a file descriptor for input in the file setup window: Background, date (i.e., Background, 8/3/00) Print a copy of the background spectrum obtained for data review.

<Note:If the current observed LCS IR spectra is not comparable to the reference LCS### spectra, then repeat the measurement to verify the unacceptable condition. Should this repeat confirm a problem exists, then begin troubleshooting the system per operators manual. DO NOT ATTEMPT TO COLLECT SAMPLE DATA UNTIL PROBLEM IS RESOLVED, as evidenced by successful repeat analysis of the LCS. >

7. Assemble the HC-32 liquid cell per reference 4 with a 0.10 mm Lead spacer.

8. Obtain an IR spectrum of the assembled empty liquid cell in transmission mode using the Spectrum 2.0 software with the following parameters: range 4000-650 cm^{-1}, 4 scans, 4 cm^{-1} resolution. Calculate the current cell path length using the equations on Form 201-3 FT-IR Test Experimental Data Sheet, as described in reference 4.

9. Insulate the assembled HC-32 liquid cell, connect the calibrated HH-22 digital thermometer (or equivalent) to the HC-32 liquid cell thermocouple, and use a Brookfield TC-500 Bath / HT-105 Controller (or equivalent) to raise the HC-32 liquid cell temperature to approximately 50°C as measured using the HH-22 Digital Thermometer.

10. Heat the crude oil sample aliquot in the 8-ml sample vial with screwed on Telflon lid to approximately 60°C in convection oven for 1 hour, shaking the sample vial vigorously every 10 minutes. Also, heat a 3 cc Luer Lock syringe in the convection oven to approximately 60°C. *Safety Note: Place the 8-ml vial in a 100 ml beaker to prevent spillage if the vial breaks, and wear safety glasses and leather gloves when shaking the heated sample vial.*

11. While wearing safety glasses and nitrile gloves, fill the HC-32 liquid cell using the preheated 3 cc Luer Lock syringe filled with ~2 cc of crude oil from the 8 ml sample vial. Angle the liquid cell during filling so that the exit port is higher than the fill port so any bubbles will be swept out of the cell. Prior to filling, protect the front cell window from spillage by tamping Kimwipes around the fill and exit ports. Place the syringe containing any remaining oil under the fume hood for later cleaning. Screw the lid onto the 8 ml sample vial tightly and place the vial (now containing ~5 ml) on the lab bench to cool back to room temperature (additional crude oil from the vial will be needed to perform a replicate analysis later). *Notes: a.) It is hoped that improved liquid cell design and procedure modification will allow direct filling of the FT-IR liquid cell from the Welker constant pressure sample cylinder to avoid loss of light ends associated with syringe filling of the liquid cell. b.)*

12. Inspect the liquid cell for any evidence of vapor pockets (bubbles) and refill the cell using the syringe containing remaining crude oil if any exist. Place the filled liquid FT-IR cell in the FT-IR Spectrometer, being careful to be sure that the liquid cell foam insulation is not in the beam path, and that the spectrometer door is not cutting off flow from the temperature bath.

13. Move the set point of the HT-105 temperature controller downward from 50°C to produce an approximate liquid cell temperature of 45°C as measured using the HH-22 digital thermometer. Manually record the time and liquid cell temperature in the laboratory notebook.
14. When the liquid cell temperature reaches thermal equilibrium at approximately 45.0°C as evidenced by the liquid cell temperature changing no more than 0.1°C in five minutes, use the Spectrum v2.0 software to obtain an IR spectrum from 4000 cm^{-1} to 650 cm^{-1} with the following instrument input parameters: 16 scans, 4 cm^{-1} resolution. Name the data file in the setup window in a sequence including: the U of U Sample Id. No., a letter starting with A for each test series, and a number corresponding to the spectra number (i.e., U####A1.sp, where U#### is the sample ID, A is the first spectra series obtained, 1 indicates the first temperature, and sp is the file designator for spectra files). Provide the following for the spectrum description in the setup window: Crude Oil Name, Temperature (°C), Date, cell path length (mm) (i.e., Crude Oil XYZ, 45.3°C, 8/3/00, 0.09987 mm). Save spectra to PC hard drive. Record the temperature, and absorbance at approximately 720.7 cm^{-1} in the laboratory notebook.

15. Decrease the HT-105 set point to produce a liquid cell temperature approximately 5°C below the last test temperature and repeat steps 13, 14 until the cell temperature can no longer be decreased (approximately -5°C). Increment each file name (i.e., U002A1.sp, U002A2.sp, U002A3.sp….etc.).

16. Complete Form 201-3 FT-IR Testing Experimental Data Sheet by summarizing observed peak data for the spectra obtained at approximately 45°C. Plot full range FT-IR spectra obtained at approximately 45°C and attach to Form 201-3.

17. Complete Form 201-4 Crude Oil FT-IR Calculation Sheet for identification of crude oil WPT and estimation of wt.% solid vs. temperature. Plot the change in peak area (735-715 cm^{-1}) over the temperature range tested and attach to completed Form 201-4. Also, attach printed output from Peak Area/Height integration performed using Spectrum v2.0 software.

18. Repeat the above steps for a replicate analysis of the crude oil aliquot, incrementing the letter designation in the filename to B, C, etc as required (i.e., for the first replicate U002B1.sp, U002B2.sp, U002B3.sp and for another replicate-if required U002C1.sp, U002C2.sp, U002C3.sp). If the WPT values, and wt.% solid vs. temperature values obtained from completion of Form 201-4 are not within 1°C and 10% respectively for the sample and replicate analyses, additional replicate analyses shall be performed to obtain representative average values for the sample aliquot tested (maximum of 3 replicates – limited by aliquot volume).

19. General Notes for Steps 13-18:

- Once the liquid cell temperature reaches room temperature (~21°C) and continues to drop, It is necessary to hook up a compressed nitrogen tube from a compressed nitrogen cylinder to the sample to prevent water from forming on the NaCl window.

Insert the two tube openings into the cell—the soft end in through the top and the stiff end in through the bottom hole in the cell (secure the stiff tube with a small cork). Keep dry nitrogen flowing until the cell temperature has come back up to room temperature.

- It is important to overlay the generated spectra throughout the procedure in order to check for any vapor pockets (bubbles) in the sample. Do not change the set point for the water bath until you have verified that no bubbles are present. The overlaid spectra should show consistent slight increasing in absorbance. If any part of the spectra is inconsistent (i.e. sudden jumps in peaks that were not in the previous spectra or a significant decrease in absorbance), rid the vapor pockets by adjusting the exit ports until the bubbles have disappeared.

