

Technique for Observing Oil-Wetting of Carbonate Surfaces Using FT-IR

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ABSTRACT

Standard methods for describing wettability and wettability changes rely on measurements of bulk properties such as contact angle or wettability indices. Information on molecular level interactions that affect reservoir wettability is scarce. A new technique for observing adsorption of oil components on carbonate surfaces is described.

Zinc selenide attenuated total reflectance (ATR) crystals were sputter coated with an 8.5 nm. layer of calcium carbonate. Coating thickness and composition were determined using X-ray photoelectron spectroscopy (XPS). Crude oil was brought into contact with the carbonate surface and Fourier Transform Infrared (FT-IR) spectra were observed over a period of time. By subtracting the initial spectrum from subsequent spectra, it was possible to observe the interactions associated with certain functional groups and a carbonate surface. Equilibration time for the adsorption process was observed to level out at approximately 130 hours in the absence of water.

INTRODUCTION

A thorough review of wettability changes of both carbonate and quartz surfaces due to crude oil, crude oil components, and simple organic compounds is given by Anderson¹. In most cases standard wettability techniques: contact angle measurement, USBM or Amott techniques were used.

Recent experimental investigations have used additional techniques to characterize physical properties of wetting films. Heslot² used ellipsometry to describe the thickness profile for films of polydimethylsiloxane and tetrakis(2-ethylhexoxy)-silane on silicone wafers. Gee *et al.*³ used ellipsometric studies to investigate surface forces of alkane films on quartz. He concluded that the alkane molecules were orientated parallel to the quartz surface.

Correlations between the nitrogen and sulfur content and oil wetness were demonstrated by Crocker⁴ and Mitchell⁵. Crocker used the standard USBM technique for wettability and high resolution mass spectrometry to analyze crude oil and crude oil fractions. He determined that the USBM index measured on Berea sandstone changed from .55 to -.06 as the concentration of nitrogen and sulfur compounds increased from 8% to 16%. Mitchell used x-ray photoelectron spectroscopy (XPS) and Laser Ionization Mass Analysis (LIMA) to confirm the presence of nitrogen-containing organic compounds on oil wet surfaces.

FT-IR Applications

Both transmission and reflectance FT-IR have been used to fingerprint oil and oil fractions^{6,7}. Baldwin⁸ recorded FT-IR spectra on crude oils extracted from chalk by sequentially more polar solvents. Internal reflectance⁹ was used to view oil removal from a porous polymer membrane by anionic surfactants.

For surface studies, Incorvia and Haltmar¹⁰ used ATR crystals sputter coated with steel to observe the structural properties at a metal/inhibitor interface.

In this study Incorvia's technique was modified to observe adsorption phenomena on CaCO₃. By sputter coating a layer of calcium carbonate onto a zinc selenide crystal, and then contacting the crystal with oil or oil fractions, we directly observed changes in the IR absorption spectra with time. Conclusions as to the relative adsorption rates, the relative effects of various crude oil components and the molecular identity of oil fractions affecting the carbonate surface were made.

Sputter Coating Process

Sputter coating of non-conductive materials onto substrates is accomplished by ion bombardment of a target and transport of the dislodged material to the substrate. The target, maintained at a negative potential using a radio frequency power supply, is bombarded with an argon plasma which dislodges target atoms. The substrate is positioned to be impacted and coated with dislodged target atoms. The sputter coating process generally coats the substrate with the same stoichiometry as that of the target¹¹.

The sputtering process has an advantage over other depositional processes in that surface coverage can be more closely controlled and adhesion is often better. Its disadvantage is that selective sputtering can give film properties different from the surface properties of the target due to high stresses¹².

EXPERIMENTAL

ATR Crystals

Zinc selenide crystals were obtained from Spectra-Tech in Stamford, Conn. Crystals were 50 x 10 x 3 mm. and had 45 degree parallel ends. These were sputter coated by a commercial firm using a cylindrical water cooled target machined from natural white marble. The target composition was determined by x-ray diffraction to be 97% calcite, 2% dolomite and a trace of gypsum. The thickness of the deposited layer was set at 8.5 nm. and varied from 8.5 to 8.7 nm. as measured with a DEC-TAC profilometer. Precautions were taken to avoid contamination of the coated surfaces. Separate crystals were used for each test.

