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The Molecular Structure of Athabasca Asphaltene. Cleavage of the Carbon–Sulfur Bonds by Radical Ion Electron Transfer Reactions

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The molecular structure of Athabasca asphaltene from northeastern Alberta has been investigated. The large asphaltene molecules of mol wt 5920 were reduced by electron transfer from naphthalene radical anions produced in situ by treatment of naphthalene with potassium in tetrahydrofuran solution. The asphaltene anions were stabilized by octylation or protonation. From the number of octyl groups and potassium atoms consumed and the number average molecular weight of the treated asphaltene it was determined that the molecular weight on an octyl-free basis decreased tenfold during reduction. The extent of hydrogen bonding in the molecule was determined from the reduction in molecular weight upon silylation and diazomethane treatment to be one bond per molecule. It was also established that at least two-thirds of the oxygen is present in hydroxyl groups and some in carbonyl groups. The average aromatic carbon and aromatic hydrogen contents were determined to be 42 and 8%, respectively, by NMR spectroscopy. From the above results and those obtained in an auxiliary study of naphthalene anion reduction of simple model sulfur compounds, it is concluded that the Athabasca asphaltene has a sulfur polymeric framework in which the average carbon moieties, consisting of an alicyclic diaromatic structure with some alkyl substituents, are held together by sulfide linkages. It is shown experimentally that at least 65% of the sulfur is present in sulfide bonds, but other considerations suggest that the true figure is at least 90%. A solvent extraction scheme allowed some fractionation of the whole asphaltene. The 15% alcohol and acetone soluble fraction contains 40% of the oxygen present in the asphaltene molecule.

Asphaltene, the ubiquitous high molecular weight pentane insoluble fraction of petroleum, is a complex mixture of polycyclic aromatic molecules. In general, petroleum asphaltene is characterized by its high heteroatom content which in the case of the northeastern Alberta Athabasca asphaltene is in the range of sulfur 8–9%, oxygen 2–3%, and nitrogen ~1%. The chemical composition and molecular weight distribution show considerable variation with the source reservoir and depth, and the concentration may also vary from a few tenths of 1% in light crude oils to 25% in the Athabasca bitumen.

The molecular structure of asphaltene poses a challenge to the structural chemist and in spite of the numerous studies addressed to the problem the crucial question of whether asphaltene is a carbon polymer or a polymer in which the smaller carbon monomers are joined together by heteroatom linkages still remains unresolved. According to currently accepted notions the heteroatoms present in asphaltene are built into the ring systems of the molecules, which view, if correct, would favor a carbon polymer skeleton. A knowledge of the molecular structure would have practical and theoretical ramifications. It could have potential significance on the refining and upgrading processes of heavy crudes and bitumens, the production of bitumen from oil sands, and the possible commercial utilization of asphaltene and could also shed light on the mode of the formation of asphaltene and the diagenetic history of the source reservoir.

Most of the earlier studies reported in the literature on the molecular structure of asphaltene employed physical methods and the few chemical investigations which appeared were rather limited in scope. The most informative study is probably that published by Sawatzky and Montgomery[1] in which the molecular weight of Mildred Lake (northeastern Alberta) asphaltene was decreased from 6110 to 3547 by a single step reduction with lithium aluminum hydride and also by three successive reductions in ethylenediamine with a large excess of lithium. The decrease in molecular weight was attributed to cleavage of sulfide or ether bonds. More recently reduction

Table I. Average Molecular Weight of Asphaltene in Various Solvents

Solvent	Mol wt
Benzene	5920
CH_2Br_2	5480
CH_2Br_2 + dioxane	5500
Pyridine	5450

of coal with potassium and naphthalene followed by alkylation has been used for solubilization of coal.[2] Cleavage of ether linkages was thought to take place but solubilization was attributed mainly to the alkylation process.

In the present chemical approach to the structural elucidation of Athabasca asphaltene we have tried several mild oxidative and reductive degradative reactions of which the most suitable one was the treatment of asphaltene with potassium in tetrahydrofuran (THF) solution in the presence of naphthalene as an electron transfer agent. The C–S and C–O linkages are known to undergo cleavage reactions on electron transfer, $RXR + e \rightarrow RX^- + R\cdot$, while C–C bonds in general are resistant to this type of cleavage. This system appeared to be promising for the clarification of the role that the heteroatoms play in the polymeric skeleton. Cleavage of the C–X bond or removal of the heteroatom would not cause degradation of the polymer if the heteroatoms are part of the ring systems but degradation and an accompanying decrease in molecular weight would result if the sulfur and oxygen atoms were essential in holding together the polymeric framework of the asphaltene molecule.

The mechanism of C–S and C–O bond cleavages by electron transfer is not well understood. Consequently, parallel to the asphaltene studies, it was necessary to carry out some cursory auxiliary studies on simple model systems.

Experimental Section

1. Materials. The asphaltene was separated from the bitumen by the standard method of *n*-pentane precipitation.[3] Oil sand from Great Canadian Oil Sand Co. obtained through the courtesy of the Alberta Research Council was extracted with benzene and the bitumen was freed from the solvent by evaporation. A 1:1 mixture of the bitumen and benzene was diluted with 60 volumes of pentane and the precipitated asphaltene collected under nitrogen on a 10–20 μm porosity sintered glass funnel. The asphaltene was Soxhlet extracted for 24 h with pentane and dried. The yield of asphaltene averaged 16%. Anal. C, 80.27; H, 8.01; N, 1.21; S, 8.18; O, 2.50. Mol wt (by vapor pressure osmometry) 5920 ± 900, as the mean and standard deviation from seven measurements. These data give the molecular formula $C_{393}H_{472}N_5S_{15}O_9$.

THF was purified by distillation from potassium under nitrogen. The potassium, which had been cleaned by melting, was weighed quickly in the THF and used for the reaction.

Diazomethane was prepared from Diazald (Aldrich) according to the manufacturer's instructions. Lithium aluminum hydride solution was prepared by refluxing a large excess of commercial lithium aluminum hydride in dry THF, filtering through dried Celite, and concentrating the filtrate slightly. The concentration of hydride was determined by adding an aliquot to wet THF and measuring the volume of hydrogen evolved. Octyl iodide was used as received (over silver) from Terochem Laboratories, Edmonton. Recrystallized naphthalene (Anachemia) and hexamethyldisilazane (Eastman) were also used as such.

Quantitative GC analysis was performed on a Hewlett-Packard HP 5730A gas chromatograph with a 3380A integrator, using the internal standard method calibrated with a mixture of known weights of products. A 6 ft × 0.125 in. column of 3% OV-17 on Chromosorb W was used with a helium flow of 20 ml/min. A 12 ft × 0.125 in. column of 3% OV17 on Chromosorb W was used for determining the more volatile products. The oven was programmed from 75 to 270 °C at 8 °C/min.

