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Chemical derivatization of Athabasca oil sand asphaltene for analysis of hydroxyl and carboxyl groups via nuclear magnetic resonance spectroscopy[☆]

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Abstract

Athabasca oil sand asphaltene was methylated with different base catalyst/solvent combinations in order to find an optimum procedure for analysis of the number and types of hydroxyl and carboxyl functional groups. High resolution carbon-13, fluorine-19, and silicon-29 NMR spectra were used to monitor the degree of methylation, trifluoroacetylation, trimethylsilylation, and aromaticity of asphaltene. Tetra-*n*-butylammonium hydroxide as phase transfer base catalyst and tetrahydrofuran or dichloromethane as solvent result in enhanced O-methylation of asphaltene. At least two types of acidic oxygen containing functionality have been detected, viz. hydroxyl and carboxyl (aliphatic and aryl). On average there are few, ≤ 4 –8, hydroxyl containing groups (including COOH) per asphaltene molecule. ¹³C NMR lineshapes suggest a broad asymmetric distribution of acidic sites. The NMR and elemental analyses allow for oxygen containing functionalities to be included in an average molecular structure. A sludge phase collected from aqueous and hydrochloric acid extractions of asphaltene has also been analyzed. A correlation is observed between the degree of O-methylation and the dielectric permittivity of the solvent and the acidity of the substrate reaction site. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Oil sand asphaltene; NMR spectroscopy; Functional group analysis

1. Introduction

Asphaltenes are complex naturally occurring components of bituminous materials such as coals and tars [1,2]. Precipitation from bitumen or petroleum solution with excess of an apolar solvent, e.g. *n*-pentane or *n*-heptane yields an asphaltene fraction comprised of polar and hydrocarbon compounds [1]. Although asphaltenes have been studied by a variety of techniques, their molecular structures have not been fully elucidated [2–6]. It is especially important to characterize the polar functional groups, as they can affect intra- and intermolecular reactions and aggregate structures through hydrogen bonding and metal chelation, etc. [7–11]. For example, high number average molecular weights (MWs) of the order of thousands of amu for asphaltene solutions have been interpreted in terms of molecular

association complexes [1,10,12,13]. This behavior is analogous to that of amphiphilic molecules, such as surfactants which form inverse micelles in apolar and low dielectric constant solvents [14], hemi-micelles with minerals and clays [15], and microemulsions with hydrocarbons in water [16].

Variation of the chemical composition of asphaltene in bituminous materials from different geological sources has also been documented [1,10,13,17]. The research described in this work deals with asphaltene from the Athabasca oil sands deposit of northern Alberta, Canada [6,18]. Elemental analysis of Athabasca oil sand asphaltene (AOSA) reveals ca. 1% nitrogen, 4% oxygen, and 8% sulfur—thus appreciable numbers of heteroatom groups [1,6,17,19–21]. Characterization of polar groups is important in understanding chemical processes involved in the formation, oxidation, degradation, refining, environmental impact, and modification of natural fuels [1–3,12,22,23]. It is the aim of this research to determine the number and types of oxygen containing acidic groups, namely, hydroxyl and carboxyl via chemical derivatization reactions, viz. O-methylation [24,25], trifluoroacetylation [26], and trimethylsilylation

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[27–30], for the introduction of site-specific NMR active nuclei (^{13}C , ^{19}F and ^{29}Si) as isotopic labels.