A freshly coated crystal was characterized by x-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA). XPS or ESCA provides surface

elemental analyses from the measurement of core-electron binding energies following bombardment by high energy x-rays. Because the photoelectron emission cross section is different for each element, the relative amounts of each element can be judged by comparing the binding energy spectra. XPS data in this study was collected using magnesium K-alpha radiation source at 300 watts x-ray power. The sample was analyzed at take-off angles of 0 and 80 degrees.

Crude Oil and Crude Oil Fractions

The crude oil used was a 27° API stock tank oil sample obtained from a Middle East carbonate reservoir. Fractions used were obtained from a USBM-API separation technique described by Jewell *et al*¹³. The procedure separates crude oil into ten fractions; asphaltenes, three acids, three bases, neutral nitrogen compounds, saturates and aromatics. The cyclohexane-asphaltenes¹⁴ were precipitated first by combining stock tank oil with a minimum forty (40) parts of cyclohexane. The cyclohexane was evaporated and the supernate was cycled to an anion exchange resin (Amberlyst A-29). Three separate acid fractions were eluted from the resin using increasingly polar solvents (toluene, methanol, and methanol-CO₂). Following the removal of the three base fractions on a cation exchange resin and the removal of neutral nitrogen fractions on attapulugus clay, the remaining components were retained on silica gel. Saturates were eluted with pentane and aromatics were eluted with chloroform. The two largest fractions, the first acid fraction (weak acids) and aromatics, were used for further tests.

Results from the USBM-API separation procedure were compared with fractions separated by an HPLC technique¹⁵ which separated the oil into saturates, aromatics, resins, and asphaltenes (SARA). Comparative results for the two separation methods are shown in Table 1. The quantity of saturates from the two techniques were comparable. Characteristically, the experimental protocol differences between the two separation techniques resulted in volumetric differences in the quantity of other fractions.

IR Spectra

FT-IR spectra were run on a Nicolet Model 170 SX Spectrometer at 4 cm⁻¹ resolution. Transmission spectra were obtained on the stock tank oil and on each fraction using KBr pellets.

Internal reflectance spectra for time studies were obtained using a Spectra-Tech variable angle ATR attachment with a liquid cell. All reflectance measurements were made at a 45° incidence angle. Spectra were obtained by filling the ATR attachment chamber either with the crude oil, the fraction or the fraction in solution (toluene). Spectral changes in the absorbance from 400 to 4000 wavenumbers (cm⁻¹) were recorded at regular intervals. Interval spectra were produced by subtracting the initial spectrum (approximately 1 minute) from each subsequent spectrum. Spectra were taken over a period of 96 hours with

additional spectra for the crude oil and the aromatics taken at 130 hours and 672 hours respectively.

A schematic for the optical path through the ATR crystal and the film is shown in Figure 1. The depth of penetration into the hydrocarbon phase is estimated to be between 0.35 and 3.5 microns¹⁶.

RESULTS

Coated ATR Crystals

IR spectra of coated crystals showed characteristic peaks for CaCO_3 at 1430 cm^{-1} and 870 cm^{-1} . There were also indications of ZnCO_3 , with peaks at 1600 cm^{-1} and 1000 cm^{-1} . Based on x-ray diffraction analyses of the sputter coating target, additional species that may have been coated onto the ATR crystals include calcium magnesium carbonate and calcium sulfate.

A survey XPS scan of the freshly coated plate at the maximum analysis depth and 0 degrees take-off angle is shown in Figure 2. The peaks show the presence of C, O, Ca, Mg, Al, and only small amounts of Zn and Se. There is some surface contamination due to aliphatic carbon. The contamination decreases with increasing depth. Carbonate carbon show no change with depth. The small amount of Zn and Se present are consistent with a fairly homogeneous coating of calcium carbonate of approximately the same thickness as the maximum analysis depth of XPS (7.7-10.0 nm).

Contacted Spectra

The first crude oil spectra taken after contacting the CaCO_3 were nearly identical to the neat spectra using the KBr pellets, demonstrated by a comparison of spectrum (a) and spectrum (b) in Figure 3. Spectrum (c) shown at the top of Figure 3 is the result of subtraction of the initial contacted spectrum (b) from the spectrum obtained after 96 hours of contact time. The peaks and valleys in spectrum (c) indicate wavenumbers where changes are occurring with time. No change in surface concentrations with contact time would result in a flat response. Increase in the surface concentration with time results in a peak formation (increased absorbance) while decreases in surface concentration result in the formation of valleys (decreased absorbance).

