

Molecular Characterization of Wax Isolated from a Variety of Crude Oils

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Petroleum waxes from sixteen different crude oils were analyzed after isolation from the crude in a two-step process. These waxes were characterized molecularly to aid in the investigation of the effect of wax type and quantity on water-in-crude oil emulsion stability. The techniques used to gather information about the waxes included elemental analysis, FTIR spectroscopy, field desorption mass spectroscopy, ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry. Two distinctly different types of petroleum waxes were discerned, microcrystalline and paraffinic. Microcrystalline waxes are aliphatic hydrocarbon compounds containing a substantial amount of branches and rings. They have large molecular weight ranges from 300 to 2500 amu and are gel-like in appearance. The rings give rise to a decreased H/C ratio relative to paraffinic waxes, often as low as 1.85. Because of the large number of different compounds and the lack of large-scale crystallinity, a distinct melting regime is not observed. FTIR spectroscopy determined that these waxes contained approximately 55% straight chain methylene, that is, methylene groups directly attached to each other. Five waxes exhibited these characteristics and thus were considered typical microcrystalline waxes. Paraffin waxes are hydrocarbon chains with few or no branches and H/C ratios between 1.96 and 2.05. They have distinct melting regions and narrow molecular weight ranges between 350 and 600 amu. They contained 63–78% straight chain methylene as gauged by FTIR spectroscopy. Six of the remaining eleven waxes exhibited all the characteristics of this paraffin category while the other five were mixtures of microcrystalline and paraffinic wax.

Introduction

Wax has been important in a variety of industries for a number of years. It has been used for everything from candles, polishes, and crayons to container coatings and impregnating paper.^{1,2} Much of this wax comes from petroleum. While wax is useful after separation from the crude, before separation it can cause or magnify a number of problems in the processing of petroleum. It can aid emulsification of the crude in the production and refining of crudes, as well as in oil spills.^{3,4} Since the wax precipitates out at low temperatures, it can cause plugging in drilling equipment and pipelines undersea and in the arctic.⁵ Because of its high viscosity, it can cause pumping problems in pipelines and when emptying tankers in regions where the water temperature is low. Our research team has focused on the role of waxes in the formation of emulsions in production and refining. These emulsions are difficult to study because of the variety of different crudes and crude waxes, the complexity of crude oil, and the lack of knowledge of the precise mechanism whereby wax stabilizes emulsions.

Numerous papers on water-in-crude-oil emulsion stability have been published recently, but the majority have focused on the role of resins and asphaltene in the stabilization of water-in-oil emulsions.^{6–10} Research has indicated that these emulsions are stabilized by a rigid film that surrounds the water droplet.^{11–13} This film is comprised of various materials, primarily resins and asphaltene. These are general terms for two different solubility classes of polar surface active molecules found adsorbed at the interface. These materials are the primary emulsion stabilizers for water-in-oil emulsions. Various solids have also been scrutinized for their capability to act as secondary stabilizers in these emulsions. One of the most common solids implicated is wax.^{3,4,11,14–17} These waxes are typically submicrometer particulate solids that can adsorb resins

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Table 1. Characteristics of the Whole Crudes

crude, full name	crude, abbrv	% organic precipitate	% wax	% resins	% asphaltenes
Malu Isan	MI	8.48	5.80	4.87	0.18
South China Sea	SCS	42.95	32.45	6.05	3.47
B6 CUSA	B6	18.76	1.08	12.05	13.13
Arab Berri	AB	3.80	1.68	3.49	0.68
Alaska North Slope	ANS	7.30	1.54	9.47	3.35
Statfjord	SF	11.10	8.10	4.02	0.09
B4 CUSA	B4	18.23	1.53	12.22	13.55
Maya	Maya	25.09	3.85	10.96	11.54
Arab Heavy	AH	12.27	1.54	9.56	8.27
Canadon Seco	CS	31.80	16.10	8.94	7.51
Gulf of Mexico	GM	12.5	7.76	5.02	0.32
Alba	Alba	10.10	1.54	10.12	1.64
Bay Marchand	BM	5.57	1.20	6.96	0.16
THUMS-1	T1	11.00	1.35	18.69	5.09
THUMS-2	T2	8.10	1.00	12.48	3.31
San Joaquin Valley	SJV	10.46	0.69	20.26	4.57

and asphaltenes to become interfacially active or are themselves interfacially active. They are then capable of adsorbing at the water–oil interface, thus stabilizing the water droplet. They play a supporting role in emulsion stability, but their importance is extremely dependent on temperature. Cooling rate and emulsion formation temperature can determine whether wax will play a role in an emulsion's stability or not.^{4,16}

Although wax has been mentioned as a possible emulsion stabilizer for years, its role in emulsion stability has not been extensively studied. Current wax research is primarily aimed at understanding the phenomenon of wax precipitation at low temperatures.^{17–21} However, wax has recently assumed more importance in crude oil emulsion stability studies. Still, data are normally limited to wax precipitation temperature and wax content of the crude in question.¹⁸ Even from these limited data, some conclusions can be drawn about the role of wax in emulsion stability. One group of researchers found a correlation between the amount of wax present in the crude and the emulsion stability which had wax content increasing as emulsion stability increased.¹⁷ However, they did not examine any properties of the wax other than the total wax content of the crude. Others have added or removed wax to examine the effect on emulsion stability.^{3,4,14,16,22} However, the wax used by these researchers has never been characterized prior to its use in these studies.

Wax has been characterized previously by some researchers. Branthaver and Holmes characterized wax from tar sand bitumens.^{23,24} Branthaver found H/C ratios of 1.9, sulfur contents of 0.07 wt %, and nitrogen contents of 0.18–0.38 wt % for waxlike substances. The melting point was between 91 and 96 °C. Solid-state ¹³C NMR showed only methyl and methylene groups, but methine could not be differentiated from methylene peaks. FTIR indicated a large peak at 720 cm⁻¹ which was indicative of long straight methylene chains. The mass spectrum indicated a mixture of *n*-alkanes with carbon numbers extending past 60. Holmes characterized wax separated from crude oil in a variety of ways. The wax FTIR spectrum showed a strong absorbance at 720 cm⁻¹. The ¹³C NMR spectrum displayed a prominent peak at 29.7 ppm, again a strong indication of long straight chain methylene. Elemental analysis indicated an H/C ratio of 1.86. Field desorption mass spectroscopy indicated an average molecular weight of 744 Da. Handoo analyzed petroleum wax from an

unnamed source.²⁵ The H/C ratio was between 1.77 and 2.21 with molecular weights between 355 and 915 Da. The melting points were between 53 and 86 °C.

The purpose of this study was to characterize the wax obtained from sixteen different crudes. They have resin contents between 3.5 and 20%, asphaltene contents between 0.09 and 13.5%, and wax contents between 0.7 and 32% as shown in Table 1. The waxes were precipitated via a modified Burger's method.²⁶ The precipitated material was then fractionated to separate the wax from the polar material that had coprecipitated. The resulting wax was analyzed by elemental analysis to determine the H/C ratio and heteroatom distribution (%S, %N, %O). The waxes were also analyzed via Fourier transform infrared (FTIR) spectroscopy to determine long straight chain methylene content. Field desorption mass spectroscopy was performed to determine the mass range of the waxes. Differential scanning calorimetry (DSC) was performed to determine the melting temperatures and enthalpies of the waxes. Information on the structure was derived from proton and carbon NMR. Gel permeation chromatography was performed to supplement the mass spectra data and to allow a better examination of the mass distribution. From these data, percentage methyl, methylene, and methine carbon were calculated and used to create average molecular structures.

