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CHARACTERIZATION OF VARIOUS BITUMEN SAMPLES FROM TAR SANDS

BY

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INTRODUCTION

Bitumen is a complex mixture of a large number of organic molecules. The composition of bitumen and the nature of their various individual components has been the subject of considerable research during the past two decades (1-11). Various modes of extraction of bitumen from oil sands such as heat, extreme mechanical force, chemical agents and solvents could significantly affect some properties of bitumen (12-13). Variations in the composition of the oil sands feed stock could also affect the properties of the extracted bitumen. However, the most commonly used analytical techniques such as elemental analyses, density and viscosity cannot detect small compositional differences in the various samples of bitumen.

With developments in instrumentation and techniques the structural characterization of complex petroleum fractions employing high resolution proton and ^{13}C nuclear magnetic resonance (NMR) spectroscopy is becoming more popular. Complex hydrocarbon mixtures are characterized using structural analysis schemes, in which the results of elemental analyses, number average molecular weight determinations and hydrogen and carbon distributions from proton and ^{13}C NMR are combined to yield a set of average structural Parameters (10, 14-21). The parameters describe structural features, such as the fraction of carbon that is aromatic, the number and length of alkyl substituents in an average moelcule, the percentage of aromatic carbons that are substituted and the number of aromatic rings per molecule. Given sufficient data these parameters can provide useful characterization of a hydrocarbon mixture.

In our laboratories we have collected a number of bitumen samples obtained from different feedstocks employing a variety of extraction techniques. It was of interest to investigate any differences between these samples from different sources. This paper reports a detailed investigation of average structural parameters by the combined use of elemental analyses, molecular weight determinations and proton and ^{13}CNMR spectroscopy. A total of twenty three bitumen samples have been studied.

EXPERIMENTAL METHODS

Materials

Table I lists brief descriptions of all bitumen samples investigated, including source and the method of extraction (22-27). The asphaltene fractions of the bitumens were prepared in the usual manner by precipitation with n-pentane (28). The precipitates were washed with pentane and vacuum dried at 80°C. Evaporation of the n-pentane from the combined filtrate and washings gave the deasphaltened oil (maltenes).

Elemental Analyses

C, H and N analyses were performed using a Perkin Elmer model 240 CHN analyser. Sulfur was analysed as total sulfur using X-ray flourescence spectroscopy. Oxygen was determined either by difference or directly (29). Asphaltene samples were also analysed

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..sing ASTM procedure D271 at the Energy Mines and Resources laboratory. These results were comparable to those obtained from the Perkin-Elmer model 240 CHN analyser. The nickel and vanadium content of the ashed bitumens were estimated, using quantitative Inductively Coupled Plasma Atomic Emission Spectroscopic methods (ICP-AES).

Ash Content

5-10 g sample of bitumen was weighed accurately into a porcelain crucible. The crucible was placed over a low bunsen burner flame in order to burn off the low boiling point components of bitumen. This was followed by ashing in a muffle furnace at 400°C to constant weight.

Instrumental Analyses

Infrared spectra were recorded using a Perkin-Elmer model 683 i.r. spectrometer. Samples were run either as solutions in CCl_4 or as KBr pellets.

Proton NMR measurements were performed on a Varian EM-360 NMR spectrometer (60 MHz) in $CDCl_3$. For quantitative ^{13}C NMR spectra the method described by Shoolery and Budde (30) was used. Spectra were recorded on a Brucker AM-400 NMR spectrometer. Samples were dissolved in deuterochloroform to give approximately 10 wt% solutions; these were run in 5 mm diameter tubes. A paramagnetic relaxation agent, chromium acetonylaceonate, $Cr(acac)_3$, was added to the deuterochloroform solution to give a 0.1 M solution. The FT ^{13}CNMR spectrum was run using a two second delay between pulses, and the proton decoupler was gated off between pulses and on during data acquisition.

Number average molecular weights of whole bitumen samples were determined by vapour pressure osometry in benzene at 40°C using a Hitachi Perkin-Elmer model 115 molecular weight apparatus. Molecular weight of maltene fractions were obtained by gel permeation chromatography in tetrahydrofuran according to the procedure described elsewhere (31).

RESULTS AND DISCUSSION

Molecular Weights and Ultimate Analyses

A comparison of the asphaltene content of the various bitumen samples leads to the following observations:

1. Bitumen obtained by centrifugation had the highest asphaltene content.

2. The asphaltene content of the bitumen samples appears to be affected by the amount of mineral fines (<44 μm particles) in the oil sand feeds. Thus, the bitumen obtained from high grade oil sands (lowest fines content) had the highest asphaltene content. Similarly, bitumen obtained from one of the low grade ores (highest fines content) gave the lowest amount of asphaltenes. This supports our previous suggestion (32) that part of the asphaltenes are strongly adsorbed by the clay component of the oil sands, and are not removed by solvent extraction.

