

AN INVESTIGATION OF OXYGEN FUNCTIONS IN BITUMEN FRACTIONS

By

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INTRODUCTION

The function of hetero-atoms (i.e. nitrogen, oxygen and sulphur) within a bitumen or petroleum has not yet been evaluated but on the basis of work carried out with a variety of petroleum asphaltenes and resins (1), it appears that they play an important part in the intermolecular forces which are necessary for the colloidal stability of petroleums, bitumens and asphalts. For example, the asphaltenes themselves are insoluble in the oils but are able to exist in bitumens (or petroleums) as micellular dispersions due to the peptising effect of the resins. Thus, the stability of the system primarily depends upon the relation of asphaltenes and resins and finally upon the relationship between the micelles and the oily medium. Whilst very little is known about the locale of the hetero-atoms in bitumens and asphalts, preliminary attempts have been made to place the hetero-atoms in aromatic or non-aromatic locations, within the Athabasca bitumen, by virtue of their retention in the cokes formed during pyrolysis (2-4). It therefore seemed worthwhile to examine the bitumen chemically and spectroscopically in order to gain some knowledge of the hetero-atom types in this material. Thus, the results of investigations pertaining to the nature of the oxygen atoms within the asphaltene and resin fractions of the bitumen are now reported.

EXPERIMENTAL

Deasphalted (pentane) Athabasca bitumen was mixed with twenty (20) parts by weight of Fuller's earth whereby extraction with pentane yielded the oil fraction. Subsequent extraction with pyridine yielded the resin fraction. Further separation of the oil fraction by a standard chromatographic technique using a silica gel-alumina column with pentane and benzene yielded the saturates and aromatics, respectively. Infrared spectra were recorded as films on sodium chloride plates using a Perkin Elmer 221 Double Beam Infrared Spectrophotometer; the films were deposited from methylene chloride solution by evaporation of the solvent.

Resin Interactions

Sodium salt of resins: The resins were dissolved in dioxane and the solution heated under reflux with normal aqueous sodium hydroxide solution for 4 hr. The sodium salt of the resins was isolated by evaporation of the aqueous dioxane under reduced pressure.

Resin acids The sodium salt was dissolved in ether and treated several times in an extraction funnel with normal hydrochloric acid solution. The ethereal solution was washed with distilled water until acid free (Congo paper), dried (anhy. sodium sulphate) and the products isolated by evaporation of the ether under reduced pressure.

Acetylated resins: Resins and acetic anhydride were heated under reflux for 24 hr. The acetic anhydride was removed by distillation under reduced pressure at 65°C. The residue was repeatedly dissolved in dry toluene and dried as before to ensure complete removal of the acetic anhydride.

Methylated resins: Resins were methylated with diazomethane in ethereal solution.

Asphaltene Interactions

Acetylated asphaltenes: Method A Asphaltenes (5 g.), acetic anhydride (50 ml.) and pyridine (2 ml.) were heated under reflux for 24 hr. The product was isolated by removal of the liquids under reduced pressure at 65°C. The residue was repeatedly dissolved in toluene and the solvent removed as before to ensure complete removal of the acetic anhydride, extracted with ether (Soxhlet) and dried (70°C/20 mm Hg); the ether extract amounted to 4% w/w of the material. The ether-insoluble material was finally purified by washing a toluene solution with water and, after drying over anhydrous sodium sulphate, the solvent was removed in the usual manner.

Method B The asphaltenes were extracted with ether (Soxhlet) prior to treatment of each fraction with acetic anhydride. As above, the ether soluble fraction amounted to 4% w/w of the asphaltenes. Thus, the asphaltene fraction (5 g.) was acetylated as described in Method A using toluene (50 ml.) as a solvent and the product was purified in a similar manner but the ether extraction step was omitted.

Acetyl group determinations were carried out by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany.

Hydrolysis of phthalic and n-butyric anhydrides: The anhydride (1 g.) and aqueous potassium bicarbonate (10% w/w, 50 ml.) were stirred at room temperature for 30 min. After acidification with normal hydrochloric acid solution, the organic product was extracted with ether and the ethereal solution was washed (water) and dried (anhy. sodium sulphate). If a precipitate formed as a result of acidification, the material was isolated by filtration, washed (water) and dried (70°C/20 mm Hg). Refluxing the reactants for 15 min. gave essentially the same results.