Materials and Methods

Materials. Sixteen crude oils from various fields around the world were investigated. Chevron supplied B4 CUSA (B4)

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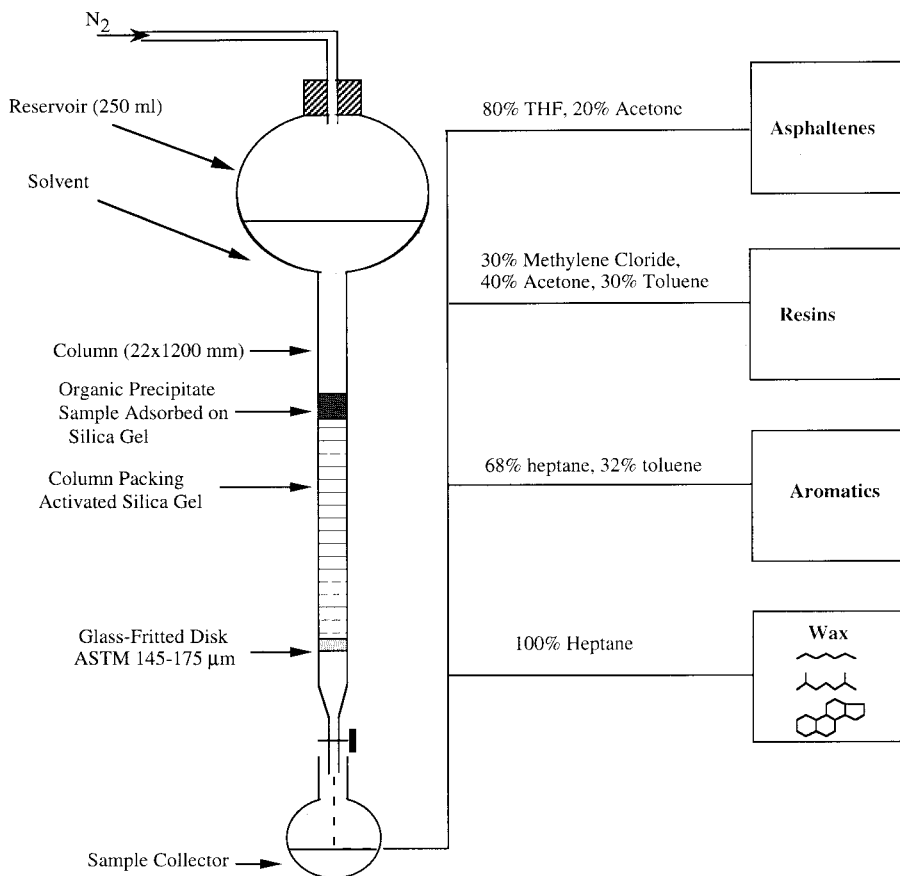


Figure 1. Sequential elution chromatography setup for separating wax precipitate into waxes, aromatics, resins, and asphaltenes.

and B6 CUSA (B6) from California, Alba (Alba) from the North Sea, Bay Marchand (BM) from off the Louisiana Gulf Coast, and Malu Isan (MI) from Nigeria. Texaco contributed Arab Berri or Arab Extra Light (AB) from Saudi Arabia, South China Sea (SCS) from China, and Gulf of Mexico (GM) from the U.S. Gulf of Mexico. Mobil furnished Arab Heavy or Safaniya (AH) from Saudi Arabia and Statfjord (SF) from the North Sea. Shell provided San Joaquin Valley (SJV) from California, Maya (Maya) from Mexico, and Canadon Seco (CS) from Venezuela. BP supplied Alaska North Slope (ANS) from Alaska. THUMS-1 (T1) and THUMS-2 (T2) from Santa Monica Bay were provided by Arco.

The methylene chloride, acetone, toluene, tetrahydrofuran (THF), pyridine, and *n*-heptane used were HPLC grade. The petroleum ether was Optima grade. The silica gel was Fisher Scientific chromatographic grade, 35–60 mesh, DAVISIL. The filter paper used was a Whatman 934 AH glass microfibre filter. All were purchased from Fisher Scientific. The sequential elution chromatography apparatus was made by University Research Glassware. All other glassware were purchased from Fisher Scientific.

Solids Precipitation. The initial stage of wax separation used a method first proposed by Burger in 1981 and subsequently modified by other researchers.^{14,18} For each precipitation, 5 g of crude oil was dissolved in 35 mL of petroleum ether. When the oil was dissolved, 110 mL of acetone was added. The sample, all of the filtration apparatus, and a wash solvent composed of acetone and petroleum ether (3:1 v/v) were cooled for 2 h at -20°C . The sample was then filtered (Whatman 934 AH glass microfibre filter) through a Buchner funnel ($d = 15$ cm) into a 1000 mL vacuum flask on which a slight vacuum was drawn. The retentate was washed with the wash solvent until clear solvent flowed. It was then rinsed into a flask with methylene chloride, and the solvent evaporated. The retentate was transferred to a tared vial and dried in a nitrogen-flushed vacuum oven at 60°C for 48 h.

Sequential Elution Chromatography. Elemental analysis established that the precipitate contained more than saturated hydrocarbons, mainly through the discovery of a low H/C ratio and significant heteroatom content. A second separation—sequential elution chromatography—was therefore performed. The material recovered in the first fraction of this chromatographic separation was the wax. One gram of organic precipitate was transferred to a flask. The material was adsorbed onto 30 g of silica gel (activated at 120°C in a nitrogen-flushed oven) using methylene chloride. It was stirred for 24 h, before solvent removal by rotary evaporation. The adsorbed sample was next dried in a nitrogen-flushed oven at 60°C for 48 h. It was charged to a standard chromatography column. These Pyrex columns were constructed with a 250 mL reservoir attached to a 14/20 joint, a 22 mm o.d. column approximately 1 m long, a fritted disk (ASTM 145–175 μm), and a detachable Teflon stopcock with removable Pyrex tip. A diagram of a packed sequential elution chromatography column is supplied in Figure 1. The material that eluted in heptane prior to the heptane's color change was considered the wax. The aromatics were eluted in 400 mL of heptane and toluene (17/8 v/v). Then the resins were eluted in 350 mL of a mix of toluene, acetone, and methylene chloride (3/4/3 v/v). Finally a fraction called asphaltenes were eluted in 350 mL of THF and acetone (4/1 v/v). The silica was then placed in pyridine for several days and the desorbed material added to the asphaltenes. The solvent was removed from all the fractions except the asphaltenes via rotary evaporation, and they were dried in a nitrogen-flushed vacuum oven at 70°C for 48 h. Because of THF oxidation, the solvent was removed from the asphaltenes via sparging with argon to evaporate the solvent before drying.

Elemental Analysis. Elemental analyses (C, H, N, S, and O) of these precipitates and their fractions were obtained with the use of a Perkin-Elmer 2400 Series II CHNS/O analyzer. A combustion method was used to determine C, H, N, and S

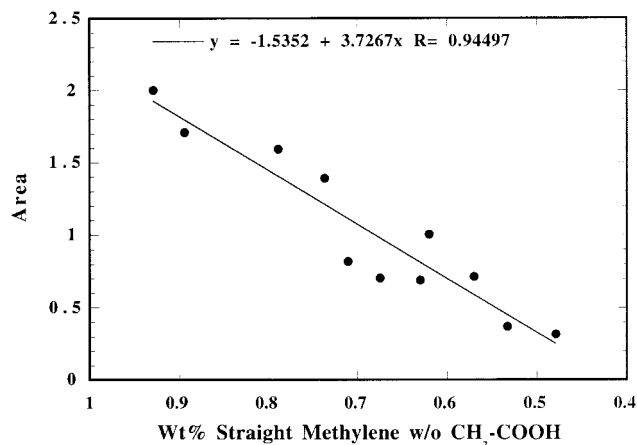


Figure 2. FTIR calibration plot for 720 cm^{-1} peak (10 g/L in cyclohexane solution) using eleven alkanes, acids, and alcohols: octane, octanoic acid, decanoic acid, decane, decanol, undecylenic acid, lauric acid, myristic acid, palmitic acid, eicosane, and triacontane.

content while the sample was pyrolyzed in a helium/hydrogen mixture to determine O content. In both methods, the homogenized gases were depressurized through a column where they were separated in a stepwise manner and detected as a function of their thermal conductivities. A known standard was first analyzed to calibrate the analyzer. The calibration factor calculated from this analysis was then used to determine unknowns. The system was specified for a precision of ± 0.3 wt % for each element. With multiple samples, the reproducibility was found to decrease to ± 0.15 wt %. The samples were weighed with a Perkin-Elmer AD-6 Ultramicrobalance.