Elemental analyses reported are the average of at least two determinations giving consistent results. In the case of the reduction and octylation experiment, the analysis is the average of several experiments each analyzed in duplicate.

The ir spectra were obtained as a 2% solution in ethanol-free chloroform using 0.5-mm NaCl cells.

The molecular weights were determined on a Mechrolab 301 vapor pressure osmometer at a concentration of 12–25 mg/ml. Benzil at various concentrations was used to calibrate the instrument. Benzene was used as solvent except where otherwise stated. Variation of the asphaltene molecular weight with solvent is shown in Table I.

2. Reduction and Octylation of Asphaltene and Model Compounds. Potassium (4 g, 0.10 g-atom) and naphthalene (0.30 g, 0.0024 mol) in 100 ml of dry THF were stirred under argon until the green-black color of the radical anion had developed. Asphaltene (4 g) or model sulfide (0.020 mol) was added and the mixture stirred for 168 h. The unreacted potassium was removed and either 24.01 g (0.100 mol) of octyl iodide or 25 ml of ethanol was added dropwise. Stirring was continued for 16 h for octylation and 2 h for protonation.

The products from the model reactions were extracted with ether and the ether solution dried over magnesium sulfate. An internal standard was added to an aliquot and the products determined by quantitative GC analysis.

The asphaltene reaction mixture was concentrated to about 50 ml, poured into 600 ml of 70% aqueous ethanol, and stirred for 2 h. The precipitated resinous product was redissolved in 50 ml of THF and precipitated again in the same manner. This procedure was repeated three or four times to ensure the complete removal of octyl iodide, inorganic salts, and naphthalene. Most of the dioctyl sulfide and alkylated naphthalene was also removed. The octylated product was pumped at 50 °C (1 mmHg) for 24 h. Analysis of the octylated product from the total asphaltene: C, 82.59; H, 11.02; N, 0.52; S, 2.88; O, 2.92. Analysis of the octylated product from the acetone insoluble asphaltene: C, 82.74; H, 11.02; N, 0.53; S, 2.35; O, 3.03. Part of the product was dissolved in THF, an internal standard was added, and the amount of dioctyl sulfide, dioctyl disulfide, hexadecane, and alkylated naphthalene remaining was determined by quantitative GC analysis. The total amount of all these by-products was about 7% of the purified product. The molecular weight of the octylated asphaltene was calculated from the experimental molecular weight M using the equation[4]

$$M = \frac{\Sigma W_n}{\Sigma(W_n/M_n)}$$

where W_n is the weight and M_n the molecular weight of the nth component.

The number of octyl groups/100C (n) is calculated from the hydrogen and carbon atoms added to the asphaltene by each octyl group.

$$\frac{120 + 17n}{100 + 8n} = \frac{H}{C} \text{ observed and } n = \frac{100\frac{H}{C} - 120}{17 - 8\frac{H}{C}}$$

It is assumed that the number of hydrogen atoms in the asphaltene part of the molecule, 120, does not change on octylation. The octyl free part of the octylated asphaltene is estimated by adding the molecular weight contributed by n octyl groups ($113n$) to the molecular weight of the asphaltene/100C (1500):

$$\text{Octyl free part} = \frac{1500}{1500 + 113n}$$

3. Treatment of Asphaltene with Reagents Capable of Blocking Hydroxyl Groups. A. Reactions with Diazomethane. Asphaltene (1.60 g), suspended in 50 ml of dry ether, was cooled in ice water. To this, a solution of 26.8 mol of diazomethane in 150 ml of ether was added. After 1 h stirring, the mixture was left to react for 72 h at 5 °C, and then allowed to stand at room temperature for 16 h. Unreacted diazomethane was removed by bubbling dry nitrogen gas through the solution. Ether was removed from the asphaltene sample by rotary evaporation. The methylated asphaltene was dried under vacuum for 24 h, yield 1.70 g (106.3% of substrate). Anal. C, 79.55; H, 8.08; N, 1.31; S, 7.79; O, 3.27.

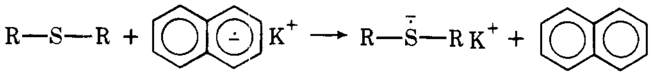
B. Reaction with Hexamethyldisilazane. Asphaltene (2.49 g) was refluxed for 4 h under nitrogen with 20 ml (0.095 mol) of hexamethyldisilazane in 60 ml of dry THF. The reaction mixture was left for 24 h at room temperature and then the solvent and unreacted reagent were removed by distillation under vacuum. The dry residue showed some solubility in pentane, so no washing was possible. Instead, the product was dried under vacuum at 0.5 mmHg to constant weight, 2.82 g (113.3% of asphaltene). Anal. C, 80.49; H, 8.72; N, 1.87; S, 7.92; O, 1.87; ash, 4.05.

4. Determination of OH Groups by Hydrogen Evolution. In control experiments, 10 ml of 3.63 M lithium aluminum hydride in

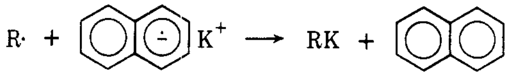
THF solution and 50 ml of dry THF were added to a flask connected to a gas buret. The pressure was equilibrated and 50 ml of THF added from a dropping funnel. The volume of hydrogen evolved was 21.4 ml. Similarly, a solution of 3.505 g of asphaltene in 50 ml of THF was added to 10 ml of 3.63 M lithium aluminum hydride in THF solution diluted with 50 ml of THF. The volume of hydrogen evolved was 115.6 ml; therefore, 3.505 g of asphaltene gives 115.6 − 21.4 = 94.2 ml of H_2 at 700.2 mmHg and 298.5 K which corresponds to 3.54 mmol. Now since 1 g of asphaltene contains 1.56 mg-atoms of O, then the amount of oxygen as OH is given by (3.54/3.505 ÷ 1.56) × 100 = 65%.