2. Experimental

2.1. O-methylation reaction

A typical methylation reaction [21,24,31–33] was performed on ca. 1.0 g of AOSA dissolved in ca. 100 ml of solvent in dry nitrogen at ambient room temperature. The base, 2 ml of 40 wt% aqueous tetra-*n*-butylammonium hydroxide (TBAH) (ALD) or 30 wt% aqueous sodium hydroxide (Anachemia), was added dropwise to a stirred solution of asphaltene in toluene (BDH), tetrahydrofuran (THF) (Anachemia), dichloromethane (Baker A.R.), or chloroform (Fisher). In one case, toluene was saturated with a 50:50 (v:v) solution of 1,4-dioxane (Anachemia) in water, and sodium hydroxide was dissolved in a 1:5 (v:v) solution of 1,4-dioxane:water in order to increase the solubility of the base. The aqueous solution of TBAH (pH 12.9) was standardized (41.35 wt%; 1.58N) by titration with 1N aqueous acetic acid (Anachemia; 99.7%) (pH 2.46) using an Accumet pH meter. After addition of 0.20 ml of 45% carbon-13 enriched iodomethane (99 at.% ^{13}C ; MSD isotopes) the mixture was allowed to stir overnight, followed by a total of ca. 30–50 extractions, first with 0.5 wt% aqueous sodium nitrate (Anachemia) and then with distilled water. THF solutions were evaporated to dryness in a stream of nitrogen gas and the residue was dissolved in toluene prior to extraction. The reaction product was dried in vacuo at ca. 80 °C for a few days. O-methylation reactions were repeated to determine the reproducibility of the technique and to observe the effects of using different amounts (0.30, 0.50, 1.0, and 2.0 ml) of TBAH and [^{13}C]-iodomethane (0.20, 0.25, 0.30, and 0.40 ml).

2.2. Trifluoroacetylation reaction

The reaction commonly involved bubbling trifluoroacetyl chloride (SCM Chemicals) for ca. 1 min through a solution of AOSA (ca. 0.2 g), plus 1–3 drops of 2,6-lutidine (ALD), in 2 ml of deuteriochloroform (MSD isotopes) in nitrogen at –55 °C in an iso-propanol/dry ice bath [21,26]. The mixture was warmed to room temperature and nitrogen was bubbled through the sample for ca. 1 h to remove excess trifluoroacetyl chloride. Residual trifluoroacetic acid was neutralized via the addition of finely powdered anhydrous potassium carbonate (Anachemia) followed by filtration.

O-methylated (with 1.0 ml of 40 wt% aqueous TBAH in THF and 0.2 ml of [^{13}C]-iodomethane) AOSA (0.067 g) was trifluoroacetylated as above with 0.005 g (0.047 mmol) of 2,6-lutidine.

2.3. Trimethylsilylation reaction

Asphaltene (1.0 g) was dissolved in 30 ml of THF and 3 ml of pyridine (Baker) was added to the solution. Trimethylchlorosilane (0.3 ml; SCM Chemicals) and hexamethyldisilazane (HMDSN) (1.0 ml; ALD) cooled on dry ice were transferred in nitrogen in glass syringes to the reaction mixture which was then refluxed at ca. 80 °C in nitrogen for ca. 1 h [28,30]. The solvent and reagent were removed in a stream of nitrogen gas at ca. 60 °C for several hours. Finally, the product was ground and dried in vacuo at room temperature overnight.

2.4. Treatment with aqueous hydrochloric acid

A solution of 10 ml of 36.5% aqueous hydrochloric acid in 40 ml of distilled water was added dropwise to a solution of asphaltene (ca. 1 g) in ca. 100 ml of toluene. The mixture was rigorously stirred and the organic layer was separated (aqueous phase; pH ~2) and extracted with distilled water until the aqueous phase was of neutral pH. After additional washings with warm distilled water, the organic phase was dried first in a stream of nitrogen gas at 80 °C and then in vacuo for several days at room temperature. The acid treated asphaltene was then methylated in THF with 1.0 ml of TBAH (aq) and 0.3 ml of [^{13}C]-iodomethane, as described.

2.5. Sludge extraction

Toluene solutions of whole, methylated, and HCl (aq) treated AOSA were each rigorously washed with warm water (ca. 80 °C) up to a 100 times. The aqueous phases were combined and extracted with toluene. The layer of sludge between the aqueous and organic layers was separated and re-extracted with toluene until the washings were colorless. Toluene was removed in a stream of nitrogen and the samples were dried at ca. 80 °C in vacuo for several days.