Cleanup / Documentation:

1. The following should be done under an operating fume hood while wearing safety glasses and nitrile gloves. Remove liquid FT-IR cell plugs, attach a 10 cc syringe full of toluene cleaning solvent to the cell sample outlet, and connect vacuum supply tubing to the cell sample inlet. Apply vacuum to remove crude oil sample via a toluene flush and collect as waste using a 50 ml Erlenmeyer Flask as a vacuum receiver, with side arm connection to a vacuum supply.

2. Disassemble liquid cell, and triple wash all parts in contact with crude oil with HPLC grade chloroform under an operating fume hood, while wearing safety glasses and nitrile gloves. After final chloroform rinse of NaCl windows, remove all residual solvent from the windows by purging with dry nitrogen for approximately 15 minutes under the fume hood (suggest placing windows in a Kimwipe lined 100 ml beaker, with tube outlet from dry nitrogen supply, covered by a watch glass). Place clean/dry NaCl windows in dessiccator for storage.

3. Rinse syringes by filling and expelling toluene-cleaning solvent (3 volumes), followed by HPLC grade Chloroform (3 volumes), and finishing with distilled water (3 volumes). Disassemble syringes, and allow to air dry after wiping free with kimwipes.

4. Backup copy all spectra obtained to a 3.5" data disc. Label the disc with the Crude Oil name, test date, and spectra filenames.

5. Provide the following to the U of U Data Review Team Leader for the sample and replicate(s) tested:

- Backup data on 3.5"disc.
- Printed background and LCS spectra.
- Completed Form 201-3 FT-IR Testing Experimental Data Sheet (with printed spectra at 45°C attached).

- Completed Form 201-4 Crude Oil FT-IR Calculation Sheet (with attached printed spectra indicating change in peak area for 735 to 715 cm-1 over the temperature testing range, and attached printed Peak Area/Height integration results from Spectrum v2.0).

< Note: Total time for the analytical and cleanup/documentation sequences of this procedure is approximately 8-11 hours each for sample and replicate analyses, excluding time spent obtaining a liquid sample aliquot per procedure U004. >

F. Data Management

F.1 Data Acquisition / Recording

- Record all notes in laboratory notebook-manual record of test temperatures.
- Form 201-2 FT-IR LCS Data Sheet.
- Form 201-3 FT-IR Test Experimental Data Sheet
- Electronic data acquisition using Spectrum v2.0 software provided with Perkin Elmer Model 16PC FT-IR.

F.2 Data Transformation

- Provided by Perkin Elmer Model Spectrum v2.00 software for mathematical calculations for calculation of absorbance / transmittance measurements.
- Provided by Form 201-4 FT-IR Calculation Sheet for calculation of WPT, and wt.% solid vs. temperature values.

F.3 Data Transmittal

- Provided by analyst turnover of lab notes, computer discs, and completed Forms-109, 150 with attached IR spectra to U of U Data Review Team Leader.
- Provided by U of U Data Review Team Leader turnover of completed Form 151 Crude Oil FT-IR Data Review/Validation/Verification-Tracking Sheet, and folder containing completed Forms-109,150 with attached IR spectra to QA manager for 2nd level review.
- Provided by QA manager turnover to Principal Investigator(PI) of Form 151 Crude Oil FT-IR Data Review/Validation/Verification-Tracking Sheet for approval to report.

F.4 Data Reduction

- Provided by data summary on Form 201-3 FT-IR Test Experimental Data Sheet.
- Provided by Form 201-4 FT-IR Calculation Sheet for calculation of WPT, and wt.% solid vs. temperature values.

F.5 Data Analysis

- Provided by analyst in completion of Form 201-3 FT-IR Testing Experimental Data Sheet.
- Provided by Form 201-4 FT-IR Calculation Sheet for calculation of WPT, and wt.% solid vs. temperature values.

F.6 Data Tracking

- Provided by completion and filing of Form 151 Crude Oil FT-IR Data Review/Validation/Verification-Tracking Sheet by the UoU Data Review Team Lead, QA Manager, and Principal Investigator.

F.7 Data Review, Validation, Verification

- Provided by 1st level review of Data Review Team Leader who will review completed Forms (Form 201-3 FT-IR Test Experimental Data Sheet, and Form 201-4 Crude Oil FT-IR Calculation Sheet) attached plotted spectra, and lab notebook entries for consistency and adherence to this laboratory procedure. The data review team lead will enter results for WPT and wt.% solid vs. temperature into a project summary Excel spreadsheet database for report generation by both Sample and Test number. The Data Review Team Leader requests QA Data Manager to provide 2nd level review to validate/verify the data for reporting.

- Provided by 2nd level review of QA Data Manager by validating/verifying that the data entry in project summary Excel spreadsheet database matches experimental results.

F.8 Data Storage & Retrieval

- Provided by project Excel Spreadsheet database (and electronic backup CD thereof).
- Provided by electronic data files on 3.5"disc, (and electronic backup copy on CD) for saved spectra/data files produced by Spectrum v2.0 software.
- Project Lab Notebook entries.
- Filed hard copies (1 copy to Test Folder, 1 copy to Sample Folder) of Form 201-2 FT-IR LCS Data Sheets, Form 201-3 FT-IR Test Experimental Data Sheets with attached plotted IR spectra, and Form 201-4 FT-IR Calculation Sheet with attached plotted IR spectra.

F.9 Data Reporting

- Provided by U of U Data Review Team Leader after approval of University of Utah project QA Data Manager and Project Manager/Principal Investigator.

F.10 Data Publication Authorization/Restriction

- Data is not to be published without approval of research sponsor.
-

G. Method Performance

1. Training Requirements - Analysts involved in sample testing must have met training requirements for the procedure to be used. Training for this procedure involves preparing and analyzing an LCS, performing the procedure for two sample batches from the same parent sample while monitored by an analyst previously trained in the procedure. Training test results produced by the student must meet procedure performance criteria. One analyst is expected to complete all work comprising a single sample batch.

2. Results reported for this procedure must be collected after successful duplication of absorbance values for an LCS.

H. Waste Management

Dispose of any contaminated material or spills per University of Utah Chemical Hazardous Waste Disposal Procedures (available online at www.ehs.utah.edu/enviro/dispose.htm).