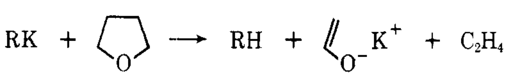
Results and Discussion

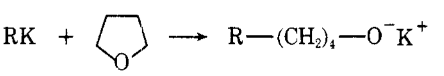
A. Reduction with Potassium in THF. The mechanism for reduction of an organic sulfide by electron transfer is not known, but by analogy with the reduction of halides[5,6] and on the basis of the nature of products observed, the following scheme appears to apply:


(1)

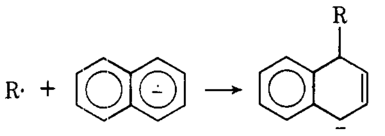
$$R{-}\overset{\cdot -}{S}{-}R \longrightarrow R{-}S^- + R\cdot \quad (2)$$


(3)


(4a)

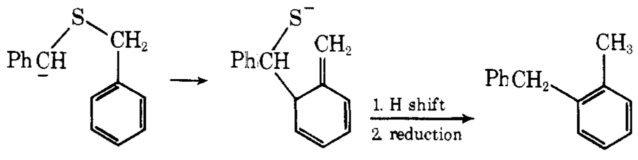

(4b)

In the absence of free-radical scavengers, reduction of the radical R· to R^-, step 3, is usually the fastest reaction of the radical. Dimerization of the radical does not compete, but addition of the radical to the naphthalene radical anion may:


(5)

$$PhCH_2K + PhCH_2SCH_2Ph \longrightarrow Ph\bar{C}HSCH_2Ph + PhCH_3$$

Organopotassium compounds can react with THF according to steps 4a and 4b. Simple organometallic compounds react with THF by proton exchange[7] but resonance-stabilized organometallic compounds such as diphenylmethyllithium react by nucleophilic ring opening (step 4b).[8] The organopotassium compounds generated in the reduction may also attack the starting material or products leading to side reactions. Known examples are[9,10]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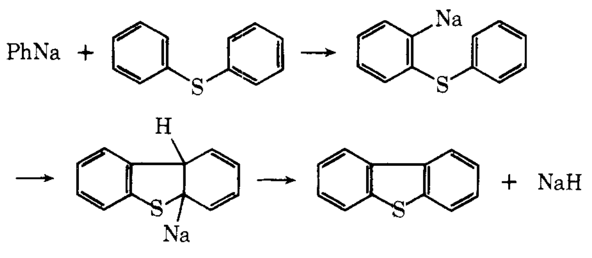
(6)


(7)

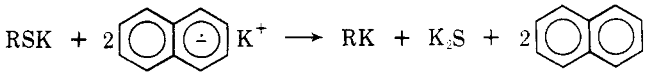
$$PhNa + PhSPh \longrightarrow PhPh + PhSNa \quad (8)$$

The reactions 7 and 8 were carried out in benzene but a related reaction

$$Ph_2NK + PhK \rightarrow PhPh + PhNK_2$$

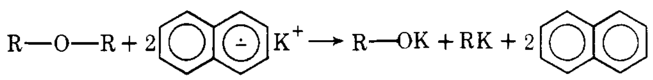
has been observed in THF.[11] Reactions 6–8 involve formation of a new carbon–carbon bond, and although carbon–sulfur bond cleavage and possibly desulfurization may occur, reduction in the gross molecular weight will be negligible.

Desulfurization during the reaction requires that the potassium thiolate produced in step 2 undergoes further reaction with potassium naphthalenide:

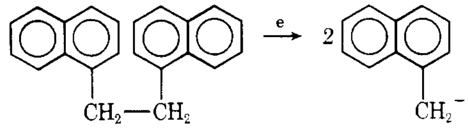


Even less is known about this reaction, but it probably proceeds via a series of steps analagous to 1–3 above.

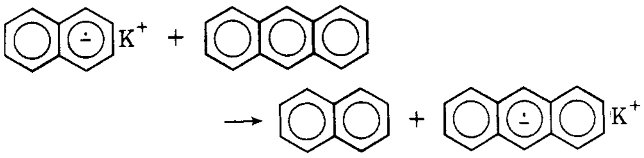
Other ways in which the asphaltene may react with potassium must also be considered. Cleavage of ethers may occur:[5]



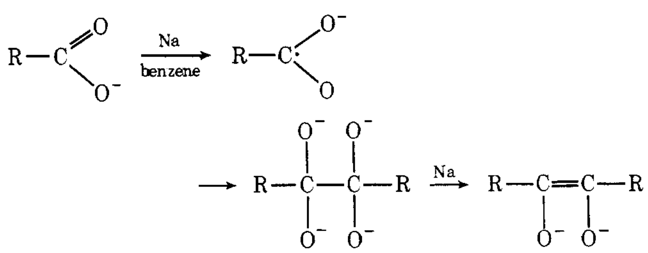
In order for this reaction to take place, one of the groups R must be aryl, benzyl, or allyl; cleavage of dialkyl ethers occurs only under very vigorous conditions. Cleavage of carbon–carbon bonds has only been observed in some 1,2-polyarylethanes:[5]



An important reaction will be transfer of an electron to polynuclear aromatic ring systems:


2

The resulting ions 2 are generally stable under the reaction conditions, giving dihydroaromatic compounds on workup. Transfer of electrons to other unsaturated groups may lead to more reactive radical ions which dimerize, as in the acyloin condensation



and the reductive dimerization of pyridine:[12]

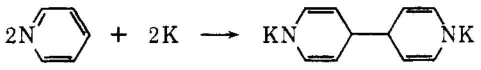
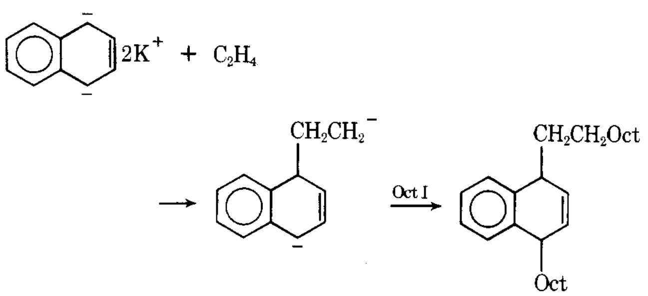


Table II. Reactions of Model Sulfur Compounds

Reactant	Products on protonation	Yield[a]	Products on octylation[b]	Yield[a]	Potassium consumed, g-atoms/mol
Diphenyl sulfide	Benzene	*c*	Benzene	91	2
	Benzenethiol	63	Phenyl octyl sulfide	96	
	Biphenyl	11	Biphenyl	16	
Dibenzyl sulfide	Toluene	72	Toluene	86	3
	1[d]	51	1[d]	11	
Dioctyl sulfide[e]	Octane	*c*			1
	Octanethiol	25			
	Dioctyl disulfide[f]	22			
	Dioctyl sulfide (recovered)	45			
Phenyl octyl sulfide	Benzenethiol	69			
	Octane	67			
Dibenzothiophene	Biphenyl	52	Biphenyl	62	5.4
2-Naphthalenethiol[g,h]	Dihydronaphthalene	36			
	Naphthalene	11			
	Tetralin	7			

[a] Moles of product per 100 mol of starting material. [b] Dioctyl sulfide was also produced when desulfurization occurred. [c] Not measured. [d] This product contained a small amount of dibenzyl by NMR. [e] This compound was reduced for 3 days only. [f] From oxidation of octanethiol on workup. [g] Reduction was by refluxing for 21 h with no naphthalene present. [h] About 15% of an unidentified by-product was formed, probably a dimer by GC retention time.