The CO_2 peak that appears at 2350 cm^{-1} is the result of carbon dioxide in the optical path and is not considered representative of CO_2 within the samples. Subtracted spectra show this peak increasing and decreasing as the amount of CO_2 in the optical path fluctuated.

Crude Oil and Cyclohexane-Maltenes

Neat and contacted spectra for the cyclohexane maltenes (crude oil minus the cyclohexane-asphaltenes) are shown in Figure 4. Comparison of the crude oil and maltenes spectra show slight differences in three areas: 860, 1250, and 2659 cm^{-1} . The spectral differences are the result of the removal of asphaltenes. The change at 860 cm^{-1} is attributed to the aromatic C-H bending of the asphaltenes while the changes at 1250 and 2659 cm^{-1} are attributed to hetero-atom activity of the asphaltenes.

Figure 5 shows the neat spectrum for the cyclohexane-asphaltenes (0.42 wt%) that were removed. The broad peak from 1000 to 1350 cm^{-1} is of particular interest. One assignment would associate the peaks with C-O stretches and O-H bends in phenolic compounds¹³. This is supported by the broad band at 3450 cm^{-1} corresponding to hydrogen bonded O-H stretching. A second interpretation would attribute the region to carbon-sulfur double bonds, sulfur-oxygen bonds or CS-NH bonds. Assignment of the broad shoulder in the region of 2600 cm^{-1} to S-H stretching would also support the presence of sulfur in the asphaltenes. Both are possible since analyses of various asphaltenes (precipitated with alkanes USBM-API method) and aromatics from the same reservoir show significant amounts of both oxygen and sulfur (Table 2).

Comparisons of the subtracted spectra of the crude oil and the maltenes (Figures 3&4), show four areas of interest: 1100 to 1192 cm^{-1} , 1610 cm^{-1} , 2850 to 2920 cm^{-1} , and 3350 to 3420 cm^{-1} . The peak at 1124 cm^{-1} can be attributed to C-O stretching, thiocarbonyls or S-O stretches. The 1610 cm^{-1} could be highly conjugated alkene links, carbonyl, or stretching of the imino carbon-nitrogen double bond. The peaks in the 2850 to 2920 cm^{-1} range are due to C-H stretching. The peak at 3400 cm^{-1} is attributed to O-H or N-H stretching and associated hydrogen bonding.

The time dependent absorption for the crude oil and the maltenes is shown in Figures 6 and 7. In both figures time is increasing from bottom to top. Spectra were measured initially every 10 minutes for 30 minutes, then at one hour intervals from 2 to 6 hours, and finally every 24 hours for four days.

Weak Acid Fraction and Aromatics

Neat and contacted spectra for the weak acid fraction and the aromatic fraction are shown in Figures 8 and 9. Compared to crude oil and the maltenes, neat spectra for these fractions show a reduction in the amount of saturated alkanes demonstrated by the decrease in absorbance at 1380, 1450, and 2920 cm^{-1} . The absence of the 720 cm^{-1} crude oil peak in the aromatic fraction indicates that the fraction contains few methylene group chains of four or more. The peak in both fractions at 1652 cm^{-1} shows additional carbonyl character not apparent in the crude oil or the maltenes.

Contacted spectra for the weak acid and aromatic fractions both show peak development at 1100 cm^{-1} range and the 2855 to 2930 cm^{-1} range. The peaks in aromatic spectra are more

distinct than those of the other components. The peaks however, are attributed to the same functional groups assigned to the crude oil and the maltenes, namely C-O stretching, thiocarbonyl or S-O stretching and C-H stretching, respectively.

The 3400 cm^{-1} peak, prevalent in the crude oil and maltenes, showed an erratic time dependent effect as indicated by the middle spectrum in Figure 8. In both the acid fraction and aromatics this peak (3400 cm^{-1}) first increased and then decreased with changes in the equilibration rate occurring at approximately 130 hours.