Form 201-1 Crude Oil Data Review/Validation/Verification Tracking Sheet

Crude Oil FTIR Data Review/Validation/Verification Tracking Sheet

For Procedure U201 Date: Analyst:

Project Title/Sponsor: ____________ **U of U Sample ID:** ________________________
Project./Acct. No.: ____________ Sub Sample No.: ________________________
Supplied Sample No.: ________________________
Lab Notebook No.: ____________ Sample Description: ________________________
Pages: ____________ ________________________
LCS No.: ________________________

1st Level Review By:______ Date:_________________

__Lab Notebook Notes - Exist/Clear/Signed & Dated
__Backup Data Disc (3.5" disc provided)
__Printed Background Spectra - Valid
__Printed LCS Replicate Spectra - Valid
__Form 201-3 Completed and spectra attached
__Form 201-4 Completed and spectra attached
__Performance Criteria Met (WPT for Sample & Replicate +/- 1^{o}C, wt.% vs. temp.10%)
__Copy of Data to Sample Folder(with 3.5" data disc)
__Copy of Data to Test Folder
__Summary Data to Project Excel Database

2nd Level Review By:______ Date:_________________

__Sample Folder Data matches Summary Project Excel Database Entry
__Performance Criteria Met (WPT for Sample & Replicate +/- 1^{o}C, wt.% vs. temp.10%)

Approved - Report To Client By:_________ Date:_

Assigned Final Report Preparation To: ___________________
Planned Reporting Date: ___________________

Reported To Client By:_________ Date:_

Form 201-2 FT-IR LCS Data Sheet (Example)

FT-IR LCS Data Sheet

For Procedure U201, U252

Date: Analyst:

Project Title/Sponsor: ______________

Project./Acct. No.: ______________

Lab Notebook No.: ______________ **Assigned LCS No.:** _______

Pages: ______________

LCS Prep. Data:

Polyethylene Film Data : ____________________________________

LCS FT-IR Analysis of Data:

	Absorbance		
Approx Wave No.:	~ 2900 cm^{-1}	~ 1470 cm^{-1}	~ 720 cm^{-1}
Duplicate#			
T1			
T2			
T3			
T4			
T5			
T6			
Ave.			
s			
RS			

Ave. = {(T1+T2+T3+T4+T5+T6) / 6 }

deviation = d# = abs{ Ave. - (T# Abs.) }

s = Std. Dev. = $\{ [(d1)^2 + (d2)^2 + (d3)^2 + (d4)^2 + (d5)^2 + (d6)^2] /5\}^{(1/2)}$

s = ________

RS = Relative Std. Dev.= (s / Ave.) x 100%

RS =%

Notes:

1.) **Precision of RS < 1 % Required By This Procedure**

Final LCS Computer Data File Name: ________________________________

Form 201-3 FT-IR Test Experimental Data Sheet (Example)

For Procedure U201, 252

FTIR Testing Experimental Data Sheet

Date:

Project Title/Sponsor: _______

U of U Sample ID: _________

Project./Acct. No.: _______

Sub Sample No.: _________

Supplied Sample No.: _________

Lab Notebook No.: _______

Sample Description: _________

Pages: _______

____

LCS No.: _________

Summary of FT-IR Spectra:

	Wavenumber (cm^{-1})	Absorbance
Strong Peaks		
Weak Peaks		

Computer Data File Name: ________________________________

Form 201-4 FT-IR Calculation Sheet (Example)

FT-IR Calculation Sheet

For Procedure
U201

Date: 8/22/00 Analyst: R. Karthik

Project Title: DOE

U of U Sample ID: Model oil (#2)

Project. Acct. No.:

Sub Sample No.: test #2

Supplied Sample No.: N/A

Lab Notebook No.: 14

Sample Description: Model oil

Pages: 42 to 44

LCS No.: N/A

		Peak Area (735 cm^{-1} - 715 cm^{-1})						Solid
File	T(°C)	Total	Corrected	Base	Adjusted	Liquid	Liquid-Solid	Wt.%
modr09.sp	44.1	16.8282	4.2098	12.6184	16.8282			
modr10.sp	39.8		4.3173		16.9357	16.9357		
modr11.sp	35.1		4.5378		17.1562	17.1562		
modr12.sp	30.2		4.8432		17.4616	17.4616		
modr13.sp	24.6		5.2097		17.8281		17.8281	0.39
modr14.sp	19.3		7.8188		20.4372		20.4372	11.69
modr15.sp	15.3		9.4988		22.1172		22.1172	17.41
modr16.sp	8.1		11.9307		24.5491			23.98
modr17.sp	3.7		12.6150		25.2334			25.09
	24.5							0