Since naphthalene is regenerated during the reduction in steps 1 and 3, we used less than stoichiometric amounts of naphthalene with respect to potassium. For most of the reactions, excess potassium was removed at the end of reduction and octyl iodide was added to convert the anions generated to their octyl derivatives. The reduced and octylated asphaltenes were more soluble and more stable than the reduced and protonated asphaltenes. To determine the products expected from the naphthalene used, a blank experiment was carried out in which naphthalene and excess potassium were stirred in THF and octyl iodide then added. The products as determined by GC–MS analysis were naphthalene (53% recovered), hexadecane (formed from octyl iodide), dioctyldihydronaphthalene (5%), and decycloctyldihydronaphthalene **3**[13] (5%) leaving 37% of the naphthalene unaccounted for. The product **3** is formed by the reaction[14]

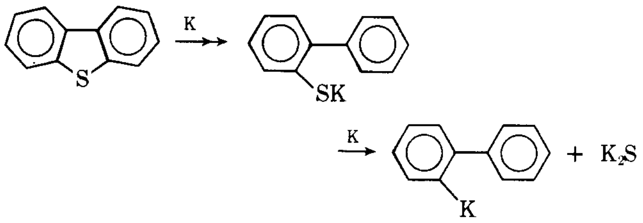


3

Oct = n-C_8H_{17}

The ethylene required is produced by decomposition of THF (as in step 4). It is reported that only the naphthalene dianion adds to ethylene; the radical anion is unreactive.[14] Formation of **3** demonstrates that the naphthalene dianion, a very strong base, is present in our reducing system in addition to the radical anion.

Reduction of several simple sulfides was carried out under the reaction conditions used for the asphaltene to assist in the interpretation of the asphaltene results and to evaluate the importance of the various side reactions discussed above. The results are compiled in Table II. Diphenyl sulfide and dibenzyl sulfide had been previously reduced with potassium in dimethoxyethane[9,15] in essential agreement with our results. From Table II it is seen that all types of organic sulfide will be cleaved by the reagent. However, desulfurization of the potassium thiolate occurs only for benzylthiolate, naphthalenethiolate, and biphenylthiolate. (Formation of biphenyl from dibenzothiophene implies that the reaction has taken place.) Phenylthiolate and octylthiolate are not reduced. In the cases of diphenyl sulfide, dibenzyl sulfide, and probably naphthalenethiol some coupled products are observed. Although the yield of biphenyl from dibenzothiophene is only 52–62%, the by-product is not biphenylthiol since elemental analysis of the total product showed that 90% of the sulfur had been removed. The average molecular weight of the unidentified product is 2428 indicating that considerable polymerization has occurred. Elemental analysis showed that desulfurization of dibenzyl sulfide is complete.



Reduction of Asphaltene. The reduced and octylated asphaltene was analyzed and the number of octyl groups added were calculated from the change in the H/C ratio. It was found on average that 18 atoms of potassium were consumed and 9.4 octyl groups were added per 100 asphaltene carbon atoms.

The number of octyl groups added as calculated from the weight increase was 13.1. Part of the difference may be due to reaction with THF, step 4b. In support of this explanation, the oxygen content of the product was found to increase from 2.5 to 5.9 atoms/100C although some of this increase might be due to oxidation during workup. Additional weight increase might also be caused by reaction of benzyl potassium compounds with ethylene,[16] and by addition of the naphthalene radical anion to asphaltene radicals generated during reduction, step 5. The difference between the atoms of potassium consumed and the number of octyl groups added can be accounted for partly by formation of potassium sulfide (1.2 molecules/100C or 2.4 atoms of potassium) and potassium

Table III. Effect of Methylation and Silylation on the Molecular Weight and Solubility of Asphaltene

Asphaltene	Mol wt	% pentane soluble
Original	5920	1.5
Methylated	2950	13.6
Silylated	3200	15.3

naphthalenide (0.8 molecules of naphthalene/100C were used). The remaining 5.4 atoms of potassium must have been transferred from the asphaltene to THF by reaction 4a. On octylation the resulting acetaldehyde enolate would be expected to give decanal and/or octyl vinyl ether. These compounds should be extracted by the 70% aqueous ethanol washes, although they were not detected by GC–MS in either the extract or the product.

The experimental molecular weight for the reduced and octylated asphaltene was 930. After correction for the octyl groups and small amounts of impurities present, the average molecular weight of the asphaltene part of the product is calculated to be 580.

In order to elucidate the mechanism of this remarkable reduction in the average molecular weight of the asphaltene, we examined the possible role that intermolecular association may play in the aggregation of the original asphaltene molecules, thus influencing the molecular weight. The average molecular weight determined in 0.006 M benzene solution from seven samples of asphaltene was 5920 ± 900. This compares well with the value of 6110 obtained by Sawatzky and Montgomery,[1a] who showed that the molecular weight was independent of concentration below 0.004 M (higher concentrations were not measured). We measured the molecular weight of the asphaltene in various solvents of different polarity. The results presented in Table I indicate that the average molecular weight of asphaltene is not significantly affected by the solvent. The role of hydrogen bonding in molecular aggregation was next explored using diazomethane, which converts carboxylic and phenolic hydroxyl groups to methyl esters and methyl ethers, and hexamethyldisilazane, which converts most hydroxyl groups to silyl derivatives. The ir spectrum of the methylated asphaltene shows carbonyl absorption at 1730 cm^{-1} with a broad band at 1250–1300 cm^{-1} typical of the C–O–R stretching vibrations in both ethers and esters. The silylated asphaltene shows the absorption of trimethylsilyl ethers at 1250, 1200, and 850 cm^{-1}, and ^1H NMR absorption near δ 0. As seen from the data given in Table III, there was a significant reduction in molecular weight, from about 5920 to 3000, and a simultaneous increase in pentane solubility. The decrease in molecular weight by about one-half shows that both methylation and silylation block the sites responsible for molecular aggregation via hydrogen bonding and means that on average there is roughly one hydrogen bond present per asphaltene molecule.

The hydrogen bonding functionality could be phenolic or carboxylic hydroxyl. The ir spectrum of the original asphaltene shows neither hydroxyl nor carboxylic acid absorption under the conditions used. The immediate effervescence on addition of diazomethane and the absorption at 1730 cm^{-1} in the methylated asphaltene suggest the possibility of the presence of carboxylic acid groups.