DISCUSSION

Absorbance Spectra

The development of absorption peaks and valleys in the subtracted spectra can be associated with three processes occurring near the surface. These would include:

- (a) physical transport process associated with the displacement of components or re-orientation of functional groups in contact with the surface,
- (b) physical adsorption with or without alteration of the vibrational modes for the adsorbed species and
- (c) chemisorption with the creation of new bonds.

Interpretation of which processes are present and/or dominant is difficult due to the complex mix of components even within a single fraction.

Transport of components in the area of the surface is the simplest interpretation of the observed results. Baldwin's work indicated that films on carbonate surfaces exhibit layering with the surface active species arranged closest to the surface. Incorvia's work demonstrated the dynamics of the migration of surface active components using ATR crystals. Both of these processes are indicated with the crude oil adsorption and absorbance.

The development of peaks at 1124 , 1611 , and 3354 cm^{-1} , along with the valleys at 2856 and 2927 cm^{-1} would indicate that more polar oxygen, sulfur, or nitrogen compounds are being adsorbed while the less polar hydrocarbons are being displaced away from the surface.

Transport of components would not explain differences seen between the crude oil contacted spectra and the maltenes contacted spectra. The reduced height of the 3354 cm^{-1} peak is expected based on the asphaltene absorbance at this frequency. However, the reversal in peak formation between the crude oil and maltenes at 1611 , 2854 and 2920 cm^{-1} can not be ascribed to particular absorbance bands in the neat spectra for the asphaltenes. All of these peaks were present in both crude oil and maltenes. The reversal would indicate that asphaltenes are not exclusively adsorbed but also facilitate the adsorption of other components. Additionally, the absence of asphaltenes allows other species to adsorb at the carbonate surface or affects the orientation of the adsorbed species restricting some vibrations while allowing others.

Chemisorption at the surface is also a possibility. The rate of absorbance change for the stock tank oil peaks at 3350 cm^{-1} and 1150 cm^{-1} is shown in Figure 10. During the time from approximately one hour to twelve hours the component responsible for the assigned O-H stretching is adsorbing faster than the component(s) assigned to the 1150 cm^{-1} peak. This would indicate that separate species are involved or that reactions are occurring. The presence of strongly bonded material supported indirectly from attempts to clean used crystals. Efforts at cleaning showed residual absorbance in areas where subtraction peaks had developed (1611, 2856 and 2926). A spectrum for one of these crystal is shown in Figure 11. Confirmation of the processes may be possible with additional XPS surface analyses of the CaCO_3 .

The time dependent response of the 3350 cm^{-1} peak may be indicative of intramolecular as opposed to intermolecular hydrogen bonding that changes with adsorption¹⁷. The peak in the stock tank oil is seen to decrease during the period from 24 to 336 hours. However, in the acid and aromatic fractions the peak increased and decreased to the initial value (approximately zero in subtraction spectrum) between 96 hours to 130 hours.

Time dependent absorbance at higher frequencies was less erratic. The peak at 1150 cm^{-1} in the stock tank oil increased with time as did similar peaks in all the fractions tested. The peak in the aromatic fraction reached equilibrium between 96 and 168 hours while in the stock tank oil the peak continued to increase but began to level off between 96 and 336 hours.

CONCLUSIONS

Methods to characterize of the surface of the ATR crystals point out the complexities and utility of surface analyses and the need for a purer target compositions. Additional XPS analyses to characterize the adsorbed species will prove useful.

The technique provides a unique and adaptable approach to wetting interpretations. The spectroscopic data is useful in identifying wetting components as well as establishing suitable time limits for sample equilibration. Specifically,

1. Dynamic adsorption of stock tank and components shows that low frequency vibrations are affected first and are variable with time. Higher frequency vibrations associated with greater aromaticity and polarity are affected more slowly and are less variable.
2. Small percentages of asphaltenes can significantly alter the chemical compositions associated with wetting.
3. Lighter fractions such as aromatics show significant adsorption similar to that of the whole crude. Absorbance data indicates that primary contributors to the adsorption process are oxygen, sulfur and possibly nitrogen.
4. Hydrogen bonding activity at the surface varies between fractions of a crude oil. This activity is enhanced and prolonged in the presence of asphaltenes.