WPT = 24.5 °C = 76.1 °F

Notes:
1

Figure 1. Preliminary WPT Data Plot

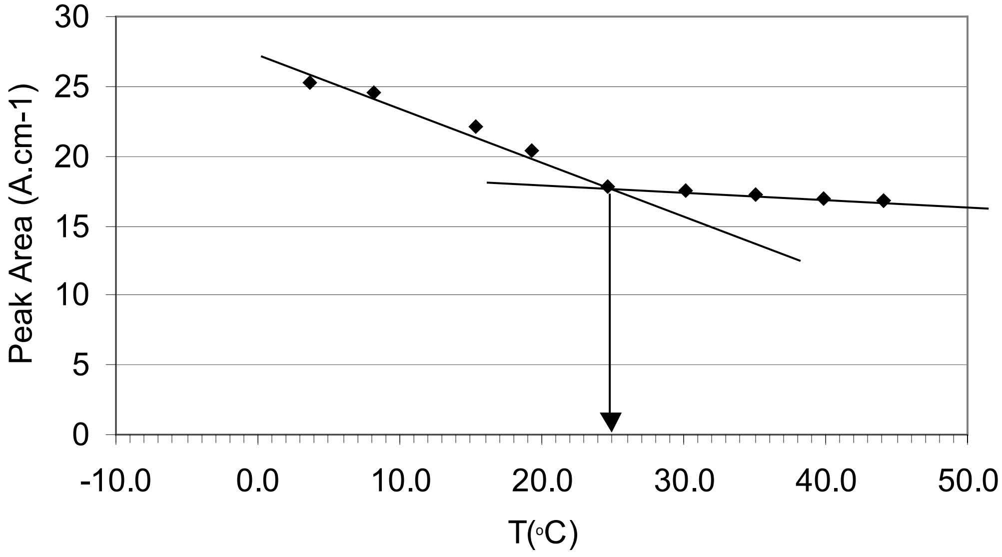


Figure 2. WPT Identification

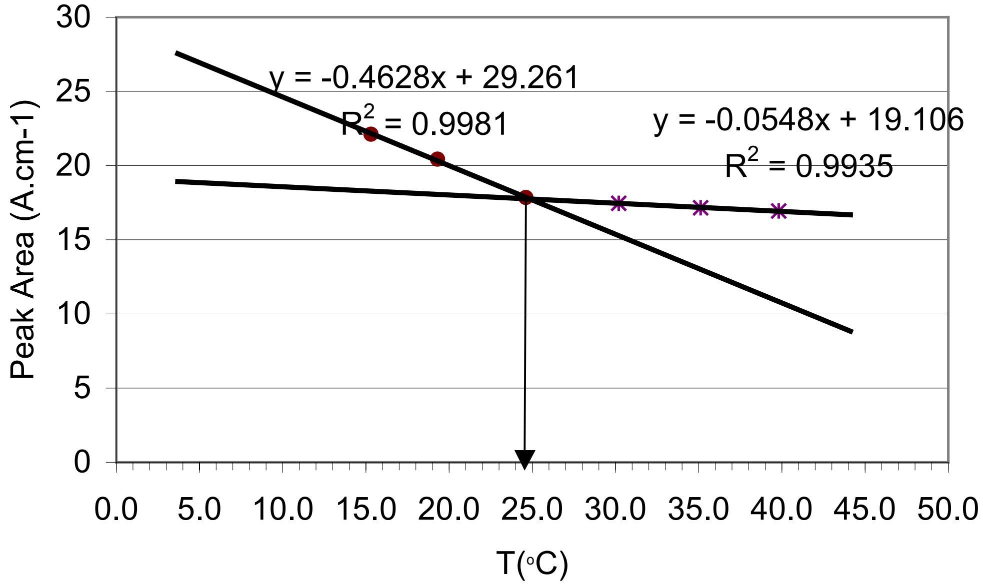


Figure 3. Wt.% Solid vs. Temperature

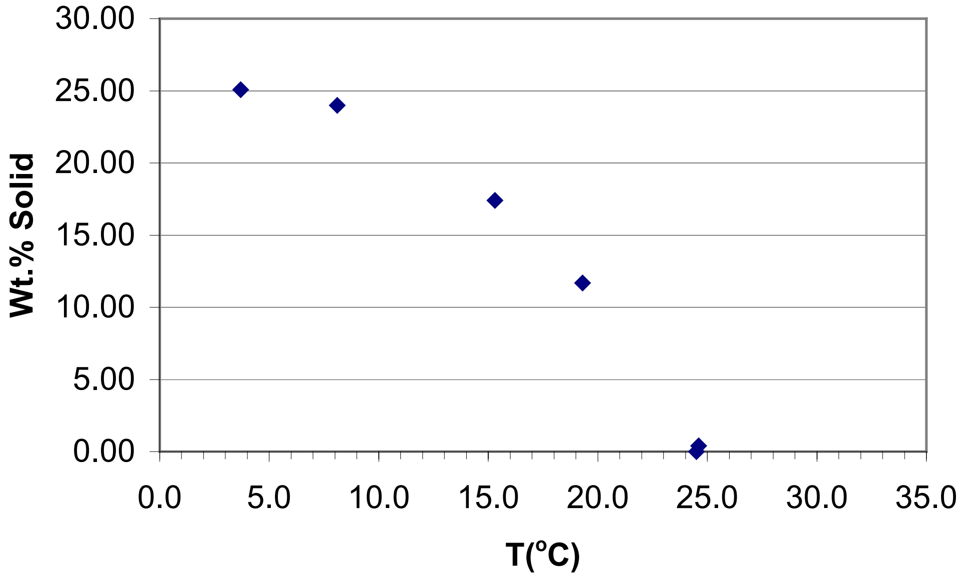


Figure 4 FT-IR Spectroscopic analyzer system I.

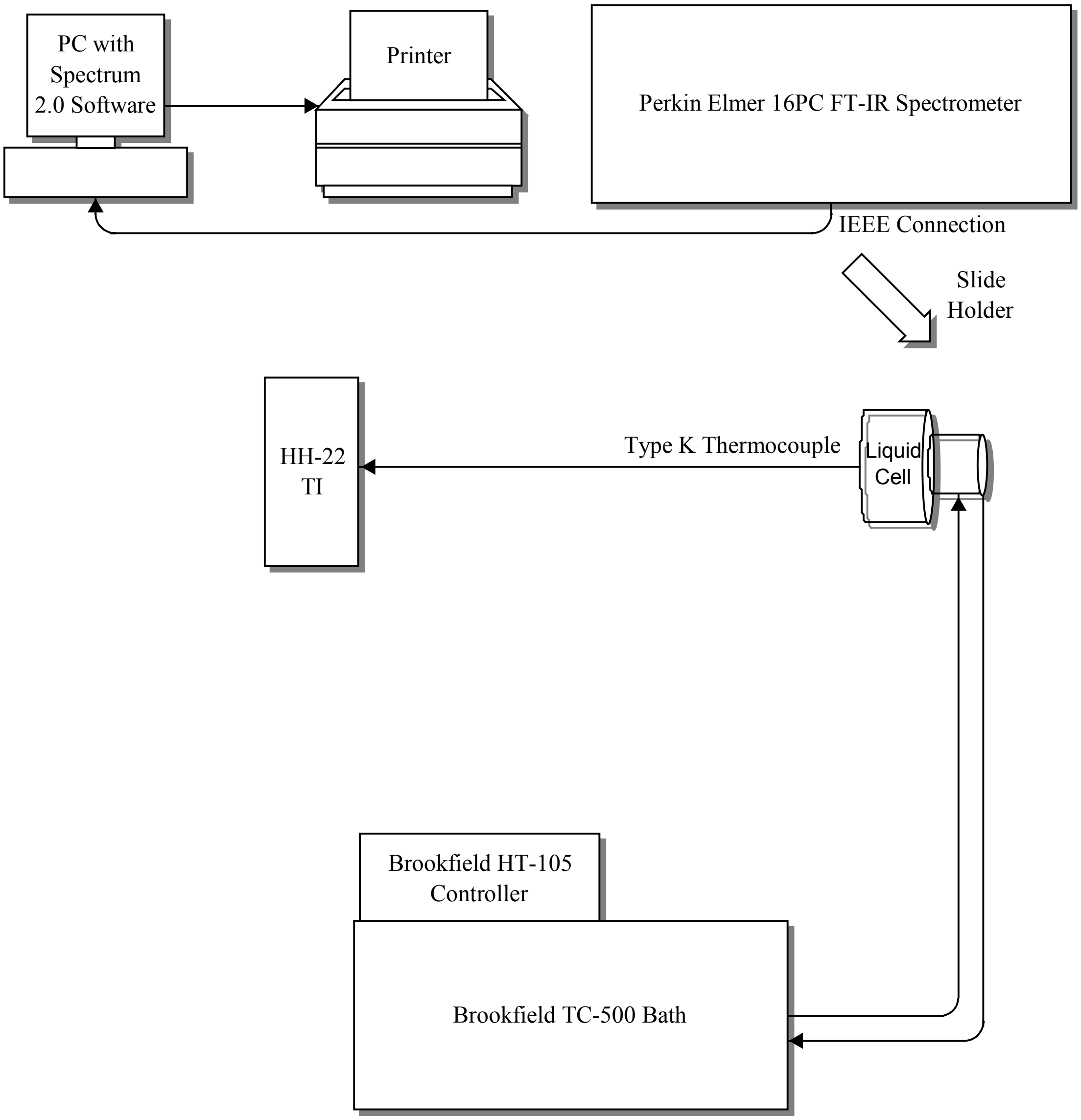
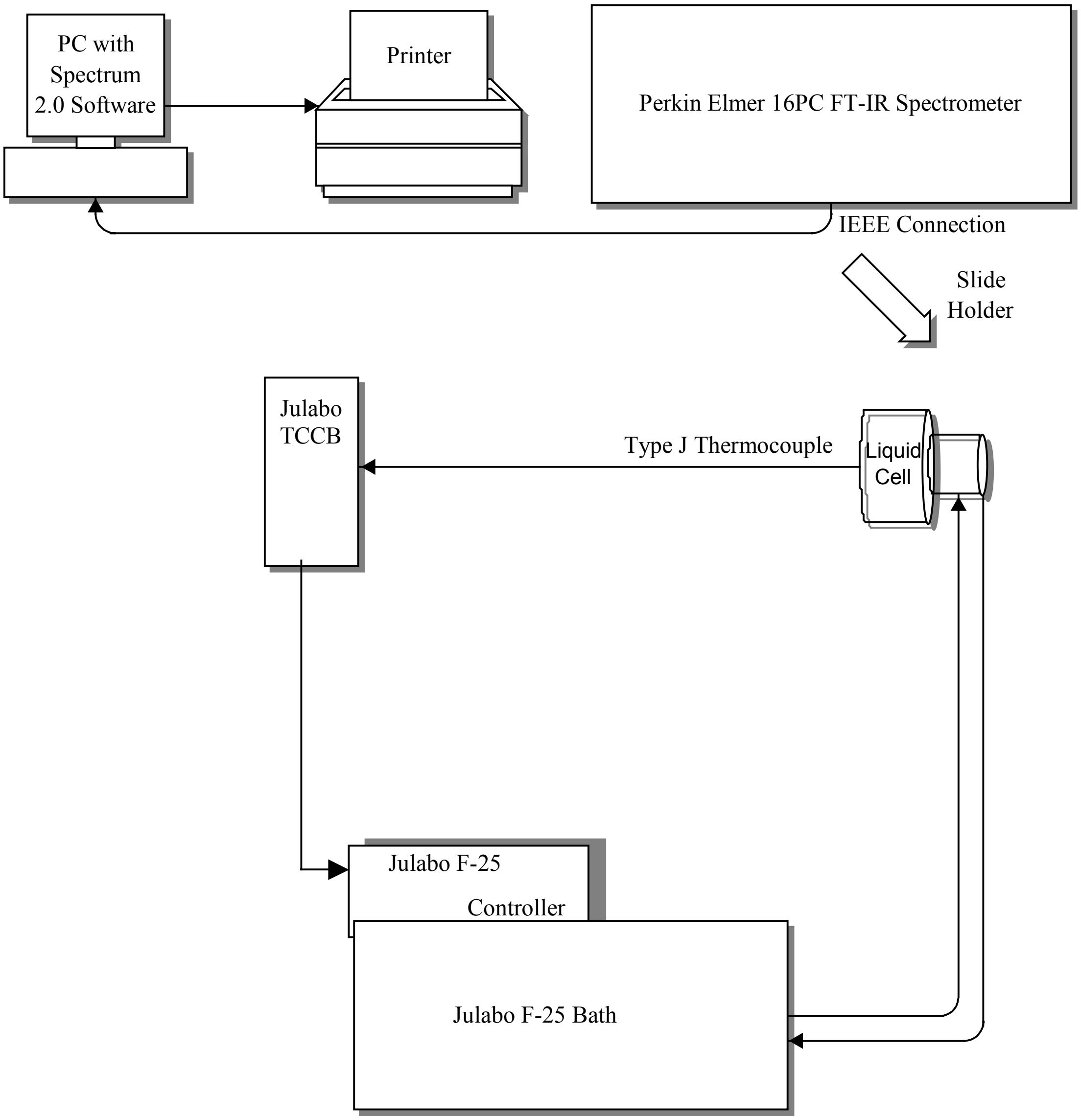