FTIR Spectroscopy. In the Fourier transform infrared (FTIR) studies, an RFX-65 FTIR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector was used to obtain the spectra from dilute solution (10 g/L) of cyclohexane through a variable path length KCl cell with a 0.2 mm spacer. The background spectrum of pure cyclohexane was integrated and automatically subtracted from the sample spectra. Sixty-four scans were taken of each sample recorded from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} in the transmission mode. Peak position and area were determined by using available software packages. The area under the absorption band of interest was used to evaluate quantitative estimates of functional group concentrations via Beer's law. The Beer's law constant was calculated from an average of the constants for a variety of straight chain hydrocarbons from decane to triacontane to palmitic acid. The calibration curve is shown in Figure 2. Spectra were recorded using the linear transmission mode of the spectrometer. Absorption band areas having the units " cm^{-1} " were then calculated by a software package integration feature.

Mass Spectroscopy. The molecular weights were found using field desorption mass spectroscopy. The sample was coated onto a silicon emitter. The cathode potential was between 1.5 and 2 kV, and the emitter currents varied from 0 to 30 mA at 2 mA/min. The detector gain was 1.0–1.4 kV, and the control field was magnetic. The acceleration voltage was 10.0 kV, and the mass scan range was 0–3000 Da. The mass spectrometer was a JEOL HX-110 double focusing mass spectrometer, Nier-Johnson configuration. The mass spectrometer was controlled by a Hewlett-Packard 9000 series 400 Unix workstation running HP/UX 8.0.

Gel Permeation Chromatography. Molecular weight distributions were found using gel permeation chromatography. Three columns, 100, 10, and 1 kDa, were linked in series. The stationary phase was a Gordi gel cross-linked polymer styrene divinyl benzene mixed bead. The mobile phase was

Table 2. Comparison of Resins and Asphaltenes Separated via Wax Precipitation and SEC versus Asphaltene Precipitation and SEC

crude	% resins		% asphaltenes		R/A ratio		asp. H/C ratio	
	wax	asp.	wax	asp.	wax	asp.	wax	asp.
MI	0.82	4.87	0.77	0.18	1.06	27.06	1.47	1.42
B6	9.14	12.05	6.49	13.13	1.41	0.92	1.23	1.23
AB	0.74	3.49	0.67	0.68	1.11	5.13	1.15	1.02
ANS	2.33	9.47	2.52	3.35	0.92	2.83	1.12	1.08
B4	7.48	12.22	7.35	13.55	1.02	0.90	1.20	1.23
AH	2.47	9.56	4.39	8.27	0.56	1.16	1.15	1.11
Alba	3.16	10.12	2.94	1.64	1.07	6.17	1.23	1.15
BM	1.82	6.96	1.46	0.16	1.25	43.50	1.22	1.26
SJV	4.25	20.26	3.82	4.57	1.11	4.43	1.20	1.17

THF. Sample concentrations were 3–6 mg/mL, and $100\text{ }\mu\text{L}$ was injected at a time. The flow rate was 1.5 mL/min , and the column temperature was $40\text{ }^\circ\text{C}$. The data were collected by an ERC Inc. RI detector with a range setting of 8. The data were recorded on a strip chart. It was then scanned into the computer and 80–120 representative points were picked via Digimatic, a program that supplies coordinates for points picked off a graph. These data were then plotted to allow the conversion of distance to molecular weight.

Differential Scanning Calorimetry. The melting temperatures and enthalpies were recorded using a Perkin-Elmer DSC 7 differential scanning calorimeter with a PC series thermal analysis system. Calibration was performed using high-purity zinc and indium. The apparatus was continually flushed with nitrogen. The samples weighed between 3 and 20 mg. Each sample was cooled to $-25\text{ }^\circ\text{C}$ for 10 min. It was then heated at a rate of $10\text{ }^\circ\text{C}$ per minute to $175\text{ }^\circ\text{C}$. It was rapidly cooled back to $-25\text{ }^\circ\text{C}$ where it remained for 10 min before reheating to $175\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}$ per minute.

^1H NMR. A General Electric GN 300 Omega NMR spectrometer with a C/H dual 5 mm probe was used for all experiments at an observed frequency of 300 MHz. All samples were approximately 5–10 mg/mL in deuteriochloroform in 5 mm sample tubes. A total of 32 scans was acquired for each sample using an $8\text{ }\mu\text{s}$ ($\sim 90^\circ$) pulse and a 4 s delay time between scans.

^{13}C NMR. A General Electric GN 300 Omega NMR spectrometer with a C/H dual 5 mm probe was used for all experiments at an observed frequency of 75 MHz. All samples were approximately 40–80 mg/mL in deuteriochloroform in 5 mm sample tubes. A total of 2560 scans was acquired for each sample using a $10\text{ }\mu\text{s}$ ($\sim 70^\circ$) pulse and a 15 s delay time between scans. During the delay, the proton decoupling power was turned off to facilitate more complete relaxation of slowly relaxing carbons.

Results and Discussion

Precipitation. A mixture of acetone and petroleum ether was used to precipitate material from the crude oil at $-20\text{ }^\circ\text{C}$. The quantity of organic material precipitated varied from 3 to 43% of the crude and was a function of the wax, resin, and asphaltene content of the crude,²⁷ listed in Table 1. While this type of precipitate is sometimes termed wax,²⁶ the relatively low H/C ratio and high heteroatom contents (see Table 2) indicated that polar material had coprecipitated with the wax. Asphaltene are the most likely coprecipitate, as they are believed to adsorb on wax particles during cooling, interfering with large-scale crystallization.^{18,28} As such, they are pour point depressants and remain

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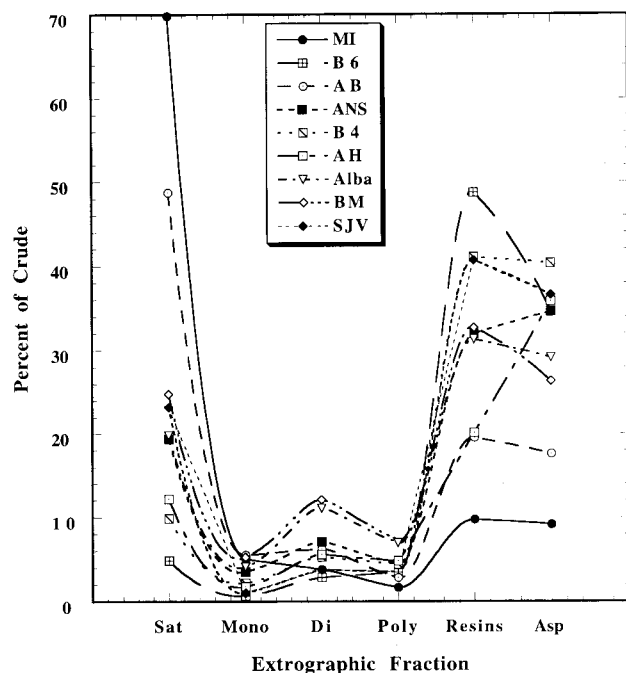


Figure 3. Percent recovery of sequential elution chromatography fractions for organic solids from nine crudes.

in the crystal matrix solubilizing it until the temperature becomes so low that they cannot prevent precipitation.

Sequential Elution Chromatography. Wax was purified following precipitation by sequential elution chromatography with the wax isolated as the first eluted fraction in *n*-heptane.^{27,29} Sequential elution chromatography (SEC) demonstrated that the precipitate was composed mainly of resins, asphaltenes, and wax as shown in Figure 3. Later chromatographies were abbreviated to only elute the wax. As shown in Table 1, the amount of wax isolated did not depend on the amount of material precipitated. However, the crudes with the least asphaltenes did have the highest percentage of wax in the precipitate. No other correlations among the percent resins, asphaltenes, wax, and precipitate have been identified.

McLean²⁷ precipitated asphaltenes in *n*-heptane and then performed sequential elution chromatography upon the filtrate. A comparison of the resins and asphaltenes separated via the two methods is shown in Table 2. The majority of the asphaltenes were recovered in the wax precipitation SEC, but these asphaltenes had generally higher H/C ratios, indicating irreversible adsorption of the more aromatic compounds. Where more asphaltenes were separated from the wax than were found in the whole crude, the additional asphaltenes were likely resins that had strongly adsorbed to the column. The majority of resins did not precipitate with the wax, causing the resin-to-asphaltene ratio (R/A ratio) to be much lower for the organic precipitate than for the whole crude, except for those with extremely high asphaltene contents and low R/A ratios.