Acetylated asphaltenes - aqueous potassium bicarbonate: Acetylated asphaltenes (1 g.) and aqueous potassium bicarbonate (10% w/w, 75 ml.) were stirred vigorously for 30 min. at room temperature. The asphaltenes were separated by filtration, washed with normal hydrochloric acid solution, water and dried (70°C/20 mm Hg). Alternatively, a solution of acetylated asphaltenes (1 g.) in chloroform (20 ml.) was stirred vigorously with aqueous potassium bicarbonate (10% w/w, 75 ml.) for 30 min. at room temperature. The organic layer was washed with normal hydrochloric acid, water and dried (anhy. sodium sulphate). The solvent was removed under reduced pressure.

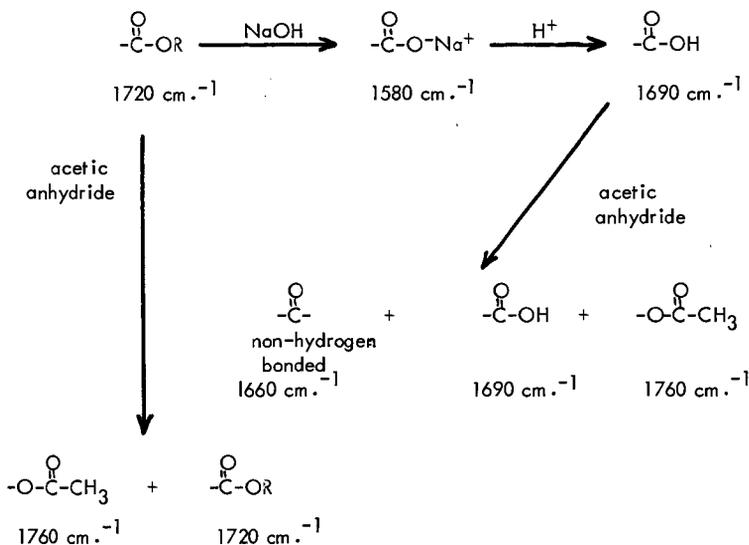
- aqueous sodium hydroxide: A solution of acetylated asphaltenes (1 g.) in benzene (50 ml.) and normal aqueous sodium hydroxide (25 ml.) was heated under reflux for 30 min. The sodium salt of the reaction product was isolated by evaporation of the liquids on a steam bath and was finally dried under reduced pressure (70°C/20 mm Hg).

RESULTS AND DISCUSSION

The use of infrared spectroscopy to identify oxygen functions, especially those responsible for carbonyl absorptions, produced during the oxidation of asphalts has received considerable attention (5). However, the recognition of organically-bound oxygen in unoxidised asphalts and bitumens has mainly been restricted to analytical data (6) and, with few exceptions (7), there has been little, or no, attempt to identify the oxygen types in natural asphalts or bitumens.

Preliminary infrared spectroscopic examination of the bitumen itself and the fractions derived therefrom (Figure 1) shows that the resin fraction exhibits the strongest absorption in the carbonyl region of the infrared (1720 cm^{-1}) and therefore was chosen as the starting material for these investigations. The infrared spectrum of the resins (Figure 2a) is characterised by two absorption bands in the $1500 - 1800\text{ cm}^{-1}$ region which are centred at 1600 cm^{-1} and 1720 cm^{-1} . The former is attributed to double bonds between carbon atoms whilst the latter is assigned to carbonyl oxygen (8). After hydrolysis, the sodium salt of the reaction product exhibits a strong absorption at 1580 cm^{-1} (Figure 2b); the original carbonyl band at 1720 cm^{-1} has completely disappeared whilst the 1600 cm^{-1} band is presumably masked by the strong and broad absorption band centred at 1580 cm^{-1} . These changes in the infrared spectra of the resins suggest formation of carboxylate anions which are derived from the hydrolysed carboxylic acid esters originally present in the resin entities. Furthermore, treatment of the resin sodium salt with hydrochloric acid results in displacement of the sodium ion and formation of the free acid. The infrared spectrum of the resin acids (Figure 2c) shows two bands centred at 1600 cm^{-1} and 1690 cm^{-1} . The latter band is assigned to the carbonyl absorption of hydrogen-bonded carboxylic acid groups. These derivatives also exhibit broad absorption in the $3200 - 3500\text{ cm}^{-1}$ region of the infrared due to the stretching vibrations of hydrogen-bonded hydroxyl groups. When the hydrolysed resins are refluxed with acetic anhydride, the result is a product with a more complex infrared spectrum. As illustrated (Figure 2d), two new bands - centred at 1660 cm^{-1} and 1760 cm^{-1} - appear. The absorption at 1600 cm^{-1} is greatly reduced when compared with the 1690 cm^{-1} band of the resin acids (Figure 2c) and the broad absorption in the $3200 - 3500\text{ cm}^{-1}$ region is also greatly reduced. It appears that reaction with acetic anhydride has caused acetylation of the free and hydrogen-bonded phenolic hydroxyl groups present in the hydrolysed resins giving rise to the absorption bands at 1660 cm^{-1} and 1760 cm^{-1} which have previously been attributed to non-hydrogen-bonded carbonyl of a ketone and/or quinone and phenyl acetates, respectively (9).