Figure 5 FT-IR Spectroscopic analyzer system II.



APPENDIX C

DIFFERENTIAL SCANNING CALORIMETRY (DSC) OF CRUDE OIL SOLIDS/MODEL OILS

Prepared by: R. Roehner / L. Shunn	
Applicable to: **Differential Scanning Calorimetry (DSC) of Crude Oil Solids and Model Oils**	

Technical Review:	N. F. Dahdah	Date:
Safety Review:	N. F. Dahdah	Date:
Quality Assurance Review:	J. V. Fletcher	Date:
Management Review:	F. V. Hanson	Date:

SCOPE:

This procedure addresses the use of a digital scanning calorimeter to generate printed thermograms for waxy solids obtained from crude oil and model oils. The solids used in this test may be obtained from low temperature centrifugation of crude oil/model oil samples, or from pipeline deposits, model flow-loop deposits, cold finger deposits, etc. This method documents the steps necessary to determine the melting onset temperature, solid-liquid transition peak temperature, and heat of fusion (J/g) for the crude oil/model oil solid. In addition, this method provides for the measurement and documentation of any solid-solid phase transitions that may occur in the tested material prior to melting.

SUMMARY OF THE METHOD:

A thermogram (heat flow in Watts/gram (W/g), versus temperature in °C) is developed for the crude oil/model oil solid using a differential scanning calorimeter. Acquisition and storage of data is provided by computer software. The thermogram is analyzed using computer software to determine values for the melting onset temperature, solid-solid and solid-liquid transition peak temperatures, and the heat of fusion (J/g) of the crude oil/model oil solid. This information is recorded in an experiment data sheet and entered into an electronic database. Raw data files containing the thermogram data are stored electronically, and a hard copy of the thermogram is filed with the experiment data sheet.

REFERENCES:

1.) duPont Instruments Differential Scanning Calorimeter 910 Operator's Manual, PN 910037.002 Rev. E, 101205 D, Issued June 1990.

2.) duPont Instruments Thermal Analyst 2000 Operators Manual, Version 8.1, PN 996524.001 Rev. D, 138017 F, Issued April 1990.

3.) duPont Instruments DSC Calibration Data Analysis Program, Version 5.0, PN 996507.001 Rev. E, 138102 D, Issued January 1989.

4.) duPont Instruments DSC Standard Data Analysis Program, Version 4.0, PN 996484.001 Rev. C, 138096 B, Issued May 1988.

5.) ASTM D 4419-90 Standard Test Method for Measurement of Transition Temperatures of Petroleum Waxes by Differential Scanning Calorimetry (DSC). *Annual Book of ASTM Standards*. ASTM, Philadelphia, PA, 1995, p. 857-859.

Note: ***The portion of duPont Industries responsible for literature references 1-4 is currently known as TA Instruments, Incorporated, New Castle, Delaware, [a subsidiary of Waters Corporation].***

RELATED PROCEDURES:

U003 Solid Sample Storage & Production Procedure

University of Utah Chemical Hazardous Waste Disposal Procedures (available online at www.ehs.utah.edu/enviro/dispose.htm).