2.6. Solvents

Solvents used for chemical derivatization reactions were purified as follows. THF (BDH; A.R.) was distilled in nitrogen over lithium aluminum hydride. Chloroform (BDH) was washed six times with 100 ml of dilute aqueous sodium hydroxide, then three times with distilled water, three times with concentrated sulfuric acid, and six times with distilled water to remove 0.75% ethanol used as stabilizer. The separatory funnel was covered with aluminum foil. The washed chloroform was distilled in the dark and the middle fraction was collected. Toluene (BDH) and methylene chloride (BDH) were used as supplied.

2.7. Nuclear magnetic resonance spectroscopy

75.47 MHz inverse-gated proton decoupled carbon-13

and gated proton decoupled 282.35 MHz fluorine-19 and 59.60 MHz silicon-29 NMR spectra were acquired at ambient probe temperature on a Bruker MSL 300 spectrometer. ^{19}F and ^{29}Si NMR spectra, respectively, involved pulse widths of 8–12 and 10 μs , relaxation delay times of 10 and 1 s, spectral widths of 8475 and 7143–11905 Hz, ≤ 8000 and 188–210 scans, and 8K of data points. A paramagnetic relaxation reagent, chromium(III)acetylacetonate (Alfa) was added to solutions of asphaltene in deuteriochloroform (99.8 at.% ^2H ; MSD Isotopes) to allow for short (typically < 2 s) relaxation delay times between pulse sequences in the acquisition of ^{13}C and ^{29}Si NMR spectra. All samples for ^{13}C NMR spectroscopy contained approximately the same weight of material, ca. 7.5 wt% asphaltene and 1.8 wt% $\text{Cr}(\text{acac})_3$ in deuteriochloroform. Chemical shifts were measured relative to tetramethylsilane for ^{13}C and ^{29}Si NMR spectra in 10 mm o.d. precision NMR tubes and relative to 1,2-difluorotetrachloroethane (SCM Chemicals) (set to 0 ppm) in deuteriochloroform for the ^{19}F NMR of samples in 5 mm o.d. precision tubes. Typical ^{13}C spectra were accumulated with 23,000–37,000 scans in 16K of memory over a spectral width of 20,000 Hz, using a 45° pulse of width 4.5 μs . In most cases no exponential line-broadening factor was applied to the free induction decay signal in order to maintain intrinsic linewidths. A five parameter curve fit was used to baseline correct each spectrum and integration limits were set where the NMR signal reached the average noise level.

Lorentzian lineshape intensity was calculated at frequency, ν , from the apparent linewidth, $\Delta\nu_{1/2}$, and peak position, ν_0 , by applying Eq. (1). T_2^* is the transverse relaxa-

tion time [34,35]:

$$g(\nu) = 2T_2^* \left[1 + 4\pi^2 T_2^{*2} (\nu_0 - \nu)^2 \right]^{-1} \\ = (2\Delta\nu_{1/2}) / \left\{ \pi \left[\Delta\nu_{1/2}^2 + 4(\nu_0 - \nu)^2 \right] \right\}; \quad (1)$$

$$T_2^* = 1/\pi\Delta\nu_{1/2}$$

The area of the resonance peak in the frequency range $\nu_2 - \nu_1 = 2(\nu_0 - \nu_1)$ can be determined by the integration of Eq. (1). The term $|(\nu_0 - \nu_1)|$ is equal to $|(\nu_0 - \nu_2)|$ and signifies an absolute value.

$$\int_{\nu_1}^{\nu_2} g(\nu) d\nu = [1/\pi(\arctan\{2|(\nu_0 - \nu)|/\Delta\nu_{1/2}\})]_{\nu_1}^{\nu_2} \quad (2)$$