3. Bitumen obtained from a second sample of low grade ore (high fines content) had a high asphaltene content comparable to that of the bitumen obtained from a high grade ore. This second sample of low grade ore was unique in that it was amenable to hot water extraction (34). The mineral composition of the ores appears to be more important in determining the quality of the ore than the actual fines content. It is obvious from these results that the asphaltene content of various bitumen samples is dependent on the absorptive capacity of the mineral constituents of the oil sand feed.

4. Bitumen extracted from Suncor sludge Pond tailings has a lower asphaltene content than the bitumen obtained from oil sand feeds (11% vs 13.4 - 17.3%). This could be due to the adsorption of the asphaltenes to the clay minerals present in the sludge pond tailings.

5. Asphaltene content of the bitumen samples; extracted from mineral agglomerates, is dependent on the mode of extraction of bitumen. Bitumen extracted using the Dean-Stark method (25) has substantially lower asphaltene content compared with the samples extracted using a Spex mixer (6.2 - 7.0% vs 11.5 - 18.4%). This can be explained on the basis of the entrapment of high molecular weight asphaltenes inside the pores of compact mineral agglomerates. Diffusion of the high molecular weight asphaltenes through the small pores of mineral agglomerates will be more difficult than the low molecular weight components of bitumen. In the Spex mixer, agglomerates are constantly being broken and reformed because of the vigorous agitation. This resulted in the release of all bitumen components thus explaining the higher asphaltene content of this bitumen compared with the bitumen extracted using Dean-Stark method.

TABLE I
BITUMEN SAMPLES DESCRIPTION

Sample #	Sample Description
(1)	Bitumen recovered from medium grade oil sands (O.S.S.#1; Bitumen content ≈ 10%) by Ultracentrifugation (22).
(2)	Suncor Coker Feed Bitumen used in a round robin study of bitumen analyses (23).
(3)	Primary production heavy oil from Husky's North Blackfoot field in the Lloydminister deposit.
(4)	Bitumen extracted from high grade oil sands (Bitumen content ≈ 15%) by modified Dean-Stark method using toluene (24).
(5)	Same as above except that the feed was a sample of medium grade oil sands (Bitumen content ≈12%).
(6)	Bitumen extracted from O.S.S.#1 by Dean-Stark method using toluene (25).
(7)	Same as in #5 except that the feed was a sample of low grade oil sands (Bitumen content ≈ 9%).
(8)	Bitumen extracted from low grade oil sands (Bitumen content ≈ 8%) by Dean-Stark method using toluene.
(9)	Bitumen extracted from O.S.S.#1 by Dean-Stark method using benzene-methanol (9:1).
(10)	Bitumen extracted from O.S.S.#1 by agitation with toluene on a Spex mixer (26).
(11)	As above except that extraction solvent was benzene-methanol (9:1).
(12)	Bitumen extracted from O.S.S.#1 by SESA* process using naphtha (27).
(13)	Bitumen extracted from O.S.S.#1 in a Waring Blendor using cyclohexane.
(14)	Secondary extract from above in cyclohexane [27].
(15)	Bitumen extracted in benzene from Suncor Sludge Pond Tailings.
(16)	Bitumen extracted in toluene using Dean-Stark method from sand agglomerates from experiment #12.
(17)	Bitumen extracted in toluene on a Spex mixer from sand agglomerates from Sample #12.
(18)	Same as #17 except that the extraction solvent was benzene-methanol (9:1).
(19)	Same as #18 except that the extraction solvent was benzene.
(20)	Bitumen extracted from sand agglomerates from sample #14 by Dean-Stark method using toluene.
(21)	Bitumen extracted from sand agglomerates from sample #14 by agitation on a Spex mixer using toluene.
(22)	Same as #21 except that it was extracted in benzene.

Cont'd.

*Solvent Extraction Spherical Agglomeration

TABLE I (CONTINUED)

Sample #	Sample Description
(23)	Same as #20 except that it was extracted in benzene.
(24)	Bitumen extracted in toluene from aqueous tailings from EMR Solvent/Bitumen contactor.

6. Asphaltene content of the bitumen extracted from sand agglomerates on the Spex mixer using benzene-methanol (4:1) is low compared to bitumen from the same sample but extracted with toluene or benzene. This is difficult to explain particularly in view of the fact that no significant solvent effect was noted when the bitumen was extracted from the oil sand feed.