SAFETY PRECAUTIONS:

Crude oil solids contain crude oil that is a flammable material, vapors can cause a flash fire. Review and consult MSDS, and/or NIOSH Chemical Hazard guides.

TABLE OF CONTENTS

List of Tables / Figures / Example Forms:

A. Equipment and Supplies

1. duPont Instruments Thermal Analyst 2000 System, including PC, plotter, external disk drive, and data analysis programs:
    a. duPont Instruments DSC Calibration Data Analysis Program
    b. duPont Instruments DSC Standard Data Analysis Program
2. IMATION 2HD, IBM Formatted 1.44 MB, 3.5” disc , or equivalent.
3. duPont Instruments 910 Differential Scanning Calorimeter
4. duPont Instruments Hermetic Sample Pan Tops, part number 900790901.
5. duPont Instruments Hermetic Sample Pan Bottoms, part number 900796901.
6. duPont Instruments Sample Pan tops, part number 900779901.
7. duPont Instruments Sample Pan bottoms, part number 900786901.
8. duPont Instruments Sample Encapsulation Press, part number 900878.902
9. Mettler AT250 Analytical Balance.
10. Metal spatulas (2)
11. Kimwipes
12. Gloves, nitrile
13. Supply of dry nitrogen at a flow rate of 80-90 ml/min (monitored by an adjustable rotameter).
14. Form 254-2 DCS Calibration Data Sheet
15. Form 254-3 DCS Experiment Data Sheet
16. TA Instruments Liquid Nitrogen Cooling Accessory (LNCA), model number CFL-50

B. Reagents and Standards

1. duPont Instruments Indium (pure) standard, part number 900660-903, or equivalent.

C. Quality Control

1. Sample Batches. A sample batch is to be comprised only of samples for a single, sponsored research project. All samples in the batch are to be analyzed during the same testing period and only after successful replicate analysis of a Laboratory Control Standard (LCS) of pure Indium has been performed.

2. Instrumentation:

   - The analytical balance to be used for weighing must have met all required maintenance and calibration requirements before analysis begins. Maintenance and calibration documentation must be completed prior to sample analysis.

   - The 910 DSC Instrument must be calibrated on a monthly basis, or whenever replicate analysis of a Laboratory Control Standard of pure Indium results in values for the melting onset temperature and enthalpy which are outside of control limits (melting point repeatable within ±1.0°C, and enthalpy values repeatable within ±5%.)

3. Analysts. All analysts involved in sample testing must have met the training requirements for this procedure, including calibration of the DSC and competent performance of the procedure while being monitored by an experienced analyst. The results generated by the student analyst must meet the performance criteria outlined in the procedure. One analyst is expected to complete all work comprising a single sample batch.

4. Accuracy. At the beginning of each testing period and prior to analysis of a sample batch, the analyst must perform a duplicate analysis of the pure Indium LCS analyzed during calibration of the 910 DSC and obtain a thermogram. The values for onset solid-liquid phase transition temperature and enthalpy of melting on this thermogram must be within ± 1.0°C and ±5%; respectively, of the known values for the onset of melting temperature and the enthalpy of melting for pure Indium. (Note: Bias for this procedure cannot be determined since there are no acceptable petroleum wax standards against which the tested waxes could be compared meaningfully. The value of transition temperatures can be defined only in terms of a test method.)

5. Precision. The precision of this procedure has been checked by performing multiple runs on a single sample and determining the standard deviation associated with those determinations. The obtained measurements of onset solid-liquid transition temperatures were repeatable within 0.2°C, and enthalpy values obtained were repeatable within 0.7%. Control limits were established as ±1.0°C for onset temperature, and ±5% for enthalpy values in order to provide a range of security narrow enough to insure for adequate precision and wide enough to accommodate the large variety of materials to be examined.

D. Calibration and Standardization

1.) Analytical balances to be used must be serviced and calibrated within one year of experimental procedure testing date.

2.) Calibration of the duPont Instruments 910 DSC involves determination of cell and onset slope calibration constants as described in the duPont Instruments DSC Calibration Data Analysis Program Manual, Version 5.0, PN 996507.001 Rev. E, 138102 D, Issued January 1989.

A. Procedure for Determination of DSC Calibration Constants

Note: This Procedure assumes the duPont Instruments Thermal Analyst 2000 system, and 910 DSC are already operating (see duPont Instruments Differential Scanning Calorimeter 910 Operator's Manual, and duPont Instruments Thermal Analyst 2000 Operators Manual for details of start-up operation).

1. Obtain Form 254-2 DSC Calibration Data Sheet and fill out initial information requested.

2. Weigh approximately 10 mg of the pure Indium standard to ± 0.1 mg.

3. Place weighed Indium into a hermetic sample pan, and crimp lid using the duPont Instruments Sample Encapsulation Press, as described in the duPont Instruments Differential Scanning Calorimeter 910 Operator's Manual

   - ***Note: be sure to cut the indium sample into small pieces or shavings that evenly cover the bottom of the pan.***

4. Position the crimped sample pan containing Indium and a crimped, empty reference sample pan into the DSC cell as described in the duPont Instruments Differential Scanning Calorimeter 910 Operator's Manual.

5. Establish/verify the nitrogen (dry) purge gas flow rate of approximately 80-90 ml/min.

6. Obtain a thermogram for the Indium sample using the duPont Instruments Thermal Analyst 2000 System Instrument Control screen, with a heating rate of 10°C/min, from 20°C to 175°C, and holding the cell at 175°C for 0.5 min prior to terminating the run. Save the thermogram data file produced as IND###.### on a 3.5" data disc, where IND### corresponds to the LCS number and .### corresponds to the run number. (Example: IND001.001 would indicate Indium LCS

number 1, run number 1; IND002.001 would mean Indium LCS number 2, run number 1; etc.)

7. During the analysis, monitor the real time data plot of W/g versus °C. To view this plot select the appropriate option on the instrument control screen.

8. When the analysis is complete, allow the Indium and reference sample pans to cool by opening the DSC cell while maintaining the nitrogen purge flow. Cooling to a safe handling temperature will typically require 10 to 20 minutes.

9. Using the DSC Calibration Data Analysis Program as described in the program documentation, determine the onset temperature and enthalpy of melting values for the Indium sample tested. These should be within ±1°C and ±5% respectively of the values 156.6°C and 28.4J/g per manufacturer's data.

10. If values measured are not within the specified limits, adjust the DSC as described in the 910 DSC Operators Manual, and repeat steps 2-9 until these limits are met.

11. If values measured are within specified limits, accept the values and have the DSC Calibration Data Analysis Program calculate/store the required cell and onset slope calibration constants.