The crudes examined here had a variety of wax contents with most having a relatively low percent wax. Other researchers have found wax contents for crude

Table 3. Elemental Analysis Data for the Organic Precipitate and Wax

crude	organic precipitate			wax (saturates)					
	wt % N	wt % S	H/C	wt % N	wt % S	wt % C	wt % H	H/C	wt % O
MI	0.24	0.51	1.85	0.00	0.26	85.25	14.59	2.05	0.42
SCS				0.00	0.05	86.12	14.23	1.98	
B6	1.53	5.57	1.34	0.00	0.50	85.32	13.92	1.96	0.57
AB	0.21	2.36	1.64	0.02	0.41	85.96	14.18	1.98	0.56
ANS	0.78	2.04	1.39	0.01	0.26	85.64	14.17	1.99	0.42
SF				0.00	0.00	86.18	14.06	1.96	
B4	1.35	5.38	1.28	0.00	0.48	85.25	13.77	1.94	0.68
Maya				0.01	0.30	86.10	13.84	1.93	
AH	0.52	5.14	1.39	0.00	0.71	85.53	13.81	1.94	0.65
CS				0.00	0.00	86.10	13.82	1.93	
GM				0.00	0.30	86.15	13.99	1.95	
Alba	0.41	1.86	1.50	0.00	0.37	85.64	13.55	1.90	0.67
BM	0.53	1.06	1.41	0.01	0.18	85.93	13.22	1.85	0.69
T1				0.00	0.13	86.12	13.41	1.87	
T2				0.00	0.16	86.34	13.28	1.85	
SJV	1.92	1.36	1.32	0.00	0.14	85.86	13.22	1.85	0.74

oils ranging from 0.0 to 16% wax.^{17,18,30} Some North Sea crudes, such as Alba and Statfjord, had wax contents ranging from 2.4 to 14.5% wax.¹⁷ Statfjord agreed with these data, but Alba's wax content was lower.

The amount and physical characteristics of wax determined by other researchers could be a function of the separation method. Both Johansen¹⁷ and Ronning- sen¹⁸ precipitated material with Burger's method and then eluted with hexane through a short silica column. However, Johansen first precipitated asphaltenes with *n*-pentane. Agrawal³⁰ precipitated with methyl isobutyl ketone at low temperatures and then decolorized the precipitate by percolation in the molten state through an activated bauxite column. Much of the older research on wax was in fact done on petroleum waxes that were commercially available.

Elemental Analysis. The elemental compositions (carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O)) of the precipitates and the wax obtained from the chromatographic separation were analyzed and collected in Table 3. They indicated that most of the nitrogen and sulfur was contained in compounds with low H/C ratios since in the eluted waxes the percent nitrogen and percent sulfur decreased while the H/C ratio increased. Thus the nonwax material in the precipitate had a low H/C ratio and high sulfur and nitrogen contents, consistent with resins or asphaltenes.

From the H/C ratio and visual inspection, preliminary categorization of the waxes could be made. Those waxes with the lowest H/C ratios, T1, T2, SJV, Alba, and BM, were translucent viscous liquids. These were considered the microcrystalline waxes. Another group was comprised of the waxes with the highest H/C ratios: AB, MI, B6, ANS, SCS, and SF. These waxes were opaque, white, or whitish-yellow solids. The yellow tinge may be a result of contamination by early aromatic elution. These were paraffin waxes. The remaining waxes, Maya, GM, CS, AH, and B4, were tackier solids with H/C ratios between those of the two groups and were mixtures of the two types.

All *n*-alkanes and isoalkanes have H/C ratios above 2 because of their terminal methyl groups. For these

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waxes to have H/C ratios below 2, they must contain rings or double bonds. An H/C ratio of 1.85 for a molecular weight near 400 amu would indicate a $C_{28}H_{52}$ formula with a maximum of 3 rings or 3 double bonds. For the same carbon content, an H/C ratio of 1.94 corresponds to $C_{28}H_{54}$ and a maximum of 2 rings, and one of 1.99 corresponds to $C_{28}H_{56}$ and 1 or 2 rings.

The sulfur content was under 0.5% for virtually all the waxes. Sulfur contents ranged from 0.0 to 0.71% and corresponded to a maximum of 0 to 14% of the wax containing sulfur. The sulfur could be thiol, thiophenic, sulfidic, or sulfoxide, though the FTIR did not indicate the presence of sulfide or sulfoxide. Since most of the organic sulfur found in crude oil is thiophenic, the sulfur in the waxes probably was as well.^{31,32} A C_{28} wax with one thiophenic ring would have an H/C ratio of 1.86, with a formula of $C_{28}H_{52}S$. Thus, sulfur thiophenic rings may account for some of the low H/C ratio. However, as sulfur is present in less than 14% of the wax molecules, it could not account for the majority of the low H/C ratio.

Oxygen in alcohols and ethers has no effect on the H/C ratio, so this decrease in H/C ratio was unrelated to oxygen content unless the oxygen was carbonyl, probably ketone or acid. Even if all the oxygen were carbonyl, it would not account for the majority of the lowered H/C ratio. The 1H NMR indicated the presence of ketone but negligible alcohol or ether. Thus the oxygen was mainly ketone or acid.

Some elemental analysis has been done on wax by other researchers, but remarkably little was on wax precipitated from petroleum. Holmes and Branthaver both examined bitumens, a close relative of petroleum. Holmes used desorptive Soxhlet extraction with heptane followed by complexation chromatography with cyclohexane to elute the saturates. The two bitumens examined had saturate fractions with H/C ratios of 1.86 and 2.07. Branthaver used Soxhlet extraction with benzene and ethanol followed by dewaxing via toluene/2-butanone at 0 °C to obtain wax. These waxes had H/C ratios of 1.87 and 1.94, a nitrogen content of 0.38%, and a sulfur content of 0.07%. The sulfur content was within the range found here, while the nitrogen content was higher. The only H/C ratio for a petroleum wax was found by Ackroyd.²⁸ The wax was separated by deasphalting the crude with benzene and adsorbing the remainder onto alumina. The pentane extract that was insoluble in acetone and that did not form a urea complex had an H/C ratio of 1.74. Since urea complexes are formed with *n*-alkanes, this H/C ratio is for branched and cyclic alkanes, thus its low H/C ratio in comparison with those here. The fraction that formed a complex with urea had an H/C ratio of 2.01, much closer to what is expected for a *n*-alkane or isoalkane.

FTIR. FTIR transmission spectra were obtained of all the waxes. The peak at 720 cm^{-1} has long been associated with long straight chain methylene,^{23,24} but no one has reported a Beer's Law constant or determined percent straight chain methylene. Few researchers have examined this peak because it is often obscured

Table 4. Weight Percent Straight Chain Methylene Obtained by FTIR, Melting Peaks, and Heats of Fusion Obtained by DSC for All Waxes

crude	% straight chain methylene	ΔH (cal/g)	peak (°C)
MI	77.91	33.19	51.34
SCS	66.38	26.13	43.43
B6	66.70	25.22	57.98
AB	68.98	17.00	47.94
ANS	62.71	19.54	46.89
SF	66.17	19.03	32.19
B4	65.30	18.00	45.82
Maya	63.40	13.37	39.42
AH	64.21	9.88	42.83
CS	60.93	11.70	30.10
GM	61.80	9.20	32.55
Alba	60.03	3.11	36.63
BM	55.49	0.88	34.06
T1	55.52	10.11	36.96
T2	53.12	3.02	32.90
SJV	51.70	0.25	30.60
eicosane		58.56	39.27

by solvent or by window opaqueness. This peak is associated with straight chain methylene at least four units long. Squalane, a branched hydrocarbon, had no peak at 720 cm^{-1} , but did have a peak at 735 cm^{-1} . This may be where methyl branched methylene chains absorb. In many cases, the percentage transmittance did not return to the baseline immediately after the 720 cm^{-1} peak, probably due to branches as demonstrated by squalane's 735 cm^{-1} peak. Therefore a symmetric peak was created by reflecting the peak through its highest point. This FTIR peak had a very small extinction coefficient of only 94.9 L/mol cm^2 . Consequently, the uncertainty in this measurement is large.