For $\nu = \nu_0$ Eq. (1) reduces to $g(\nu_0) = 2/(\pi\Delta\nu_{1/2})$ and this allows for normalization of the Lorentzian function using the spectral intensity I_0 at the peak maximum:

$$g(\nu)_N = I_0 g(\nu)/g(\nu_0) = [\pi\Delta\nu_{1/2}I_0/2]g(\nu) \quad (3)$$

Normalized Lorentzian lineshapes calculated using Eq. (3) were fitted to the observed spectra. Integration of Eq. (3) via Eq. (2) generates Eq. (4) which yielded the areas of observed and calculated peaks.

$$\int_{\nu_1}^{\nu_2} g(\nu)_N d\nu = [(\Delta\nu_{1/2}I_0/2)\arctan\{2(\nu_0 - \nu)/\Delta\nu_{1/2}\}]_{\nu_1}^{\nu_2} \\ = (\Delta\nu_{1/2}I_0)\arctan\{2|(\nu_0 - \nu_1)|/\Delta\nu_{1/2}\} \quad (4)$$

Integrals were measured for the total methoxy band and also were calculated from the sum of the component integrals (Eq. (4)) of the resolved peaks (Eq. (3)). In the few cases, where extraneous peaks from reaction

Table 1

Relative proportions of hydroxyl and carboxyl groups from integrated areas of the components of the ^{13}C NMR methoxy spectral region of phase transfer methylated Athabasca oil sand asphaltene in various solvents using different amounts of aqueous catalyst solution and ^{13}C -iodomethane. ($f(\text{O}^*\text{CH}_3)$) is the relative degree of O-methylation determined from the ratio of the integrated areas of the total methoxy carbons to that of the aromatic carbon atoms. ϕ' , sterically hindered aryl; ϕ , aryl; R, alkyl; #, little or no O-methylation observed)

Solvent/catalyst (ml)/ $^{13}\text{CH}_3\text{I}$ (ml)	$\phi'\text{OCH}_3$	ϕOCH_3	XOCH_3^a	$\phi\text{CO}_2\text{CH}_3$	RCO_2CH_3	$f(\text{O}^*\text{CH}_3)$
THF/TBAH (0.30)/0.25	0.41	0.22	0.05	0.13	0.19	0.52 ± 0.02
THF/TBAH (0.50)/0.20	0.37	0.18	0.05	0.15	0.25	0.49 ± 0.02
THF/TBAH (1.0)/0.20	0.37	0.19	0.07	0.10	0.27	0.53 ± 0.08
THF/TBAH (1.0)/0.20	0.37	0.16	0.07	0.11	0.27	0.38 ± 0.02
THF/TBAH (1.0)/0.30 ^b	0.39	0.16	0.07	0.15	0.23	0.42 ± 0.04
THF/TBAH (2.0)/0.20	0.36	0.20	—	0.15	0.29	0.41 ± 0.02
Dichloromethane/TBAH (1.0)/0.20	0.35	0.25	0.03	0.05	0.33	0.47 ± 0.04
Chloroform/TBAH (1.0)/0.20	0.32	0.16	0.02	0.12	0.38	0.16 ± 0.01
Toluene/TBAH (1.0)/0.20	0.48	0.22	0.10	0.09	0.11	0.38 ± 0.03
Toluene/TBAH (2.0)/0.40	0.50	0.28 ^c	—	—	0.22 ^c	0.41 ± 0.01
THF/NaOH (4.4)/0.40	0.53	0.24	0.09	0.05	0.09	0.20 ± 0.02
Toluene/NaOH (9.8)/0.40	#	#	#	#	#	#
Toluene + 1,4-dioxane + water/ NaOH (3.0)/0.20	#	#	#	#	#	#

^a From component resonance peak at ca. 56 ppm.

^b PTM reaction with AOSA which was treated with aqueous HCl.

^c Unresolved (total $\phi\text{OCH}_3 + \text{XOCH}_3$) and $(\phi\text{CO}_2\text{CH}_3 + \text{RCO}_2\text{CH}_3)$, respectively.