12. Print the thermogram with onset liquid-solid transition temperature, peak liquid-solid transition temperature, and enthalpy of melting clearly marked as described using the DSC Calibration Data Analysis Program.

13. Save the sample pan containing the Indium sample tested in a small vial with a Teflon coated screw top lid. Label the vial with an IND### descriptor, date prepared, sample weight, and analyst initials.

14. File Form 254-2 DSC Calibration Data Sheet with the printed thermogram from the above steps as follows:

    - Original to project file folder for LCS.

    - Copy to project file folder for Test 254 (data sheets filed sequentially by date).

E. Procedure

Keep all notes in numbered project lab notebook.

Note ***This Procedure assumes duPont Instruments Thermal Analyst 2000 system, and 910 DSC are already operating (see the duPont Instruments Differential Scanning Calorimeter 910 Operator's Manual, and the duPont Instruments Thermal Analyst 2000 Operators Manual for details of start-up operation).***

Analytical Sequence:

1. Record entries in a numbered lab notebook, and on Form 254-3 DSC Experiment Data Sheet.

2. Obtain the last pure Indium LCS used to calibrate the DSC, place it in the DSC cell with an empty reference sample pan as described in the duPont Instruments Differential Scanning Calorimeter 910 Operator's Manual.

3. Establish / verify nitrogen (dry) purge gas flow of approximately 80-90 ml/min.

4. Obtain a thermogram for the Indium sample using the duPont Instruments Thermal Analyst 2000 System Instrument Control screen, with heating rate of 10°C/min, from 20°C to 175°C, and holding the sample at 175°C for 0.5 min prior to ending the analysis. Save the thermogram data file to be produced as IND###.### (i.e. IND001.001, IND002.001, etc.) on a 3.5" data disc.

5. During analysis, monitor the real time data plot of W/g versus °C by selecting the appropriate option on the instrument control screen.

6. When the analysis is complete, allow the Indium and reference sample pans to cool by opening the DSC cell and maintaining the nitrogen purge flow. Cooling to a safe handling temperature will typically require 10 to 20 minutes.

7. Using the DSC Standard Data Analysis Program, as described in the program documentation, determine the onset temperature and enthalpy of melting values for the Indium sample tested. These should be within $^{\pm}1$°C and $^{\pm}5$% respectively of the values 156.6°C and 28.4J/g per manufacturer's data.

8. If the measured values are not within the specified limits, investigate / troubleshoot problem and repair or re-calibrate the DSC as required prior to analysis of the crude oil solids sample.

9. If the measured values are within the specified limits, document the LCS test result on Form 254-3 DSC Experiment Data Sheet.

10. Prepare a crude oil solids/model oil sample (while wearing safety glasses and nitrile gloves) by obtaining approximately 5 to 15 mg of crude oil solid/model oil from the appropriate sample container (see also U003 Solid Sample Storage & Production Procedure). Weigh the sample to +/-0.0001g; place the sample in a hermetic sample pan, and crimp the sample pan and lid to form a hermetic seal (using an encapsulation press).

11. Obtain a thermogram for the crude oil solids/model oil sample using the duPont Instruments Thermal Analyst 2000 System Instrument Control screen. This should include a thermal pre-cycle that cools the sample to 0°C, then heats the sample to 95°C at 10°C/min. This melts the entire sample prior to data collection to ensure intimate sample-to-pan contact and establish the same thermal history for each sample. The sample is again cooled to 0°C, and heated to 120°C at 10° C/min. During both the pre-cycle and the data collection cycle the sample is held isothermally at the maximum and minimum temperatures for 0.5 minutes before proceeding with either cooling or heating. Only data from the final stage (0°C-120°C) is used to generate the thermogram.

    Note: ***If a second test of the same sample is to be performed the thermal pre-cycle can be bypassed.***

12. Save the thermogram data file as U####.### (i.e. U0001.001, U0001.002, etc. as required) on 3.5" data disk, where U#### refers to U of U sample number, and .### refers to sample duplicate number.

13. During the analysis, monitor the real time data plot of W/g versus °C. This plot can be viewed as an option of the instrument control screen.

14. When the analysis is completed, allow the crude oil solid/model oil and reference sample pans to cool by opening the DSC cell and maintaining the nitrogen purge flow. Cooling to a safe handling temperature will typically require 10 to 20 minutes.

15. Using the DSC Standard Data Analysis Program as described in program documentation, determine the onset temperature, the solid-liquid transition peak temperature, and enthalpy of melting values for the sample tested. Print a copy of the thermogram with data values given on the plot. Provide required information on Form 254-3 DSC Experiment Data Sheet.

16. File Form 254-3 DSC Experiment Data Sheet with printed the thermograms as follows:

    - Original to project file folder for parent sample per UoU Sample ID.

- Copy to project file folder for Test 254 (data sheets filed sequentially by date).

Cleanup/Documentation:

1. Wipe clean all tools, shutoff nitrogen purge flow, and dispose of unused sample aliquot and contaminated solvents which cannot be used for other tests as described in University of Utah Chemical Hazardous Waste Disposal Procedures (available online at www.ehs.utah.edu/enviro/dispose.htm).

2. *Make backup copy of computer data files (U####.###) on 3.5"data discs.*

3. *Provide data discs (with label indicating data files), and a copy of completed Form 254-3 DSC Experiment Data Sheet (with attached printed thermograms U####.###) to the project Data Review Team Leader.*

Note: Total time for the analytical and cleanup/documentation sequences of this procedure is approximately 2 hours.

F. Data Management

F.1 Data Acquisition / Recording

- Record all notes in numbered project laboratory notebook.

- Complete Form 254-2 DSC Calibration Data Sheet.

- Complete Form 254-3 DSC Experimental Data Sheet, and attach hard copy print out of sample thermograms obtained.

- Data acquisition using duPont Instruments Thermal Analyst 2000 Operators Manual, Version 8.1, PN 996524.001 Rev. D, 138017 F, Issued April 1990.

F.2 Data Transformation

- Provided by duPont Instruments DSC Calibration Data Analysis Program, Version 5.0, PN 996507.001 Rev. E, 138102 D, Issued January 1989, duPont Instruments DSC Standard Data Analysis Program, Version 4.0, PN 996484.001 Rev. C, 138096 B, Issued May 1988 to obtain thermogram data from electrical response/data log.

F.3 Data Transmittal

- Provided by turnover of lab notes, computer discs, and completed Form 254-3 DSC Experimental Data Sheet with attached printed thermograms to U of U Data Review Team Leader.

- Provided by manual entry of data file names U####.###, and summarized results from completed Form 254-3 DSC Experimental Data Sheet into Excel Spreadsheet Database by U of U Data Review Team Leader.

F.4 Data Reduction

- Provided through entering of mean values, obtained through use of Form 254-3 DSC Experiment Data Sheet, into project Excel spreadsheet database.