A variety of compounds were used to calculate the Beer's law constant for straight chain methylene. Because of the wax's heterogeneity, acids, an alcohol, and *n*-paraffins were used in the determination of the Beer's law constant. Octane, octanoic acid, decanoic acid, decane, decanol, lauric acid, myristic acid, palmitic acid, undecylenic acid, eicosane, and triacontane were used in this calculation. The best fit for the data was if the methylene group next to the acid group was not included.

From this FTIR measurement, the waxes were gauged to contain between 50 and 80% straight methylene chains at least 4 methylene units long (see Table 4). In addition, the waxes likely contain shorter chains, rings, and branches. On the basis of the measurements, SJV, Alba, BM, T1, and T2 fell at one end of the spectrum with 60% or less straight methylene. AB, B6, MI, SCS, and SF were at the other end with more than 66% straight methylene.

Mass Spectroscopy. The mass spectroscopy data definitively separated the waxes into the two categories mentioned previously. Several of the waxes in this study (AB, NS, B6, MI, SCS, and SF) had mass spectra reflecting a normal distribution of *n*-alkane or isoalkane hydrocarbons. The peaks were evenly spaced, 14 amu apart, covering a range from 350 to 600 as shown in Figure 4. However, five of the waxes, SJV, Alba, BM, T1, and T2, had very different mass spectra. These spectra began at near 350–400 amu but continued to 2000–3000 amu as in Figure 5. On the basis of the principles of the field desorption method, it is presumed that the profile shown accurately reflects the mass

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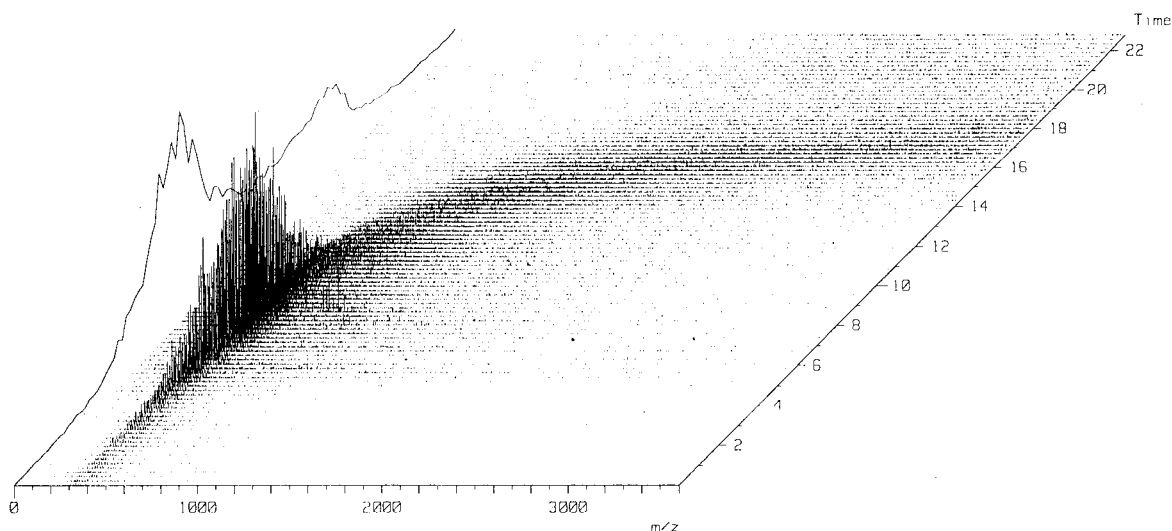


Figure 4. Malu Isan mass spectrum (field desorption mass spectroscopy) showing paraffin character.

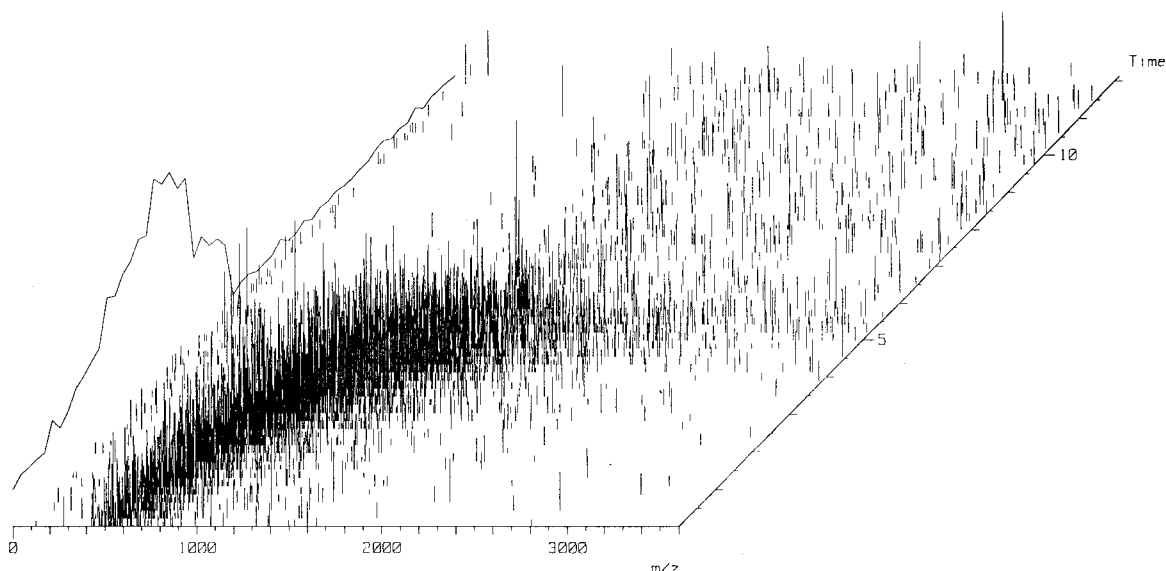


Figure 5. San Joaquin Valley mass spectrum (field desorption mass spectroscopy) showing microcrystalline character.

distribution of parent ions or molecules. Also, these waxes were not a simple 14 amu apart in the lower mass region. Some waxes, B4, Maya, GM, AH, and CS, were largely paraffinic in the lower mass regions, but contained a significant amount of higher molecular weight compounds as shown in Figure 6.

A few researchers have used a variety of methods to obtain molecular weight data for waxes. The data varied considerably, and only an average molecular weight was recorded. Some listed average molecular weights between 250 and 500 amu,^{2,18,33} or between 500 and 800 amu,^{5,23,34} or even higher, between 814 and 1078 amu.²⁸

Gel Permeation Chromatography (GPC). GPC was performed to determine an accurate median molecular weight. The median molecular weight was between 300 and 700 amu for all the waxes. As shown in Figures 7 and 8, most tailed off before 2000 amu. This may be incorrect as the baseline was determined visually, and thus a relatively small amount of material

could have been obscured by baseline variability. A few of these waxes, SCS, SF, MI, and B6, had a relatively narrow molecular weight range. Some also had small peaks near 100–200 amu which may be the result of contamination.

For SJV, Alba, BM, T1, and T2, the plots were inconsistent with the mass spectroscopy. Either the higher molecular weight compounds did not alter the refractive index much or field desorption mass spectroscopy falsely exaggerated the higher molecular weight peak heights. A propagation of error analysis was performed on the data. Even though the error depended on the molecular weight, the deviation was only 200 at 2000 Da. Thus, errors in reading the data cannot account for all the inconsistency.