Fig. 1. Carbon-13 NMR spectrum of a deuteriochloroform solution of phase transfer methylated (with TBAH (aq) (0.3 ml) in THF) Athabasca oil sand asphaltene. Inset: partially resolved methoxy resonances using Lorentzian calculated (---) lineshapes: A(ν_0 = 51.5 ppm; $\Delta\nu_{1/2}$ $\approx$ 36 Hz); B(ν_0 = 52.7 ppm; $\Delta\nu_{1/2}$ $\approx$ 144 Hz); C(ν_0 = 55.4 ppm; $\Delta\nu_{1/2}$ $\approx$ 82 Hz); D(ν_0 = 56.4 ppm; $\Delta\nu_{1/2}$ $\approx$ 91 Hz); E(ν_0 = 60.9 ppm; $\Delta\nu_{1/2}$ $\approx$ 182 Hz).

byproducts or reagents appeared, the measured and calculated values for these peaks were subtracted from the total methoxy integral. The upfield limit of integration was taken from the point (ca. 49 ppm) where the calculated line for the alkyl methyl ester peak reached the baseline, and the downfield limit was at ca. 68 ppm. These allowed for a relative degree of total (OH and COOH) O-methylation, $f(\text{O}^*\text{CH}_3)$, to be determined from the ratio of the total integrals of the methoxy to the aromatic carbon bands. These values are listed in Table 1 along with the relative proportions (P_i) of each type of acidic oxygen functional group. P_i values were determined from the component integrals using Eqs. (3) and (4). In turn, the relative degree of methylation of each constituent is available from the relation: (relative proportion of OH or COOH) $\times$ (total relative degree of O-methylation) = $P_i \times f(\text{O}^*\text{CH}_3) = f_i$; where $i = \phi\text{OH}$; $\phi'\text{OH}$; XOH ; ϕCOOH ; RCOOH .

Distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR spectra were acquired using the technique of Bendall and Pegg [36]. Pulse widths for 90° flip angles were also calibrated and tested on benzene ($J(\text{C}-\text{H}) = 159.8$ Hz (obs.)) in deuteriochloroform and on 1.5 molar solutions of sucrose in deuterium oxide via Ad Bax's method [37]. In both cases, the pulse length was determined from the zero crossing point of signal intensity to be 10 and 90 μs , respectively, for the ^{13}C and ^1H (decoupler) channels. The latter is in good

Fig. 2. Carbon-13 NMR spectra of Athabasca oil sand asphaltene: (a) methylated with TBAH (aq) (2.0 ml) and ^{13}C -iodomethane (0.40 ml) in toluene; (b) whole untreated asphaltene; (c) methylated with TBAH (aq) (1.0 ml) and ^{13}C -iodomethane (0.20 ml) in toluene; (d) methylated with TBAH (aq) (1.0 ml) and ^{13}C -iodomethane (0.20 ml) in THF; (e) methylated with NaOH (aq) in THF; and (f) methylated with NaOH (aq) in toluene.

agreement with literature results [37]. A polarization transfer delay time of 3.93 ms ($1/2J$; $J(\text{CH}) = 127.2$ Hz is the carbon-proton spin coupling constant) was used along with carbon-13 (9.1 and 18.2 μs) and proton (18.0 and 36.0 μs) 90° and 180° pulses, respectively. A value of 8.75 μs was employed for the 135° ^1H sorting pulse.

2.8. Elemental analysis

Weight percent hydrogen, carbon, and nitrogen were determined on a Perkin-Elmer 240 CHN analyzer. Sulfur content was analyzed via X-ray fluorescence spectroscopy and weight percent oxygen was calculated by difference from the total CHNS values.

3. Results and discussion

3.1. Carbon-13 NMR spectroscopy of O-methylated asphaltene

O-methylation of AOSA with base and isotopically labelled methyl iodide, according to the following net reaction (Eq. (5)), is evident from comparison of the carbon-13 NMR spectra of the original and product materials (Figs. 1 and 2).