ACKNOWLEDGMENTS

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Crude Oil Analyses		
Fraction	USBM-API	SARA
Saturates	48.9	42.1
Aromatics	28.4	44.6
Resins	22.3*	5.7
Asphaltenes	0.42	7.6

* By Difference

Table 1. Crude Oil Analyses

Elemental Analysis - Crude Oil Fractions - Weight %						
Fraction	C	H	O	N	S	H/C
asphaltenes	82.55	7.00	4.37	0.54	5.54	1.01
aromatics	81.75	9.75	2.15	0.55	5.8	1.42

Table 2. Elemental Analyses

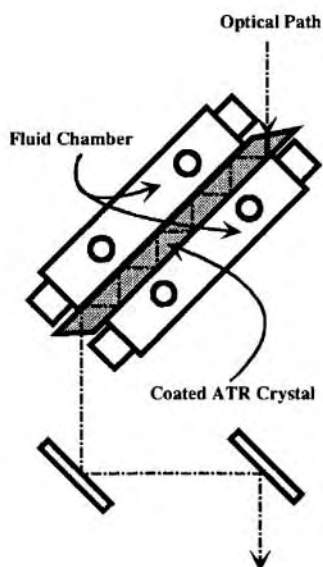


Figure 1
FT-IR ATR Schematic

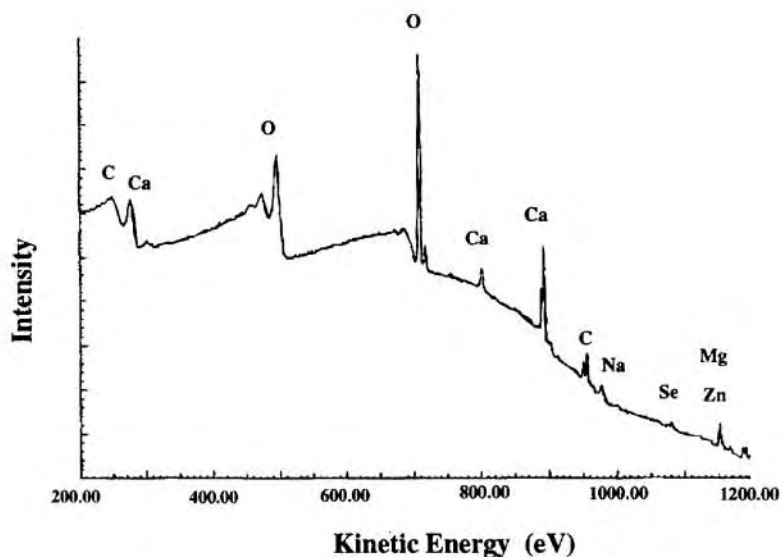


Figure 2