Differential Scanning Calorimetry. The differential scanning calorimetry data confirmed the separation of the waxes into two distinct groups (see Table 4). SJV, Alba, T1, T2, and BM had very indistinct peaks even at significantly higher sample weights than those necessary for the other waxes as shown in Figure 9. These waxes melt over such a large region that no real discernible melting range could be found, as the enthal-

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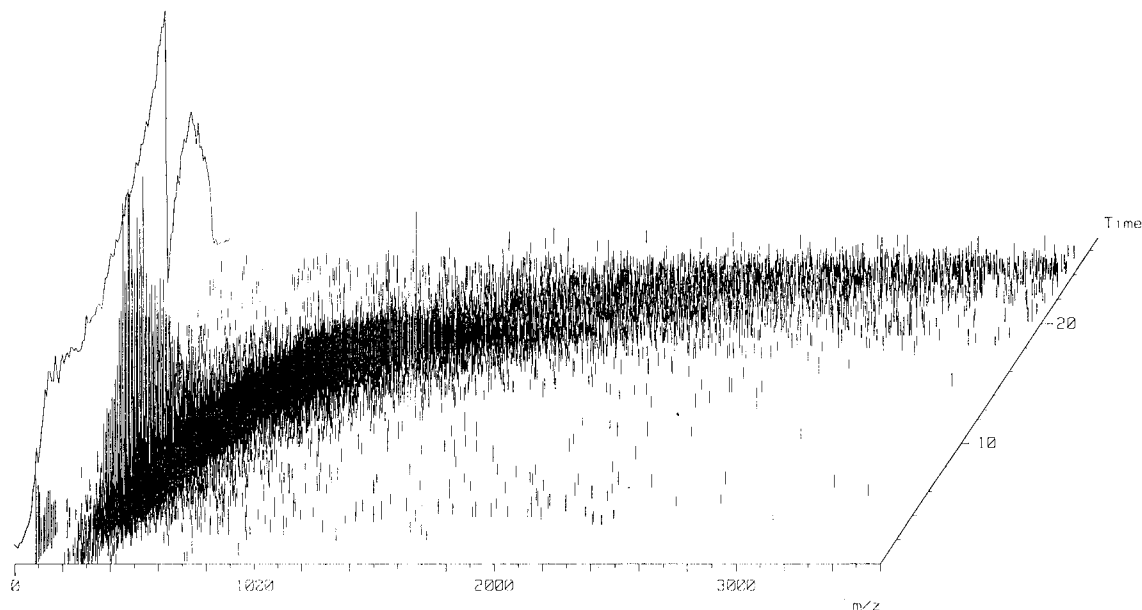


Figure 6. Canadon Seco mass spectrum (field desorption mass spectroscopy) showing a mixed paraffin-microcrystalline character.

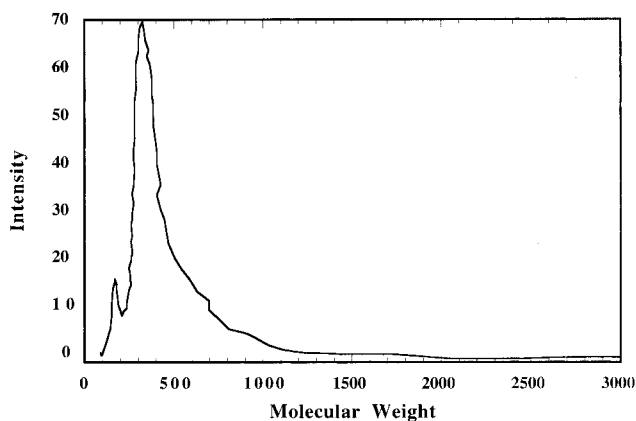


Figure 7. Malu Isan gel permeation chromatography for 0-3000 Da.

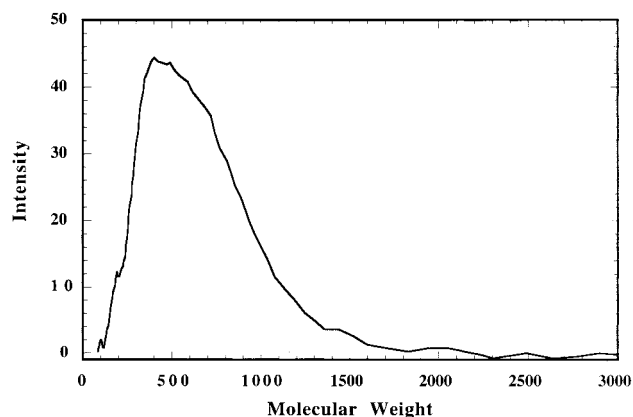


Figure 8. San Joaquin Valley gel permeation chromatography for 0-3000 Da.

pies found for the slight bulges seen are too small to be those of wax. The absence of a true melting region for these waxes has several possible explanations. The heat of fusion decreases with the increased isoparaffin content.³⁵ Thus these waxes could be mainly composed of isoparaffins or cycloparaffins. Also, the higher the

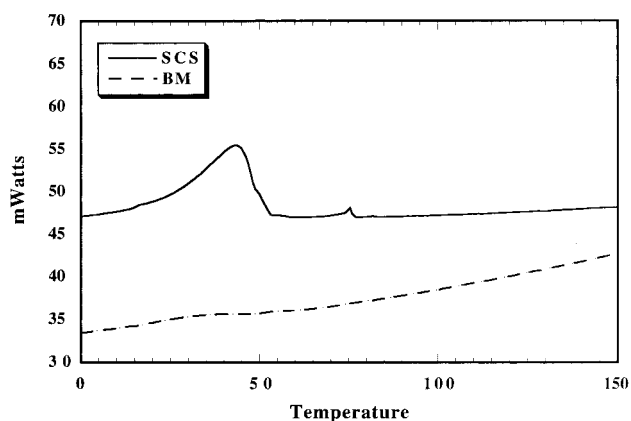


Figure 9. Differential scanning calorimetry thermograms of Bay Marchand and South China Sea wax from 0 to 100 °C.

molecular weight is, the lower the start of the melting range.³⁶ This would account for the slight bulge in the lower temperature regions for these five waxes. This further indicated that these five waxes had high molecular weights, branches, and rings. Eicosane was run as a standard to verify the accuracy of the melting enthalpies.

The remaining waxes all had distinct melting peaks as for SCS in Figure 9. MI was the only wax to have a definite transition peak and that merged into the melting peak. All had peak melting temperatures between 30 and 57 °C and melted over a range of 20-25 °C. Most had melting enthalpies between 10 and 35 cal/g. GM, Maya, AH, and CS had relatively low melting enthalpies, around 10 cal/g.

The melting temperatures of these paraffinic waxes were consistent with melting temperatures of waxes determined elsewhere. Several had melting temperatures very close to those found here, between 40 and 60 °C^{23,25,36} while some went as high as 93 °C, but none were lower than 40 °C.^{1,5,23} Other researchers' heats of fusion were near those determined here. Most were

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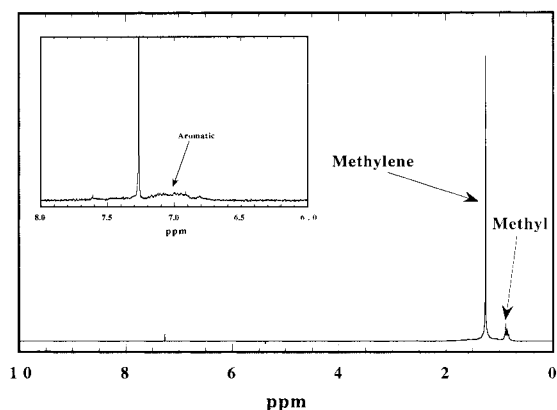


Figure 10. Arab Heavy in chloroform ^1H NMR spectrum at 5 g/L, with aromatic region expanded in inset.