The decrease in molecular weight on reduction might also be associated with the broad range of molecular weight distribution in the asphaltene, which is separated only on the basis of pentane insolubility. In particular it was thought that the asphaltene might contain some relatively low molecular weight compounds which were insoluble in pentane only on account of their high polarity, or were adsorbed strongly on the surface of the asphaltene. To remove any such compounds, the asphaltene was Soxhlet extracted successively with methanol, 98% ethanol, and acetone. The results of two experiments are summarized in Table IV and as seen from the data 86% of the asphaltene is insoluble in acetone. The only major change in the elemental composition is a decrease in the number of oxygen atoms/100C from 2.34 to 1.29. The alcohol and acetone fractions are correspondingly enriched in oxygen, and their ir spectra show carbonyl absorption at 1710 cm^{-1} which is not discernible in the spectrum of the whole asphaltene.

The molecular weight of the acetone insoluble asphaltene is about 9000. The molecular weight calculated for the combined fractions is about 4400, compared to 5920 for the whole asphaltene, which suggests that solvent separation breaks up some of the association. The acetone insoluble asphaltene from the second experiment (mol wt 9884) was silylated and the molecular weight decreased to 4062. Reduction and octylation of this acetone insoluble asphaltene decreased the octyl-free average molecular weight to 534 which is very close to the value of 580 obtained on reduction of the whole asphaltene.

From the above results it appears to be securely established that the average molecular weight of the whole asphaltene is decreased from 5920 to 580 on reduction, and the average molecular weight of the acetone insoluble asphaltene is reduced from 9884 to 534. The decrease in molecular weight corresponds to cleavage of 9.2 bonds per molecule in the whole asphaltene (2.09 bonds/100C) and to cleavage of 17.5 bonds per molecule in the acetone insoluble asphaltene (2.44 bonds/100C).

In order to determine how many of the bonds cleaved could be the carbon–oxygen bonds of ethers, the number of oxygen atoms present in hydroxyl groups was measured. The maximum number of ether oxygen atoms can then be found by subtraction. Two methods were found to be useful for measurement of the number of hydroxyl groups. The number of trimethylsilyl groups introduced on silylation of the asphaltene can be readily determined from the integration of the ^1H NMR spectrum. This method gave 1.5 silyl groups/100C for the whole asphaltene and 1.7/100C for the acetone insoluble asphaltene. From the increase in the H/C ratio the number of silyl groups introduced was found to be 1.8/100C for both samples. The whole asphaltene contains 2.34 oxygen atoms/100C so that 1.5/2.34 = 64% of the oxygen is present as hydroxyl groups, leaving 36% or 0.84 oxygen atoms/100C which may be in ether groups. Supporting evidence for this value came from the volume of hydrogen evolved on addition of the asphaltene to lithium aluminum hydride solution. This corresponds to 65 and 81% (two determinations) of the oxygen atoms being present as hydroxyl groups. Not all of the 36% of the oxygen atoms which are not hydroxyl need be in ether groups; some of this oxygen may be present as ketones, esters, or possibly amides. The 1.7 silyl groups/100C introduced on silylation of the acetone insoluble asphaltene account for slightly more than the total number of oxygen atoms (1.23/100C in this sample), so it appears that all the oxygen atoms in the acetone-insoluble asphaltene are present as hydroxyl groups. The amount of hydrogen evolved, 1.96 and 2.17 mmol/100C from duplicate runs, corresponds to a greater number of oxygen atoms than were actually present.

Since all of the oxygen atoms in the acetone insoluble asphaltene appear to be present as hydroxyl groups, none are present as ether groups, and all of the 2.44 bonds/100C which are cleaved on reduction must be carbon–sulfur bonds (where the sulfur atoms are not in a ring). The remaining 3.68 − 2.44 = 1.24 sulfur atoms may be in rings or may not have been reduced. Every coupling side reaction of the type discussed

Table IV. Extraction of Asphaltene with Polar Solvents

	Yield		H/100C		N/100C		S/100C		O/100C		Mol wt		Mol wt calcd from combined fractions	
Solvent	1[a]	2[a]	1	2[b]	1	2	1	2	1	2	1	2	1	2
Methanol	2.4	1.7	139		0.73		2.12		11.23		571			
				129		1.20		3.49		6.13		1108		
98% ethanol	2.9	4.4	129		0.84		3.62		4.29		947		3890	4891
Acetone	9.6	8.4	126	124	0.93	1.43	3.45	3.14	2.78	3.46	1167	1325		
Benzene	85.1	86.6	121	121	0.90	1.67	3.97	3.68	1.35	1.23	8363	9884		

[a] Data are given for two experiments, 1 and 2. [b] In experiment 2 the methanol and ethanol fractions were combined prior to analysis.

above reduces the apparent number of bond cleavages by one, which will lead to underestimation of the number of nonring carbon–sulfur bonds cleaved.

In the case of the whole asphaltene 0.84 oxygen atoms/100C may be in ether groups and could account for part of the 2.09 bonds/100C cleaved. However, it is not likely that all these oxygen atoms will be present as aryl ethers, some of the oxygen atoms may be in rings (e.g. benzofurans) and/or carbonyl groups, and comparison with the result from the acetone insoluble asphaltene suggests that cleavage of carbon–oxygen bonds is not important. Thus, the decrease in molecular weight of the total asphaltene on reduction is probably also due to the cleavage of nonring carbon–sulfur bonds.

Reductive Removal of Octyl Groups. Further treatment of the reduced and octylated asphaltene with potassium and naphthalene is expected to remove those octyl groups attached to sulfur and phenolic oxygen atoms. Octyl groups attached to carbon and alkyl oxygen atoms will be unaffected. Of the 9.4 octyl groups/100C added to the asphaltene after reduction and octylation, 6.0 remained after deoctylation so that 3.4 were attached to sulfur or phenolic oxygen atoms. The reduced and octylated asphaltene contained 2.7 sulfur atoms and 5.9 oxygen atoms per 100 asphaltene carbon atoms. Of the 3.4 octyl groups/100C removed, a total of 1.6 were found as octane (0.6), octanol (0.7), octanethiol (0.1), and hexadecane (0.2). The low value for octyl groups found, relative to those removed, may be caused by the difficulty of measurement, particularly for octane, and by the addition of octyl groups to naphthalene radical anion (reaction 5). Since all of the 2.7 sulfur atoms should have been octylated according to the model reactions, $3.4 - 2.7 = 0.7$ octyl groups must have been removed from phenolic oxygen atoms.