Number average molecular weights of various bitumen samples were determined in benzene using vapour pressure osometry. There was a considerable variation in the data for various bitumen samples. The bitumen extracted from Suncor sludge pond tailings had the lowest molecular weight. This might be due to the fractionation of bitumen by clay minerals present in the sludge. It is probable that the higher molecular weight components of bitumen are strongly associated with the clay component of tailings either by adsorption or by clay organic interactions (33).

Bitumen samples extracted from sand agglomerates have relatively lower molecular weights than the samples extracted directly from bituminour feed-stocks. Again this can be explained on the basis of entrapment of high molecular weight components of bitumen inside the pores of sand agglomerates.

The Bitumen sample prepared using centrifugation had a considerably lower molecular weight compared with the solvent extracted samples in spite of the fact that it had the highest asphaltenes content. Bitumen samples prepared using centrifugation are known to have a greater proportion of low boiling components (13). It is possible that the greater proportion of low boiling components offsets the higher asphaltenes content thus accounting for lower molecular weight.

Molecular weights of maltenes were not as meaningful as those for bitumen for the following reasons:

1) These molecular weights were determined using a gel permeation chromatographic method which has been shown (35,36) to give different results to vapour pressure osometry.

2) The molecular weights were determined in THF, which has been shown (31) to give anomalour results with bitumen and maltenes.

3) Complete removal of the last traces of solvent from bitumen and maltenes is very difficult. However, the effect of residual solvent will be more pronounced for the low molecular weight maltenes compared with bitumen.

The H/C ratios for the different samples were of almost the same magnitude : 1.48 ± 0.04 for bitumen, 1.17 ± 0.04 for asphaltenes and 1.55 ± 0.05 for maltenes.

Trace metal analyses of crude oils usually leads to information of geochemical significance (37). The V/Ni index in particular has been extremely studied in relation to oil maturation (38,39) oil migration (40) or depth and age of reservoir rocks (41). There is substantial variation in the nickel and vanadium content of the various bitumen samples. The bitumen sample extracted from Suncor sludge pond tailings had the lowest concentration of both nickel and vanadium. This suggests that the nickel and vanadium containing components of bitumen in the sludge, have become strongly associated with the clay components and cannot be easily extracted.

Bitumen obtained using cyclohexane in a blendor has the highest nickel and vanadium content. This is consistent with our previous findings (42). In that investigation it was demonstrated that heavy metals can be concentrated in a blendor due to an effect similar to flotation.

Although the absolute concentration values for vanadium and nickel show considerable variations, the V/Ni index is fairly uniform (3.6 ± 0.3). This suggests that the V/Ni index is independent of any compositional differences. The uniformity of the index suggests that vanadium and nickel might have been incorporated during the genesis of bitumen. The uniformity of the V/Ni index also suggests that all bitumen samples are genetically related, that is they are all of the same origin. The V/Ni concentration ratios of various bitumen samples suggest that these are middle cretaceous oils.

Figures 1 and 2 illustrate the correlation between the asphaltene content of various bitumen samples and their vanadium and nickel content. Except for a few cases there is a fairly good correlation between the asphaltene content and the metal content of various bitumen samples. This suggests that in most cases Ni and V complexes are associated with the asphaltene fraction of the bitumen. Since the petroleum asphaltenes are known to have the capacity to complex heavy metals (43), it is probable that at least a part of vanadium and nickel are associated with the asphaltenes.

The V/Ni index for the Loydminister heavy oil suggests that it is a lot more mature oil than the oil sand bitumen.

Infrared Spectra

Because of the difficulty of removing the last traces of solvent from bitumen and its maltene fractions the differences in the infrared spectra of these samples were difficult to interpret. The infrared spectra of various asphaltenes samples were remarkably similar resembling the typical infrared spectra for petroleum asphaltenes.

Interpretation of NMR Spectra

Figure 3 and 4 illustrate typical proton and ^{13}C NMR spectra for bitumen and its asphaltene and maltene fractions. All spectra were essentially similar. Proton NMR spectrum of asphaltenes consists of two broad resonances. The strongest band, centered around 1.0 ppm, is due to various types of methyl and methylene hydrogens; and the weak band centered at 7.0 ppm results from aromatic hydrogens. Bitumen and maltene samples show proton NMR spectra with at least 4 well defined regions. Two sharp peaks at 1.3 and 0/9 ppm correspond to the saturated alkyl and naphthenic hydrogens, and γ and further methyl hydrogens, respectively. A broad region extending from 2 to 3.5 ppm is due to the hydrogens attached to the α carbon bonded to aromatic rings.