XPS Survey scan of freshly coated ZnSe crystal

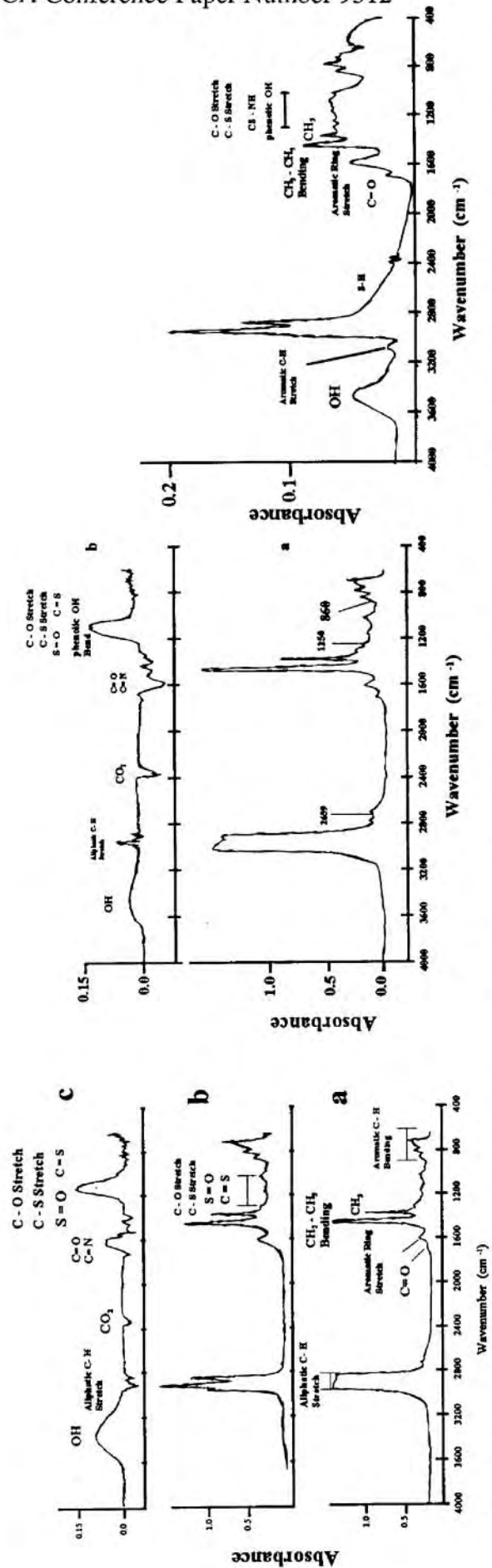


Figure 3 Stock Tank Oil Spectra (a) KBr pellets, (b) Contacted $t = 0$, (c) Subtracted $t_{96} - t_0$

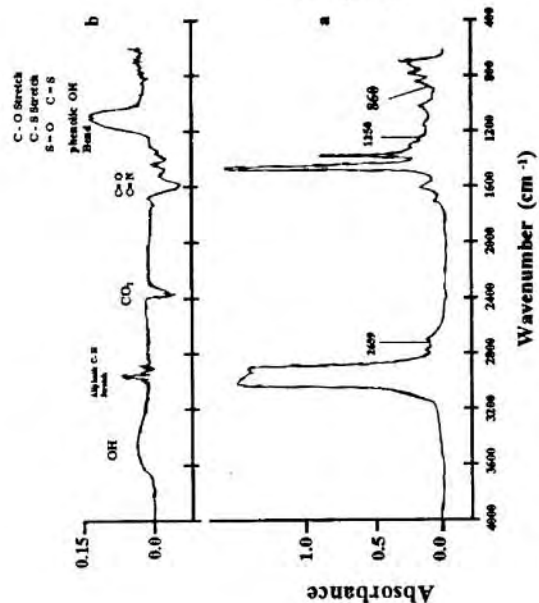


Figure 4 Cyclohexane Maltenes Spectra (a) KBr pellets, (b) Subtracted $t_{96} - t_0$

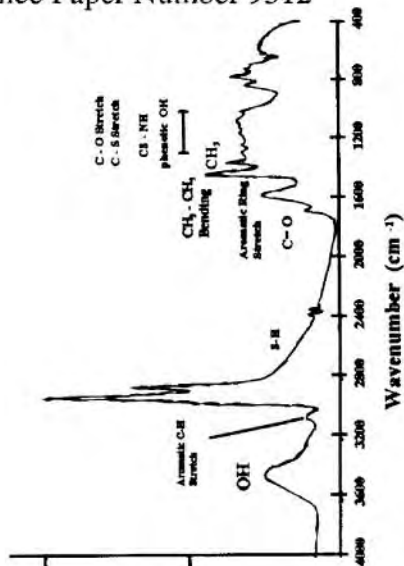


Figure 5 Neat spectra for asphaltenes precipitated from cyclohexane.

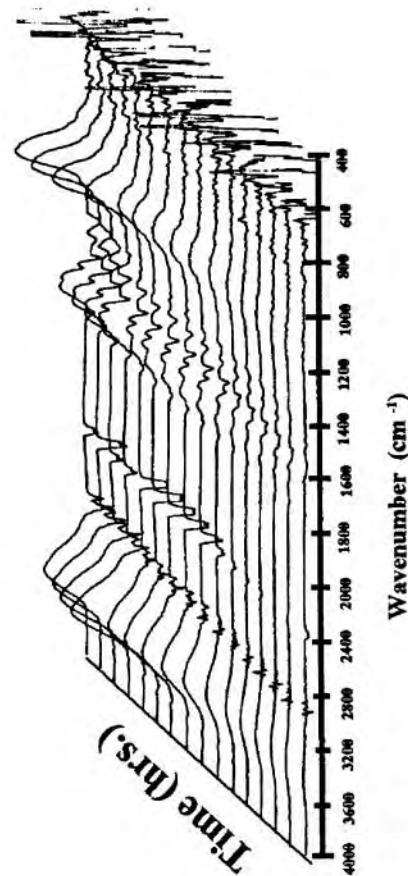


Figure 6 Stock Tank Oil Subtracted Contacted Spectra ($t-t_0$) from 5 mins. to 96 hours