Decrease in Sulfur Content. Reduction of the asphaltene with potassium and naphthalene removed 30% of the sulfur, decreasing the number of sulfur atoms/100C by 1.1, from 3.8 to 2.7. On the basis of the model reactions this result implies that 1.1 sulfur atoms/100C in the asphaltene are attached to polyaryl or benzyl groups and 2.7 attached to phenyl or alkyl groups. The desulfurization of the acetone insoluble asphaltene was slightly higher, 39%, so of the 3.7 sulfur atoms/100C, 1.4 were attached to polyaryl or benzyl groups and 2.3 to phenyl or alkyl groups.

Role of Naphthalene. Sternberg et al.[2] used naphthalene in the reaction of coal with potassium because neither coal nor potassium have appreciable solubility in THF. Asphaltene is soluble in THF and almost certainly contains some polycyclic aromatic nuclei which can act as electron transfer agents. Therefore, it seemed possible that asphaltene would react with potassium without naphthalene present. When the asphaltene was treated with potassium in the absence of naphthalene, but otherwise under the same conditions as before, reaction did take place but the decrease in molecular weight and sulfur content was lower than that found when naphthalene was present. These results are shown in Table V for both the whole asphaltene and the acetone insoluble asphaltene. since the extent of desulfurization and the number of octyl groups added are lower without naphthalene present, the simplest explanation for the smaller decrease in molecular weight is that the reaction is slower, i.e., fewer bonds are cleaved, because the concentration of reducing agent in solution is lower without added naphthalene. It may also be that the radicals generated during the reduction are less efficiently reduced when the concentration of reducing agent is lower so that addition of the radical to another asphaltene molecule (polymerization) competes with reduction of the radical.

Table V. Comparison of the Reduction of Asphaltene by Potassium with and without Naphthalene Present

Reaction	Mol wt of product (octyl free)	% of sulfur removed	Octyl groups added per 100C
Whole asphaltene with naphthalene present	580	30	9.4
Whole asphaltene without naphthalene present	1900	18	5.9
Acetone insoluble asphaltene with naphthalene present	530	33	9.3
Acetone insoluble asphaltene without naphthalene present	1600	15	5.9

B. Derivation of an Average Molecular Structure for the Asphaltene. The experimental evidence that the asphaltene can be readily cleaved by reduction into relatively small molecules requires reevaluation of some asphaltene structures suggested in the literature. One of the problems in determining a reasonable average structure for the asphaltene has been the difficulty in obtaining a value for the proportion of aromatic carbon. Methods adequate for lower boiling petroleum fractions based on density and refractive index correlations, are not fully satisfactory for large molecules relatively rich in heteroatoms. We have determined the ^{13}C NMR spectrum of the asphaltene in order to assess the proportion of aromatic carbon more directly. Combination of this value with the degree of unsaturation, determined by the H/C atomic ratio, and the percent of hydrogen atoms which are attached to aromatic rings (from the ^{1}H NMR spectrum) makes it possible to propose a structure for the average asphaltene molecule, although assumptions must still be made.

The ^{13}C NMR Spectrum of the Asphaltene. There are two problems in obtaining ^{13}C NMR spectra in which the peak areas correspond quantitatively to the number of carbon atoms.

Firstly, it is general practice to run the spectra with broad-band proton decoupling. This increases the signal intensity but the intensity enhancement is variable for different kinds of carbon. In the present case this problem was avoided by running the spectra with proton coupling and compen-

Table VI. Double Bond Equivalents per Carbon Atom (DBE/C) and the Ratio of Non-Ring-Junction to Ring Junction Carbon Atoms (C_4/C_5) for Some Aromatic Compounds

Compd	DBE/C	C_4/C_5
Benzene	0.67	∞
Naphthalene	0.70	4.00
Anthracene	0.71	2.50
Tetracene	0.72	2.00
Pyrene	0.75	1.67
Coronene	0.79	1.00
Ovalene	0.81	0.78
Graphite (C_∞)	1.00	0

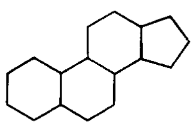
sating for the loss of intensity by using the maximum amount of sample. The second more difficult problem is that some carbon atoms, particularly those without attached protons, have very long relaxation times T_1, as high as 100 s. This means that the carbons are not completely relaxed between pulses. The time required for virtually complete relaxation is $5T_1$ s, and the practical limit for pulse repetition is 1 s or less, owing to the cost and availability of machine time. For the asphaltene this problem was solved by reducing the T_1's by three mechanisms: (1) dipole–dipole relaxation induced by the high viscosity of the solution;[17,18] (2) the application of a relatively low magnetic field, 15.08 MHz, since relaxation times are lower for a given correlation time at lower fields;[19] and (3) the use of a paramagnetic reagent, chromium acetylacetonate, to cause relaxation by spin–spin coupling. This reagent has been shown to reduce the relaxation time for an unprotonated carbon atom in cholesteryl chloride from 4.3 to 0.23 s.[18] Complete relaxation in the asphaltene sample was demonstrated experimentally by increasing the time between pulses from about 0.7 s used initially, to 1 s. No change in the relative signal intensities occurred. Under these conditions, using a concentrated sample containing chromium acetylacetonate, running the spectrum with proton coupling, low field strength, 1 s repetition time, and 90° pulses, the proportion of aromatic carbon was found to be 42%. The spectrum shows two broad peaks for the aliphatic and aromatic carbons with well-defined steps in the electronic integration curve. The aromatic peak occurred between 100 and 160 ppm from tetramethylsilane, centered at 135 ppm, and the aliphatic peak occurred between 0 and 60 ppm, centered at 30 ppm. The proportion of aromatic carbon in the acetone insoluble asphaltene was found to be slightly lower at 35%.

The proportion of hydrogen atoms which are attached to aromatic rings was found from the conventional ^1H NMR spectrum to be 8% for both the total asphaltene and the acetone insoluble asphaltene. The aromatic peak occurred between δ 5.8 and 8.5 and the saturated peak between δ 0.1 and 4.5. The H/C ratio is 1.2 for both fractions. It follows that of the 120 hydrogen atoms/100C $0.08 \times 120 = 10$ are attached to aromatic carbon atoms. Therefore, the fraction of substituted aromatic carbon atoms, including ring junctions, is $32/42 = 0.76$.

Structural Analysis of the Average Asphaltene Molecule. The degree of unsaturation or number of double bond equivalents (DBE) of a molecule is given by the formula DBE $= (2N_C + 2 - N_H)/2$ where N_C is the number of carbon atoms and N_H the number of hydrogen atoms. For the asphaltene there are 120 hydrogen atoms/100C, so that DBE/100C $= (200 + 2 - 120)/2 = 41$.