In order to obtain stronger evidence and to substantiate further the weak absorption band at 1660 cm^{-1} , methylated resins were treated with refluxing acetic anhydride in the absence of a catalyst. This method has been found effective by Moschopedis (9) on coal humic acids and was later employed by Mathur (10) during studies of soil humic acids. Thus, examination of the infrared spectrum of the product (Figure 2f) again showed prominent absorptions at 1660 cm^{-1} and 1760 cm^{-1} . It was also noted that the 1660 cm^{-1} carbonyl band was much more intense when the resins were methylated prior to treatment with acetic anhydride in agreement with previous work (9-12) that acetylation takes place much more readily after the material has been methylated. In an attempt to ascertain the proximity of the various oxygen functions in the natural resins with respect to each other, the resins and the hydrolysed resins were heated in sulpholane under reduced pressure in the manner outlined elsewhere (11). In both cases, anhydride formation failed to occur thus indicating that any carboxylic acid functions in the original resins and, for that matter, similar functions in the hydrolysed material are not located in such close proximity which would be conducive to anhydride formation (11). It is also noteworthy here that whilst such carbonyl oxygen functions exist in isolated locations, the results of preliminary studies into the quantitative analysis of oxygen functions in the resins indicate that esters are the predominant locale for oxygen in the resin fraction. These latter observations notwithstanding, the results described above lead to the conclusion that the 1720 cm^{-1} infrared absorption band of the natural resins is mainly due to the presence of esters in this material and, thus, the following transformations are proposed:



At this stage, attention was turned to the asphaltene fraction of the bitumen. An examination of the infrared spectrum of the asphaltenes (Figure 1) shows that characteristic absorptions due to oxygen-containing functional groups are largely restricted to the 3200-3500 cm.^{-1} region; this broad absorption has previously been assigned to hydrogen-bonded hydroxyl groups (13, 14). Lack of any absorption in the 1670 - 1800 cm.^{-1} region of the spectrum indicates that carboxylic acid carbonyl groups are absent from the asphaltene molecule (14). Nevertheless, it is known that hydrogen-bonded carbonyl groups of ketones and/or quinones appear in the 1600 cm.^{-1} region (14) and, consequently, will be masked by the 1590 cm.^{-1} band present in the asphaltene spectrum; the 1590 cm.^{-1} band in the infrared spectrum of asphaltene has been mainly assigned to carbon-carbon double bonds (8).

When asphaltenes are heated with acetic anhydride in the presence of pyridine, the infrared spectrum of the product (Figure 3a) exhibits prominent absorptions in the 1680 - 1800 cm.^{-1} region. Examination of the expanded infrared spectrum shows that the infrared bands of the acetylated material are centred at 1680 cm.^{-1} , 1730 cm.^{-1} and 1760 cm.^{-1} . The relative intensities of the 1730 cm.^{-1} and 1760 cm.^{-1} bands appears to depend upon the method by which the asphaltenes were treated with acetic anhydride. For example, when the asphaltenes were acetylated in suspension (Method A) the 1760 cm.^{-1} absorption was more intense than the 1730 cm.^{-1} band. The converse is true when the asphaltenes were acetylated in solution (Method B); in this case the 1730 cm.^{-1} band was more pronounced. Therefore, it is apparent that when asphaltenes were treated in toluene solution acetylation is much more extensive and presumably includes acetylation of hydroxyl groups which may otherwise be

sterically hindered when the material is in suspension and which are relatively difficult to acetylate in this state.

The observed changes in the infrared spectrum of the asphaltenes as a result of treatment with refluxing acetic anhydride suggest acetylation of free and hydrogen-bonded phenolic hydroxyl groups which are present in the asphaltenes (13). The absorption bands at 1680 cm^{-1} and 1760 cm^{-1} have previously been attributed to non-hydrogen bonded carbonyl of a ketone and/or quinone and to phenolic acetates, respectively (9). If the 1680 cm^{-1} band is, in fact, due to the presence of non-hydrogen bonded ketones or quinones, the appearance of this band in the infrared spectra of the products could conceivably arise by acetylation of a nearby hydroxyl function which had served as a hydrogen-bonding partner to the ketone (or quinone) thereby releasing this function and causing the shift from ca. 1600 cm^{-1} to higher frequencies.