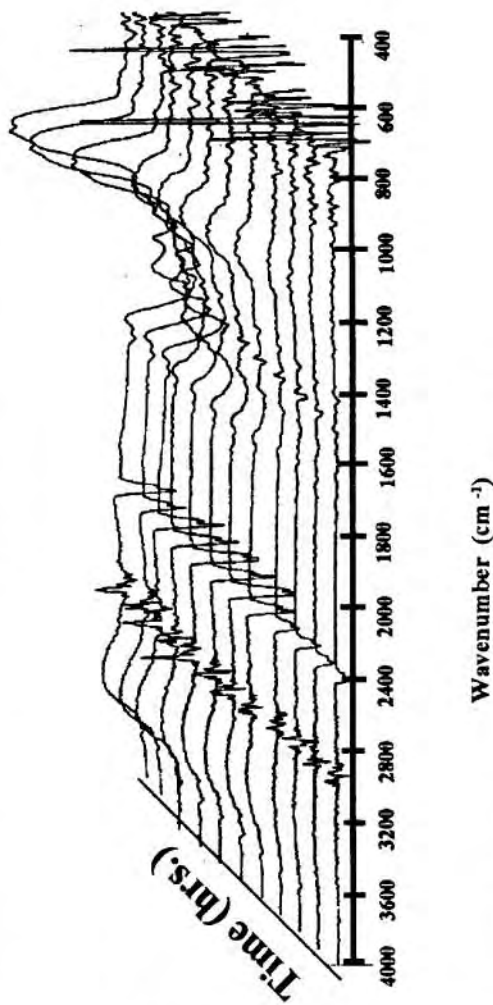


Figure 7 Cyclohexane Maltenes Subtracted Contacted Spectra ($t-t_0$) from 5 mins. to 96 hours

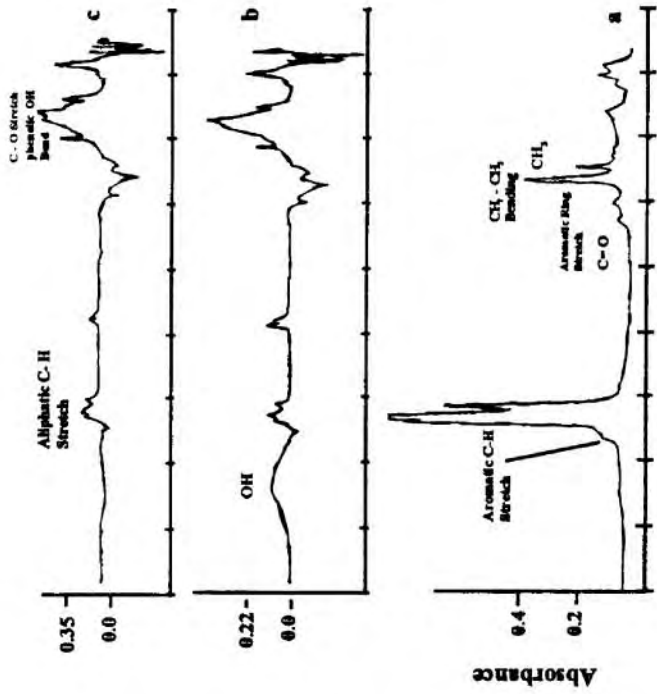


Figure 9
Aromatic Spectra (a) KBr pellets, (b) Subtracted $t_{96} - t_0$,
(c) Subtracted $t_{77} - t_0$