Table 5. Percent Hydrogen for All Waxes Obtained by HNMR

crude	ratio CH_2/CH_3	ketone/ benzylic H			
		acid H	alcohol H	aromatic H	
MI	7.22	0.11	0.15	0.01	0.23
SCS	4.47	0.28	0.35	0.00	0.44
B6	4.83	0.18	0.36	0.02	0.45
AB	5.10	0.26	0.38	0.00	0.50
ANS	4.89	0.15	0.27	0.00	0.46
SF	4.51	0.19	0.20	0.00	0.34
B4	4.90	0.17	0.33	0.02	0.52
Maya	4.57	0.15	0.29	0.00	0.52
AH	4.43	0.25	0.43	0.02	0.63
CS	4.63	0.28	0.40	0.01	0.54
GM	4.10	0.20	0.21	0.00	0.43
Alba	4.37	0.19	0.30	0.01	0.52
BM	3.25	0.27	0.32	0.00	0.55
T1	2.89	0.32	0.50	0.00	0.62
T2	2.45	0.29	0.38	0.00	0.53
SJV	2.47	0.28	0.31	0.00	0.65

between 18 and 34 cal/g^{25,37,38} with some as high as 50–60 cal/g.^{1,25}

Proton Nuclear Magnetic Resonance Spectroscopy. Proton NMR did not show as obvious a separation of the waxes as did the previous methods. A sample ^1H NMR spectra is shown in Figure 10. SJV, Alba, T1, T2, and BM did have a much lower ratio of methylene to methyl carbons as shown in Table 5. This implied a number of branches larger than those the other waxes, validating the DSC and FTIR data. The proton NMR spectra did show a small region of aromatic proton as in the inset in Figure 10, but none contained more than 1% aromatic. One percent aromatic carbon means that 7% of the wax contains an aromatic ring. Much of this aromatic carbon could be present in thiophenic rings as the sulfur present in the waxes was likely thiophenic. Also, among the paraffin waxes, an increase in sulfur content is accompanied by a corresponding decrease in H/C ratio. If the sulfur was thiophenic, then the aromatic carbons in the thiophene would serve to reduce the H/C ratio as was observed.

All the waxes contained near 1% aromatic carbon, not completely accounting for the decrease in the H/C ratio. For example, for a H/C ratio of 1.85, a $\text{C}_{28}\text{H}_{52}$ formula is required. This has over 14% CH. Since the wax has only an average of 1% aromatic carbon, most of the

Table 6. Percent Carbons from ^{13}C NMR for Several Waxes

crude	CH_2/CH_3	%	methine for	
	ratio for straight CH_2		methyl branch (19.7 ppm)	methyl branch (32.8 ppm)
MI	17.20	18	0.0	0.4
SCS	17.69	29	1.4	0.6
B6	16.78	19	2.0	1.5
AB	14.75	30	1.4	1.1
ANS	13.90	35	0.6	0.9
SF	10.24	36	1.7	1.2
B4	16.38	33	1.6	1.1
Maya	12.39	32	1.6	1.3
AH	21.10	37	1.1	0.7
CS	15.38	49	1.1	0.9
GM	9.85	47	1.2	1.2
Alba	15.33	42	1.9	1.3
BM	11.90	55	1.6	1.8
T1	19.91	31	2.0	1.5
T2	11.13	45	4.5	2.9
SJV	9.71	64	2.3	1.6

decrease must be attributable to naphthenic rings. Two rings would give 10% methine with a H/C ratio of 1.96. Since the methine peak is hidden in the methylene peak, this is probably what occurs. One group of researchers found aromatic contents of 0.3–4.6% aromatic carbon for wax fractions from petroleum.³⁹

The ^1H NMR spectra also indicated the type of oxygen present in the waxes. Most protons on carbons adjacent to alcohols or ethers absorb between 3 and 4 ppm. Less than 0.02% proton was located there, so virtually none of the oxygen was alcohol or ether. A peak at 2.3 ppm often occurred when protons were on a carbon adjacent to an acid group. Another peak at 2.55 ppm could be attributed to protons adjacent to a ketone or on a carbon adjacent to an aromatic ring. All of these peaks were less than 1% of the hydrogen in the molecule. Both methine and naphthenic peaks were obscured by the methylene peak.

^{13}C Carbon Nuclear Magnetic Resonance Spectroscopy. Carbon NMR has often been a useful tool in the characterization of compounds though it is less useful for petroleum wax because of the wax's heterogeneity. In ^{13}C NMR, the position of carbons four atoms away from the one being studied can affect the peak location. Thus peaks only exist where a large fraction of the wax molecules have the same characteristics.

Since most waxes contain long straight chains, eicosane was used to identify some of the peaks. The peak at 14.1 ppm was the methyl end of the chain. The peaks at 22.7, 31.9, and 29.1 ppm were methylene units successively further from the methyl group. The large peak at 29.7 ppm was long internal methylene.^{40,41} The ratio of these methylene to the 14.1 ppm methyl peak is tabulated in Table 6. This is an indication of the average length of a straight methylene chain terminated by a methyl group. Sample spectra are shown in Figure 11. The MI, B6, AB, ANS, SF, and SCS wax spectra were almost exactly like the spectra of eicosane. The spectra for AH, CS, GM, Maya, and B4 were much the same with a few additional small peaks. The peak at

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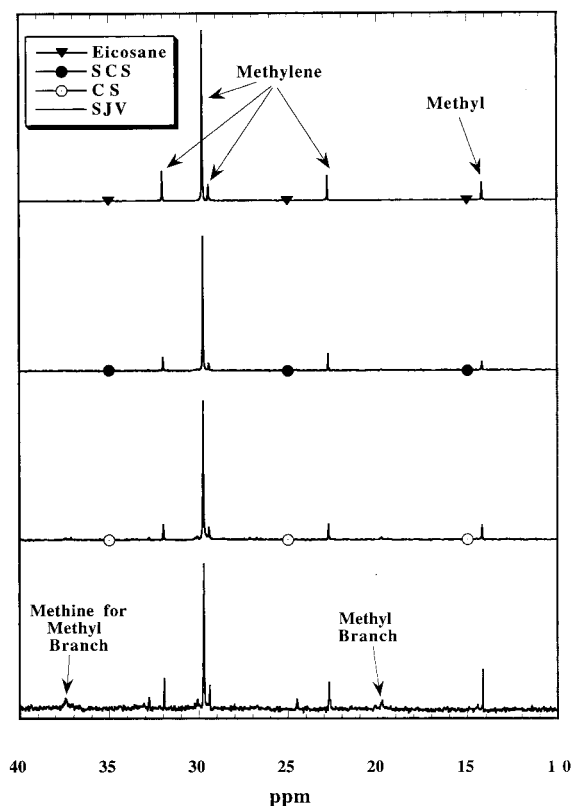


Figure 11. ^{13}C NMR for eicosane, South China Sea (SCS), Canadan Seco (CS), and San Joaquin Valley (SJV) waxes.

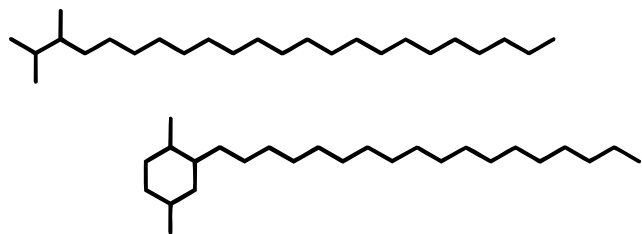


Figure 12. Average structure of a paraffin wax—Malu Isan.

19.71 ppm is indicative of methyl branches on a straight methylene backbone, and the peak at 32.8 ppm is the methine associated with that methyl branch. The percent of each of these peaks is shown in Table 6. The other waxes, SJV, BM, Alba, T1, and T2, also exhibited such peaks, as well as several unknown peaks. These waxes showed significantly more clutter under the baseline as tabulated in Table 5 as “% unknown”. This was likely the result of a number of peaks overlapping. Thus, these waxes were more heterogeneous than the others.

None of the waxes exhibited any aromatic, ketone, or acid peaks. This was not surprising considering the high concentration of an identical region necessary for a peak to be formed. Given the high number of possible neighborhoods for any of the groups, the possibility of having enough of any to show in a spectra is unlikely.

Average Structure of Wax Molecules. Several of the data sets, when combined, were used to produce an average structure for each of the waxes (see Figures 12 and 13). From the data, three independent equations could be written for an overall wax molecule. Because four independent variables exist, one of the variables must be fixed. Quaternary carbon was chosen because

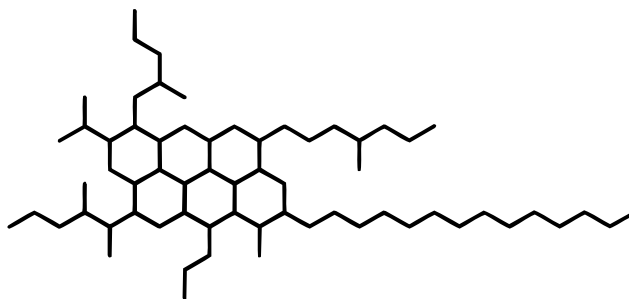


Figure 13. Average structure of a microcrystalline wax—San Joaquin Valley.