The 1730 cm^{-1} band, the third prominent feature in the spectrum of the acetylated products is also ascribed to phenolic acetates and, like the 1760 cm^{-1} band, falls within the range $1725 - 1760\text{ cm}^{-1}$ assigned to esters of polyfunctional phenols suggesting that a considerable portion of the hydroxyl groups present in the asphaltenes may occur as collections of two, or more, hydroxyl functions on the same aromatic ring or on adjacent peripheral sites or on sites adjacent to a carbonyl function in a condensed aromatic system (11).

To check the possibility of anhydride formation which could also account for the 1730 cm^{-1} and 1760 cm^{-1} absorption bands in the products, the acetylated asphaltenes were treated at room temperature with aqueous potassium bicarbonate. The failure of this procedure to cause any changes in the spectra of the acetylated asphaltenes, when model anhydrides were hydrolysed by this reagent, is strong evidence for the exclusion of anhydrides from the products of the acetylation process.

The infrared spectrum of the ether-soluble asphaltene fraction (Figure 1d) is characterised by a broad absorption band at $3200-3500\text{ cm}^{-1}$ and a moderately strong band centred at 1690 cm^{-1} . The former band is assigned to hydrogen-bonded hydroxyl groups of phenols and/or carboxylic acids whilst the latter band is assigned to the carbonyl group of carboxylic acids (14). After refluxing in an acetic anhydride-pyridine mixture, the product also had a band at 1690 cm^{-1} but with shoulders on the high frequency side which consisted of absorptions at 1730 cm^{-1} and 1760 cm^{-1} . These two bands are again assigned to the presence of polyfunctional phenol acetates since, after treatment with aqueous potassium bicarbonate, no changes were observed in the position of these two bands in the infrared. Additional evidence for the assignment of the 1730 cm^{-1} and 1760 cm^{-1} absorptions to phenol acetates was obtained by hydrolysis of the acetylated products, in particular hydrolysis of the acetylated ether-soluble asphaltene as the original material contains carboxyl functions (Figure 3d) which could conceivably lead to anhydride formation. Thus, treatment of the acetylated product with normal aqueous sodium hydroxide yielded a product with a strong absorption centred at 1580 cm^{-1} (Figure 4), assigned to the presence of the carboxylate ion (14), with no absorptions in the $1700-1800\text{ cm}^{-1}$ region. Since treatment with aqueous potassium bicarbonate did not cause any changes in the infrared but hydrolysis with aqueous sodium hydroxide caused marked changes in the infrared spectrum, it is evident that the 1730 cm^{-1} and the 1760 cm^{-1} absorption bands are due to phenolic acetates and not to carbonyl functions of anhydrides.

Finally, acetyl group determination in the products produced some interesting information (Table). The results showed that 40 - 60% of the oxygen present in the unreacted asphaltenes is accessible to acetylation and, in accordance with the absorption band at 1200 cm^{-1} in the infrared spectra of the acetylated materials, is presumed to be in the form of phenolic hydroxyl groups (14). However, it seems that some of these particular groups may

be inaccessible to acetylation because of steric factors since infrared spectroscopic examination of the acetylation products in dilute solution (13) showed the presence of absorption bands due to non-hydrogen bonded hydroxyl groups. It is conceivable that groups of this type may be sterically hindered by virtue of their location in "hole" structures - if such structures do in fact exist within the asphaltene molecule (15). Nevertheless, it is apparent that the majority of the oxygen in the asphaltenes is in the form of hydroxyl groups. The remainder of the oxygen, apart from that in sterically-hindered hydroxyl groups, could well exist as carbonyl functions (such as ketones and quinones), ethers, sulphur-oxygen functions as well as carboxyl functions in the ether-soluble fraction.