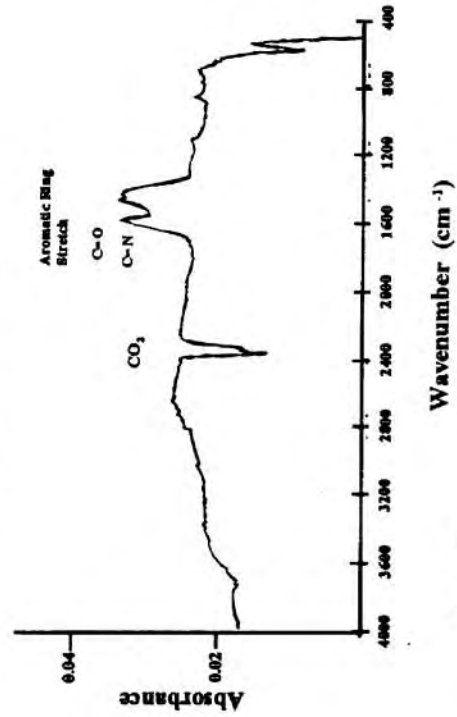


Figure 11
FT-IR Spectra for coated ZnSe crystal

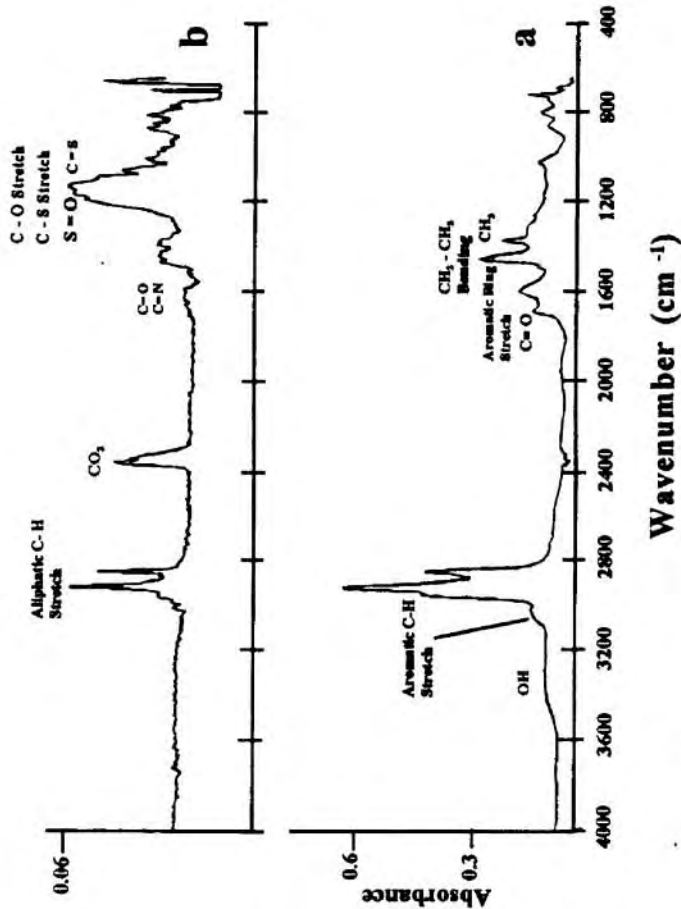


Figure 8
Weak Acid Spectra (a) KBr pellets, (b) Subtracted $t_{96} - t_0$

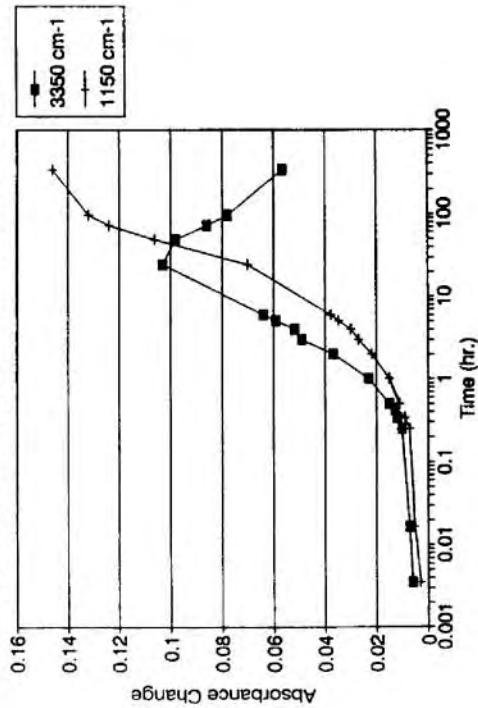


Figure 10
Stock Tank Oil absorption change