There are 42 aromatic carbon atoms/100C and each aromatic carbon atom contributes about 0.72 double bond equivalents (vide infra). Therefore, the 42 aromatic carbon atoms contribute $42 \times 0.72 = 30$ DBE leaving $41 - 30 = 11$ DBE to be contributed by the alicyclic carbon atoms. If it takes an average of four alicyclic carbon atoms to contribute one degree of unsaturation (as a ring), then the proportion of alicyclic carbon is $11 \times 4 = 44\%$. This leaves $100 - 42 - 44 = 14\%$ of paraffinic carbon atoms.

This analysis required assumptions to be made about the number of double bond equivalents per aromatic carbon atom and per alicyclic carbon atom. This data, determined by inspection of the structures, is given for a number of simple aromatic and alicyclic compounds in Tables VI and VII.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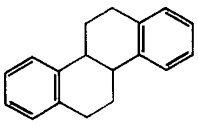
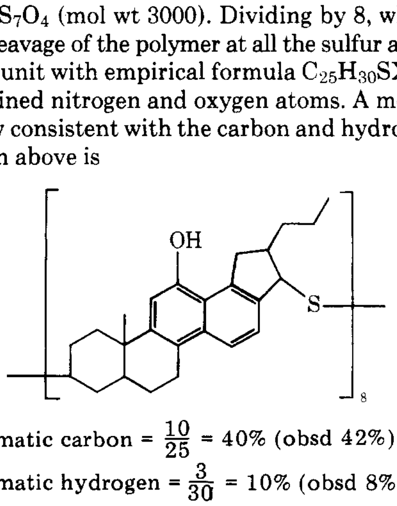

5

It can be seen that the DBE/aromatic carbon atom and alicyclic carbon atoms/alicyclic DBE used above (0.72 and 4) are middle of the range. Another reason for the use of 0.72 for the DBE/aromatic carbon atom is that the corresponding C_4/C_5 ratio is the minimum value of the range given by the Montgomery–Boyd analysis.[20] The value for alicyclic carbon atoms/alicyclic DBE cannot be higher than 5.3 or the number of paraffinic carbon atoms becomes negative. Values much lower than four seem unlikely because then the alicyclic proportion of the molecule must consist entirely of a very restricted range of structures, for example, it is unlikely that the asphaltene consists entirely of fluorene units joined together. Also, the alicyclic protons of fluorene absorb at δ 4 where the asphaltene shows virtually no absorption. However, a value of 3 for the number of alicyclic carbon atoms/alicyclic DBE is not unreasonable. This would reduce the number of alicyclic carbon atoms to 33% and increase the number of paraffinic carbon atoms to 25%. Greater accuracy cannot be expected without a means of measuring the number of alicyclic or paraffinic carbon atoms directly.

These qualitative estimates are useful in the construction of reasonable model structures for the average asphaltene molecule. The molecular formula of the average asphaltene molecule, after allowing for hydrogen bonding, is $C_{200}H_{240}N_2S_7O_4$ (mol wt 3000). Dividing by 8, which corresponds to cleavage of the polymer at all the sulfur atoms, gives a monomer unit with empirical formula $C_{25}H_{30}SX$, where X is the combined nitrogen and oxygen atoms. A molecule approximately consistent with the carbon and hydrogen distribution given above is



$$\% \text{ aromatic carbon} = \frac{10}{25} = 40\% \text{ (obsd 42\%)}$$

$$\% \text{ aromatic hydrogen} = \frac{3}{30} = 10\% \text{ (obsd 8\%)}$$

$$H/C = 1.2 \text{ (obsd 1.2)}$$

$$\text{aromatic DBE/aromatic carbon atom} = \frac{7}{10} = 0.70$$

$$\text{alicyclic carbon atoms/alicyclic DBE} = \frac{11}{3} = 3.67$$

$$\text{proportion of substituted aromatic carbon atoms} = \frac{7}{10} = 0.70$$

$$\% \text{ alicyclic carbon atoms} = \frac{11}{25} = 44\%$$

$$\% \text{ paraffinic carbon atoms} = \frac{4}{25} = 16\%$$

Since 64% of the oxygen atoms are present as hydroxyl groups, there is one hydroxyl group for every three of the monomer units shown. Of course a considerable variety of ring and substituent arrangements are possible and an enormous variety of structures will actually be present, leading to the average values given above. The degree of homogeneity of the hydrocarbon framework is not known. We can only assume that it is mainly derived from triterpenes.

The acetone insoluble asphaltene has slightly lower aromaticity, 35%. The carbon distribution, 35% aromatic, 64% alicyclic, and only 1% paraffinic, is obtained assuming that the DBE/aromatic carbon atom is 0.72 and that the alicyclic carbon atoms/alicyclic DBE ratio is 4. If the latter ratio is only 3, then the distribution becomes 35% aromatic carbon, 48% alicyclic carbon, and 17% paraffinic carbon.

This type of analysis was first attempted by Montgomery and Boyd[20] 15 years ago, prior to the availability of NMR, but a brief discussion seems appropriate. Their method involved correlating the number of various types of carbon atom with molar volume (mv) and molar refraction (mr) in a number of model compounds. The mv and mr of the asphaltene are then used to derive the number of each type of carbon atom in the asphaltene molecule. The carbon atoms were divided into five types: C_1, paraffinic carbon atoms; C_2, non-ring-junction alicyclic carbon atoms, including substituted ones; C_3, ring junction alicyclic carbon atoms, including substituted ones; C_4, non-ring-junction aromatic carbon atoms, including substituted ones; and C_5, ring junction aromatic carbon atoms. With five unknowns three more equations are required. One is available from the carbon balance, $C_1 + C_2 + C_3 + C_4 + C_5 = \Sigma C$. The next one used was $C_4 + C_5 = C_a$, the total number of aromatic carbon atoms. For lower molecular weight petroleum fractions, methods were available for estimating C_a, but these methods were not applicable to the asphaltene. Therefore this relation was essentially replaced by the condition that the number of carbon atoms C_1–C_5 all be greater than zero, which left a range of possible values instead of a unique solution. Finally, Montgomery and Boyd used the relation $2C_1 + 2C_2 + C_3 + C_4 = \Sigma H$ which follows from the definitions of these groups.