^{13}C NMR spectra of all samples had a sharp peak around 29 ppm which indicates the presence of interior methylene groups, $-(CH_2)-$, of long straight-chain side chains. Other peaks such as those at 14, 22 and 32 ppm are all characteristic of long alkyl side chains (44). A peak at 19 ppm may be assigned to branched methyl groups in long alkyl substituents. The region between 37 and 50 ppm has a number of peaks in addition to a broad envelop. This region contains resonances from bridgehead and other CH naphthenic carbons, some methylene bridge carbon (between site, where one has no adjacent ring or group), alkyl CH other than in isoalkyl groups, and alkyl CH_2 adjacent to alkyl CH (45). Precise assignments in this region are difficult, but it appears that most of the above groups could be present.

Carbon and Hydrogen Distribution From NMR Data

Carbon and hydrogen distributions in the bitumen and some of its asphaltene fractions were calculated from the integrated areas of various regions as shown in Table II. Considering the accuracy of nmr measurements, there was not much variation in the data for the distribution of carbon and hydrogens in bitumen and asphaltenes. Ca, the ratio of aromatic carbon to total carbon (carbon aromaticity) for different samples were of almost the same magnitude: 0.24 ± 0.02 for bitumen and 0.39 ± 0.03 for asphaltenes. This suggests that 1/4 of the total carbons in bitumen and 2/5 of the total carbons in asphaltenes are in aromatic locations. Data for the distribution of various types of hydrogens suggests that H_β, the saturated alkyl and naphthenic hydrogens and H_γ the γ and further methyl hydrogens together constitute about 80% of the total hydrogens. Aromatic hydrogens constitute only 6.4% of the total hydrogens. However, the proportion of aromatic hydrogens in asphaltenes is greater than in bitumens (9.3% vs 6.4%). This is consistent with the higher carbon aromaticity of asphaltenes compared with bitumens. The ratio of H_α to total hydrogens in asphaltenes is also considerably higher than in bitumens (0.27 ± 0.015 vs 0.14 ± 0.014). Subsequently, the proportion of H_β and H_γ hydrogens is lower in asphaltenes than in bitumens (0.798 ± 0.016 vs $0/639 \pm 0.016$).

TABLE II
ASSIGNMENT OF PROTON AND CARBON-13 NMR SPECTRA

Proton: Symbol	Definition	Chemical Shift Range (PPM from TMS)
H_a	Aromatic protons	6.00 to 9.00
H_α	Hydrogen in saturated groups α to aromatic rings	2.00 to 4.00
H_β	Hydrogen in saturated groups β to aromatic rings	1.00 to 2.00
H_γ	γ-CH_3 to aromatic ring and straight-chain or branch alkane methyl hydrogens	0.50 to 1.00
C-13		
C_a	Aromatic carbon atoms	100.00 to 150.00
C_{al}	Saturated carbon atoms	0.00 to 70.00

The Average Molecular Structural Parameters

Average molecular structural parameters of various bitumen samples and some of its asphaltene fractions were calculated using data obtained from the integration of the areas of the various carbons and hydrogen regions in the respective NMR spectra. The equations used to calculate average moelcular parameters were similar to those used by Knight (46), Dickinson (18), Takegami et al (44), Suzuki et al (10) and Seshadri et al (47). Heteroatoms, such as sulfur, oxygen and nitrogen were neglected in the calculations in order to simplify the average structures. The absolute accuracy of calculated average molecular parameters is probably not high. However, the accuracy is usually considered to be sufficient to provide useful comparisons between samples. From the values of structural parameters it was deduced that an average bitumen moelcule contains 1.5 to 2 aromatic rings and 4 to 5 naphthenic rings with 4 to 5 alkyl substituents of chain length ranging from 6 to 7 carbon atoms. There were some differences in the magnitude of these parameters for various samples. However, these differences were small, and consequently it was deduced that the various samples bear a close resemblance to each other in terms of their chemical nature.

CONCLUSIONS

1. In a previous publication (32) we demonstrated that the bitumen extraction efficiency of the Clark hot water process depends mainly on the mineral fines (<44 μm particles)content of the bituminous feedstock. However, the data in this report suggests that the composition of the mineral fines also plays a significant role in determining the effeciency of extraction of a process.

2. There appears to be a correlation between the asphaltene content of bitumens and the grade of the bituminous feedstock.

3. The high molecular weight asphaltenes are entrapped in the pores of mineral agglomerates and are not easily removed, using simple solvent extraction such as the Dean-Stark method.