Acknowledgements

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TABLE

Sample	Unreacted material		Product	
	%O	m.eq./g.	% acetyl	m.eq./g.
Asphaltene product (Method A)	---not determined---		2.73	0.63
Asphaltene (ether- insoluble) product (Method B)	2.49	1.56	3.08	0.72
Asphaltene (ether- soluble) product (Method B)	1.82	1.14	2.74	0.64

FIGURE 1 Infrared spectra of Zibicos - Ethicon on acrylnitrile fractions

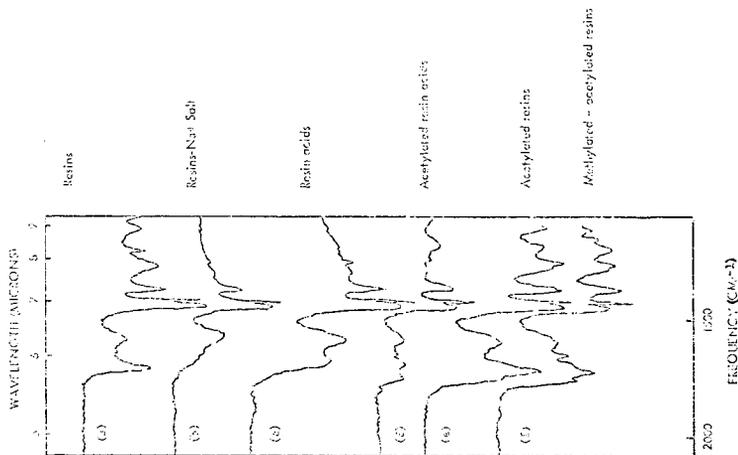
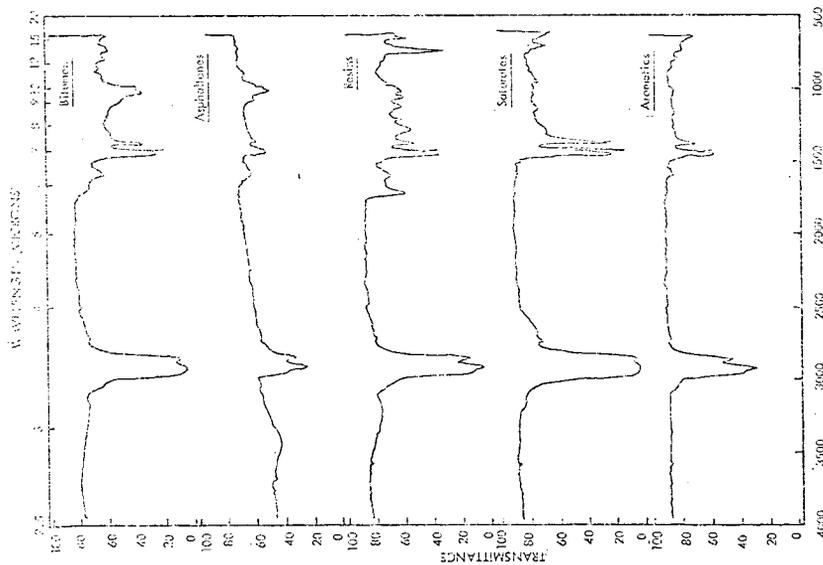


FIGURE 2 Infrared spectra of the resin fraction and derived products

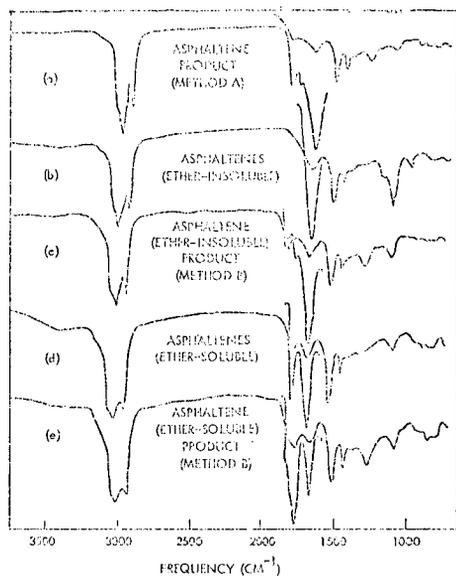


FIGURE 6: Infrared spectra of acetylated products

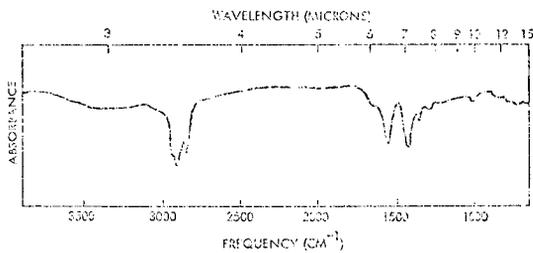


FIGURE 7: Infrared spectrum of acetylated (Method A) ethionolacetic asphaltene after hydrolysis (eq. 10.20)