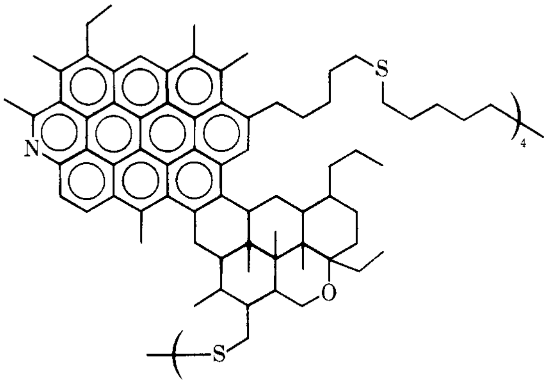
Employing this method, Sawatzky, Boyd, and Montgomery[1b] reported the following values for the Athabasca asphaltene: C_1, 33.8–34.2%; C_2, 0–6.5%; C_3, 10.3–0%; C_4, 45.2–41.2%; C_5, 11.2–18.0%, with the percent aromatic carbon ($C_4 + C_5$), 56.1–59.2%. (It should be noted that their asphaltene was prepared by extracting the oil sand with pentane and then with benzene.) In view of the limited amount of data and the rather crude analytical techniques available at the time, this analysis yielded surprisingly good results. In particular, the degree of condensation of the aromatic rings agrees with our results. The somewhat high value derived for the percent aromatic carbon results in correspondingly low values for the percent alicyclic carbon. The original classification did not distinguish between ring junction carbon atoms and carbon atoms linking aromatic rings (as in biphenyl). The latter were designated C_7, and the following distribution, applicable only when $C_3 = 0$, was calculated: C_1, 38.8%; C_2, 22.0%; C_4, 41.3%; C_5, 10.02%; C_7, 7.7%. Other work on density ring number correlations has been reported recently.[21]

Another structural analysis of the Athabasca asphaltene was attempted by Speight.[22] In this method the saturated ^1H NMR peak was dissected into areas attributed to benzylic, alicyclic, chain methylene, and chain methyl groups. The number of non-ring-junction aromatic carbon atoms is then the number of aromatic hydrogen atoms plus half the number of benzylic hydrogen atoms. The total number of aromatic carbon atoms is obtained by subtracting the saturated carbon atoms from the total carbon atoms. The number of saturated carbon atoms was calculated by dividing the estimated number of benzylic, alicyclic, and chain methylene hydrogen atoms by 2, and the chain methyl hydrogen atoms by 3. The ratio of non-ring-junction to ring junction aromatic carbon atoms (C_4/C_5 in the Montgomery–Boyd analysis) obtained in this way is 0.67, much lower than any value in the range of the Montgomery–Boyd analysis.[20] The low C_4/C_5 value corresponds to a highly condensed aromatic structure such as naphthoovalene. Determination of the number of each type of carbon atom from the number of hydrogen atoms is difficult because an assumption must be made about the extent of substitution of the carbon atoms. The saturated proton peak in our spectrum shows too much overlap to be resolved as suggested by Speight. Estimation of the relative number of alicyclic and chain methylene hydrogen atoms is particularly uncertain.

Table VII. The Number of Alicyclic Carbon Atoms per Alicyclic Double Bond Equivalent in Various Compounds

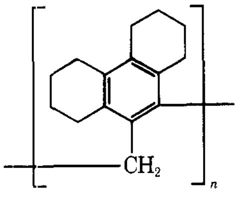
Compd	Alicyclic carbon/ alicyclic DBE
Cyclohexane	6
Cyclopentane	5
Decalin	5
4	4.25
Tetralin	4
5	3
9,10-Dihydroanthracene	2
Fluorene	1
Diamond (C_∞)	1

The percent aromaticity has also been determined by Yen and co-workers[23] from the intensity of the γ and (002) bands in the x-ray spectrum. Unfortunately these bands overlap substantially and considerable speculative curve resolving is necessary. The percent aromaticity reported for the Athabasca asphaltene was 31%,[24] slightly lower than the 42% we find from the ^{13}C NMR spectrum. Yen[25] recently proposed the following average structure for the Lagunillas asphaltene.



This asphaltene has an H/C ratio of 1.12, and 41% aromaticity as determined by the x-ray method. The highly condensed aromatic and alicyclic ring system in Yen's structure, with the lower H/C ratio and higher aromaticity, results in a small proportion of alicyclic carbon atoms. However, it should be noted that the value of F/C_A,[26] which determines the degree of ring condensation, is based on the assumption of a rectangular aromatic sheet, and also depends critically on the number of rings per carbon atom, which is determined from a density–ring number correlation.[27] The difficulties with these correlations have been discussed by Montgomery and Boyd[20] and by Yen.[27] In addition, the number of rings per carbon atom obtained from the density correlation is the total number of rings, whereas the number required for calculating

F/C_A is the number of aromatic rings. Use of the value for the number of rings obtained from densimetric analysis in the calculation of F/C_A implies the assumption that there are no alicyclic rings. This difficulty becomes very apparent in the analysis[24] of the octahydrophenanthrene–formaldehyde copolymer, e.g.



In calculating F/C_A a value of C/R[28] $= 15$ (i.e., $R = 1$) is used. Densimetric analysis should give $R = 3$ which would lead to an unreasonably high value of F/C_A.

It seems that an aromatic–alicyclic–paraffinic division of the carbon atoms is the most that can be expected. Combination of the aromatic–aliphatic NMR peak areas with molar volume and molar refraction correlations might provide a narrower classification.

Conclusions

In the present study it has been clearly established that Athabasca asphaltene is a sulfur polymer in which the average carbon moieties consisting of alicyclic diaromatic structures with some alkyl substituents are held together by sulfide linkages. Since most asphaltenes are rich in sulfur[29] irrespective of origin, it is probable that they also possess a sulfur polymer framework.

In the vast Athabasca oil sand formation of northeastern Alberta the concentration of asphaltene varies between 16 and 25% of the raw bitumen. In light of the molecular structure of the asphaltene, the high sulfur content of the bitumen cannot be construed upon as evidence for an old geological age or a significant geothermal history of the formation. The asphaltene probably arose from the interaction of microbiologically produced sulfur with the primary lighter crude oil, a process which can occur under mild conditions.

Further work is in progress.

Acknowledgments. The authors are grateful to the National Research Council for financial support and to Mr. Cleve Murray for technical assistance. It is also a pleasure to express our appreciation to Dr. D. S. Montgomery for many stimulating discussions on oil sand chemistry.

Registry No.—Naphthalene dianion, 23013-60-7; methanol, 67-56-1; ethanol, 64-17-5; acetone, 67-64-1; benzene, 71-43-2; potassium, 7440-09-7; naphthalene, 91-20-3; naphthalene radical anion, 34509-91-6; dibromomethane, 74-95-3; dioxane, 505-22-6; pyridine, 110-86-1.

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