4. Clay minerals fractionate bitumen. High molecular weight components of bitumen appear to be associated with clay minerals either by adsorption or by clay-organic interactions.

5. V/Ni index for various bitumen samples is fairly uniform suggesting that it is independent of any compositional differences. The uniformity of V/Ni index suggests that all bitumen samples are genetically related. The value of the V/Ni index is characteristic of middle cretaceous oils.

6. Average molecular parameters calculated from proton and ^{13}C NMR spectroscopic data do not differ significantly for different bitumen samples.

7. An average bitumen molecule appears to contain 1.5 to 2 aromatic rings and 4-5 naphthenic rings with 4-5 alkyl substituents of chain length ranging from 6-7 carbon atoms.

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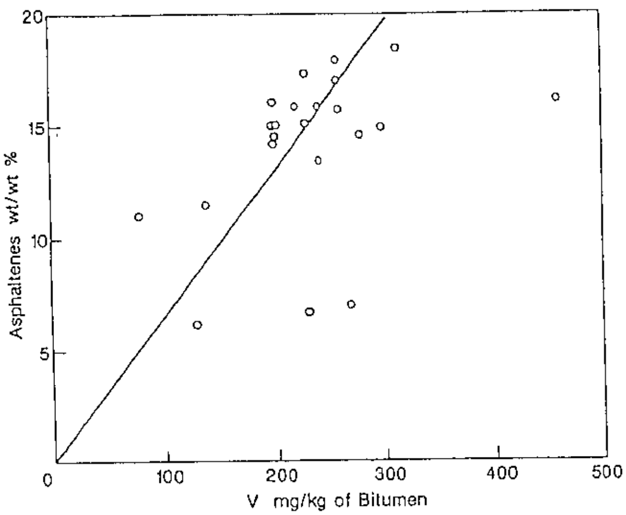

Figure 1: Correlation between Vanadium and Asphaltene Content of Bitumens

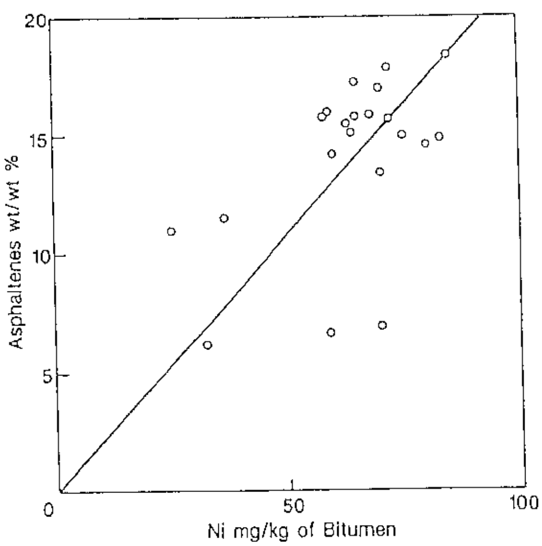

Figure 2: Correlation between Nickel and Asphaltene Content of Bitumen.

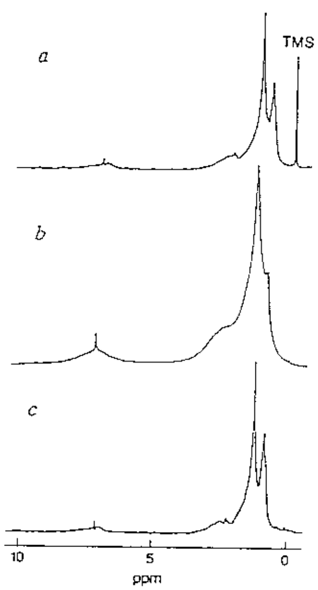

Figure 3: Typical Proton NMR spectra of (a) Bitumen, (b) Asphaltenes, (c) Maltenes

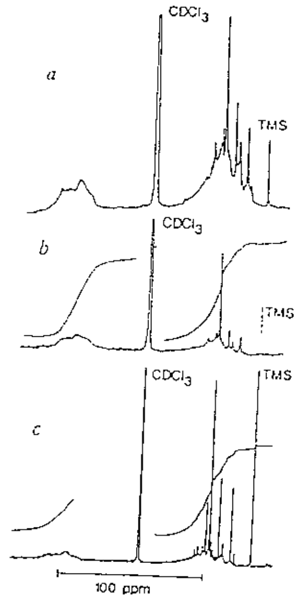

Figure: 4 Typical ^{13}C NMR spectra of (a) Bitumen, (b) Asphaltenes, (c) Maltenes.

determinations of maltenes using GPC and to Drs. B. D. Sparks and John A. Ripmeester for reading the manuscript and making many valuable comments.

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