Table 7. Percent Methyl, Methylene, Methine, and Quaternary Carbon for All Waxes

crude	% methyl	% methylene	% methine	% quaternary carbon
MI	12.2	82.3	5.3	0.2
SCS	16.4	68.3	15.1	0.3
B6	15.1	68.2	16.5	0.3
AB	14.9	70.7	14.1	0.3
ANS	14.9	71.1	13.7	0.2
SF	15.9	66.7	17.2	0.2
B4	14.7	67.1	17.9	0.3
Maya	15.3	65.2	19.3	0.3
AH	15.8	65.2	18.7	0.4
CS	15.1	65.3	19.2	0.4
GM	16.8	64.2	18.7	0.3
Alba	15.3	62.3	22.1	0.3
BM	17.6	53.1	28.9	0.3
T1	19.3	52.1	28.2	0.4
T2	20.7	47.3	31.7	0.3
SJV	20.6	47.7	31.3	0.4

of its relative scarcity. The percent quaternary carbon was determined from the aromatic and acidic proton percentages from ^1H NMR. All of the aromatic proton was assumed present in benzylic rings. The acidic carbons and the benzene ring joints were assumed to be the only quaternary carbon present in the wax molecule. The three equations used to calculate methyl, methylene, and methine percentages are shown below

$$\#C + \#CH + \#CH_2 + \#CH_3 = \#C_{\text{total}} \quad (1)$$

$$\#CH + 2\#CH_2 + 3\#CH_3 = \#H_{\text{total}} \quad (2)$$

$$\frac{\text{CH}_2}{\text{CH}_3} = A \quad (3)$$

where A is the methyl-to-methylene ratio from ^1H NMR. The three equations were solved, and the numbers converted to percentages. These percentages are shown in Table 7.

For all of the waxes, the estimated percent quaternary carbon was below 0.5 wt %. The waxes averaged 12–21% methyl, 48–82% methylene, and 5–31% methine. Discrepancies between these data and the methylene content from FTIR was attributable to uncertainty in the data used to determine the percents methyl, methylene, and methine carbon. MI, SCS, B6, AB, ANS, and SF had, overall, the lowest percent methine, and methyl and the highest percent methylene. The extremely high percent methine of Alba, BM, T1, T2, and SJV combined with the percent methyl indicated a large number of rings. For every methyl group, there must be a corresponding methine, excepting the two terminal methyls present in any ringless molecule. The additional me-

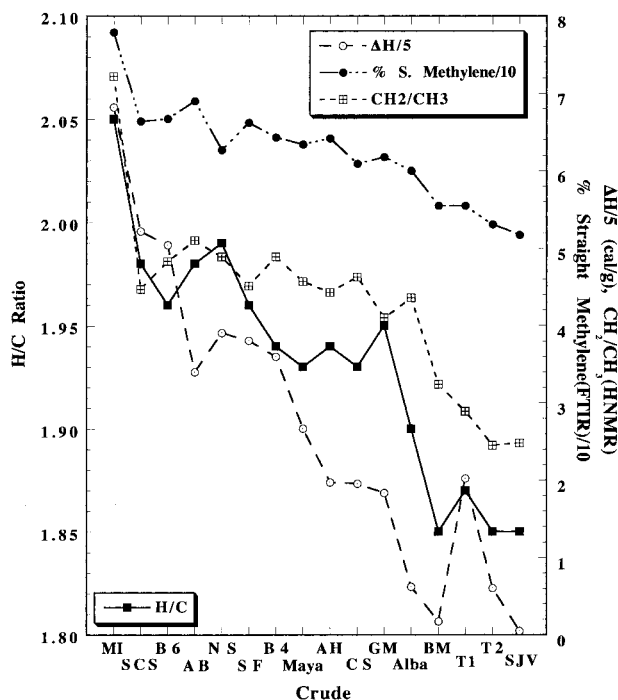


Figure 14. Comparison of ΔH , CH_2/CH_3 (^1H NMR) ratio, H/C ratio, and % straight chain methylene from FTIR for waxes from a variety of crudes.

thine above the number required for the methyl groups are ring joints. These five waxes had 7–11% more methine than methyl. This indicated a significant number of rings. MI, SCS, B6, AB, ANS, and SF, however, had about as many methine as methyl. This indicates that these waxes contained 0–2 rings per molecule.

Comparison of Different Techniques. BM, Alba, SJV, T1, and T2 were identified by several techniques as being different from other waxes. They had a large molecular weight range and lower H/C ratios. They had broad, indefinite melting regions. They had a smaller number of methylene groups per methyl than the other waxes, were a different color, and behaved much like gels. They had a lower percentage of straight chain methylene and a significant amount of unknown material in the ^{13}C NMR. They had a higher percent methine than methyl groups. These waxes were different from the others in a variety of ways and were thus a different type of wax called microcrystalline or amorphous wax.⁴² AB, NS, B6, MI, SCS, and SF had very different characteristics from the previous group. They had a narrow molecular weight range, between 300 and 650 amu. They had higher H/C ratios and identifiable melting regions. They had a higher number of methylene groups per methyl and were solids. They had a higher percentage of straight chain methylene. They had the near the same percent of methyl groups as methine, or more. These were labeled paraffin waxes. Five crude waxes did not fit neatly into either category. B4, AH, Maya, GM, and CS were mixtures of both types of wax with paraffinic wax at low molecular weight but a distinct tail of higher molecular weight compounds. A comparison of all these characteristics is shown in Figure 14. The mixed waxes tend to be high

in some respects but low in others because they are mixtures. In fact, most of the waxes were probably mixtures of both types, but the majority had one type dominating to such a degree that its characteristics almost completely obscured the other type.

Conclusions

The wax from sixteen crude oils was characterized. All of the waxes contained small amounts of oxygen which ^1H NMR indicated was primarily acid or ketone. All had small amounts ($\sim 1\%$) of aromatic carbon, a significant portion of which was probably involved in thiophenic rings. All contained at least 50% straight chain methylene.

The waxes fell into two different categories based primarily on molecular weight, H/C ratio, and melting ranges. Several of the waxes were composed of paraffinic hydrocarbons such as *n*-alkanes and isoalkanes. Their molecular weight range was between 350 and 600 amu with H/C ratios between 1.92 and 2.05. They displayed definite melting peaks and heats of fusion. These were paraffin waxes. Five other waxes, SJV, Alba, BM, T1, and T2 had a much longer molecular weight range continuing to 3600. These waxes also had slightly lower H/C ratios, between 1.85 and 1.90, with no identifiable melting peak. They had a much lower ratio of methylene to methyl carbons and contained a number of methyl branches. They had a large amount of clutter in their ^{13}C NMR spectra. Analysis indicated a large excess of methine compared to methyl groups. These were microcrystalline waxes.⁴² B4, AH, Maya, GM, and CS were a mixture of both types of wax, with the majority being paraffinic but with a significant amount of microcrystalline as well.

Precipitation by itself was not a viable method for the measurement of the wax content of a crude because material often coprecipitated with it. Two different types of wax were found in crude oil. They had differing H/C ratios, DSC plots, mass spectra, CH_2/CH_3 ratios from ^1H NMR, and ^{13}C NMR spectra.

Acknowledgment. The authors are grateful to the Petroleum Environmental Research Forum (PERF), through grants 91-05 and 95-02, and to the National Science Foundation (NSF), through a predoctoral fellowship to Barbara J. Musser, for supporting this research. We acknowledge the work of the undergraduate researchers who contributed to this study: Joe Todd and Robert Hughes.

Nomenclature

#C = number of quaternary carbon in wax molecule
 #CH = number of methine groups in wax molecule
 #CH₂ = number of methylene groups in wax molecule
 #CH₃ = number of methyl groups in wax molecule
 #C_{total} = total number of carbons in wax molecule (wt % C × given molecular weight)
 #H_{total} = total number of hydrogens in wax molecule (wt % H × given molecular weight)
 A = methylene/methyl ratio for wax from FTIR (Table 4)

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