F.5 Data Analysis

- Provided by duPont Instruments DSC Calibration Data Analysis Program, Version 5.0, PN 996507.001 Rev. E, 138102 D, Issued January 1989, duPont Instruments DSC Standard Data Analysis Program, Version 4.0, PN 996484.001 Rev. C, 138096 B, Issued May 1988.

- Provided by Form 254-3 DSC Experiment Data Sheet comparison of experimental thermogram data.

F.6 Data Tracking

- Provided by U of U Data Review Team Leader through completion and filing of Form 254-2 DSC Calibration Data Sheet and Form 254-3 DSC Experimental Data Sheet, electronic file backup, and entry of data file names into project Excel spreadsheet database for samples tested.

F.7 Data Review, Validation, Verification

- 1st level review by 1st Level Data Review Team Leader, who will review Form 254-3 DSC Experimental Data Sheet, U####.### and U####.### duplicate thermograms, lab notes, and enter summary data into Excel Spreadsheet Database. The Data Review Team Leader requests the QA Data Manager to provide 2nd level review to validate data for reporting.

- 2nd level review by QA Data Manager, who reviews/approves data entry in the project Excel spreadsheet database, through comparison with Form 254-3 DSC Experimental Data Sheet.

- The data review, validation and verification will be documented by completion of Form 253-1 Differential Scanning Calorimetry Experimental Data Review/ Validation/Verification Tracking Sheet by the 1st and 2nd Level Reviewers.

F.8 Data Storage & Retrieval

- Provided by project Excel spreadsheet database (and electronic backup using CD format).
- Provided by electronic data files on 3.5"disc, (and electronic backup thereof by unspecified means) for U####.### thermogram data files.
- Lab Notebook entries.
- Filed hard copies of Form 254-2 DSC Calibration Data Sheet, Form 254-3 DSC Experimental Data Sheet, and printed thermograms.

F.9 Data Reporting

- Data Review Team Lead reports data after approval of same the project QA Data Manager and the Project Manager/Principal Investigator.

F.10 Data Publication Authorization/Restriction

- Data is not to be published without approval of research sponsor.
-

G. Method Performance

1. Training Requirements - Analysts involved in sample testing must have met training requirements for this procedure, including calibration of the DSC and competent performance of the procedure while being monitored by an experienced analyst. The results generated by the student analyst must meet the performance criteria outlined in the procedure. One analyst is expected to complete all work comprising a single sample batch.

2. Results reported for this procedure should result from acceptable thermograms (duplicated within ±1°C for temperatures, and ± 5% for enthalpy values) and are to be collected only after a successful replicate analysis of a pure Indium LCS.

H. Waste Management

Dispose of any contaminated material or spills as directed in the University of Utah Chemical Hazardous Waste Disposal Procedures (available online at www.ehs.utah.edu/enviro/dispose.htm).

Form 254-1 Differential Scanning Calorimetry Data Review/Validation/ Verification Tracking Sheet

Form 254-1 Rev. D, 10/10/00 Date: ______ Analyst: ________

Differential Scanning Calorimetry (DSC) of Crude Oil Solids
Data Review/Validation/Verification Tracking Sheet

Procedure U254

Project Title/Sponsor: __________________ UofU Sample ID: __________________
Project/Acct. #: __________________ Sub Sample #: __________________
Lab Notebook #: __________________ Supplied Sample #: __________________
Pages: __________________ Sample Description: __________________

LCS #: __________________

1st Level Review By: ________________ Date: ________________

________ Lab Notebook Notes – Exist/Clear/Signed & Dated
________ Backup Data Disk Provided
________ Form 254-2 (DSC Calibration Data Sheet) completed and LCS thermogram attached
________ Form 254-3 (DSC Experiment Data Sheet) completed and sample thermogram attached
________ Original Form 254-2 and LCS thermogram to Indium LCS file folder
________ Copy of Form 254-2 and LCS thermogram to U254 Procedure Folder
________ Original Form 254-3 and sample thermogram to Parent Sample Folder
________ Copy of Form 254-3 and sample thermogram to U254 Procedure Folder
________ Summary Data to Excel Project Database

2nd Level Review By: ________________ Date: ________________

________ U254 Procedure Folder Data Matches Summary Data in Excel Project Database
________ Performance Criteria Completed (Indium LCS: onset melting temperature is within ±1°C of 156.6°C and enthalpy of melting value is within ±5% of 28.4 J/g per manufacturer's data. Crude Oil Solid Sample: onset melting temperatures from subsequent runs are within ±1°C of each other and enthalpy of melting values are within ±5% of each other.)

P. I. Approval, Report to Client By: ________________ Date: ________________

Assigned Final Report Preparation: ______________
Planned Reporting Date: _________

Report To Client By: ________________ Date: ________________

Form 254-2 DSC Calibration Data Sheet (Example)

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DSC Calibration Data Sheet

For Procedure U254

Date: Analyst:

Project Title/Sponsor: ____________________

Project./Acct. No.: ____________________

Lab Notebook No.: ____________________

Pages: ____________________

Assigned LCS No.: ____________________

Indium - LCS Prep. Data:

Indium Sample Weight (gr/mg): ____________________/____________________

DSC Set-up Data:

Heating Rate: ________deg. C per ________min.

Nitrogen Purge Gas Flow: __________ml/min

Data Analysis:

	Onset Temp. (deg. C)	Enthalpy of Melting (J/g)
Reference Value	156.6	28.4
Measured Value		
Difference		
% Difference*	N/A	

* Note: % Difference = {ABS[Reference Value - Measured Value]} x 100% / Reference Value

Final LCS Computer Data File Name: ____________________________________

Form 254-3 DSC Experimental Data Sheet (Example)

1

DSC Experimental Data Sheet

For Procedure U254

Date: Analyst:

Project Title/Sponsor: ____________________

Project./Acct. No.: ____________________

Lab Notebook No.: ____________________

Pages: ____________________

Sample No.: ____________________

LCS No: ____________________

LCS File: ____________________

DSC Set-up Data:

Heating Rate: __________deg. C per__________min.

Nitrogen Purge Gas Flow: __________ml/min

Indium - LCS Data Analysis:

	Onset Temp. (deg. C)	Enthalpy of Melting (J/g)
Reference Value	156.6	28.4
Measured Value		
Difference		
% Difference*	N/A	

* Note: % Difference = {ABS[Reference Value - Measured Value]} x 100% / Reference Value

Crude Oil Solid Sample Data Analysis:

Crude Oil Solid Sample Wt. (g/mg):____________________/____________________

Sample (U####)	Temperature (Deg. C)			Enthalpy of S-S trans. (J/g)	Enthalpy of Melting (J/g)
	S-S peak	S-L Onset	S-L peak		
(If Reqd.)					
Average					

Computer Data Files: ______________________________

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