The three prominent overlapping peaks at ca. 50–65 ppm are in the methoxy chemical shift range, as observed for other asphaltic substances [2,21,38,39]. Integrated areas of the methoxy peaks suggest that of the different catalyst/solvent combinations studied, phase transfer methylation (PTM) with TBAH/THF yields the highest degree of O-methylation (Table 1). This is not unexpected, as TBAH has a higher solubility than sodium hydroxide in toluene or THF. In fact, utilization of sodium hydroxide/THF attenuates O-methylation, whereas sodium hydroxide/toluene results in little or no reaction with AOSA (Fig. 2).

Noteworthy is the increase in intensity with decrease in linewidth of the methoxy NMR peaks in order of increasing acidity of the methylatable group (Fig. 1). Interpretation of lineshape changes necessitates consideration of structural and dynamic properties of asphaltene solutions. For instance, AOSA can aggregate in organic solvents, as shown from NMR self-diffusion measurements [21] and vapor pressure osmometry [1,17,19]. In addition, the association complexes are probably different in toluene, THF, dichloromethane, and chloroform owing to solvent effects. Polar solvents can hydrogen bond to acidic groups and solvate metal counterions thereby facilitating derivatization via exposure of reactive sites. Such an observation would support the view that dipolar interactions are a major factor in the formation and stabilization of asphaltene aggregates. The NMR linewidths generally follow the order, $\Delta\nu_{1/2}(\text{RCOOCH}_3) \approx 30 \pm 4 \text{ Hz} < \Delta\nu_{1/2}(\phi\text{OCH}_3) \approx 88 \pm 13 \text{ Hz} < \Delta\nu_{1/2}(\phi'\text{OCH}_3) \approx 174 \pm 15 \text{ Hz}$, where R = alkyl, ϕ = aryl, and ϕ' = sterically hindered aryl, and are consistent in value (± 1 standard deviation) among the different solvent/catalyst systems. The alkyl methyl ester linewidth is similar to those of the large alkyl carbons resonances at 10–40 ppm. Based on linewidths, the distribution of acidic sites follows the trend $\phi'\text{OH} > \phi\text{OH} > \text{RCOOH}$. In terms of chemical shift, the overlapping resonances at 50–65 ppm can be interpreted as methyl derivatives of: (i) carboxylic acids at 50–53.5 ppm; (ii) phenols and mono *ortho*-substituted phenols at ca. 54–57 ppm; and (iii) sterically hindered phenols, e.g. di-*ortho*-substituted phenols at ca. 59–63 ppm [21,33,39,40]. Primary alcoholic methyl ether groups usually resonate in the narrow range at 58–59 ppm [40]. There is also the possi-

bility of S-, N-, and C-methylations of thiol, thiophene, amine, amide, imine, pyrrole, pyridyl, fluorenyl, etc. groups appearing at 18–50 ppm [21,25,31,41]. Indeed, comparison to the aliphatic spectral regions before and after PTM reactions, particularly in toluene or THF (Fig. 2), suggests the methylation of heteroatom groups [21]. PTM of active heteroatom sites can diminish intra- and intermolecular linkages via disruption of hydrogen and chelation bonds, and alkaline hydrolysis, with resultant conformational modifications, such as unfolding or loosening of asphaltene complexes, along with a decrease in the aggregation number. Published reports confirm that methylation reduces the MWs of asphaltenes [10,13]. Further outcome of the above reaction effects is alteration of correlation times for molecular and group rotations resulting in NMR linewidth and intensity changes.

NMR linewidths are influenced by many factors, in particular, magnetic susceptibility and spin–spin relaxation processes. For instance, the rotational mobility of hydrocarbon chains can reduce the width of the alkyl methyl ester peak at ca. 51 ppm, whereas groups attached to the rigid aromatic structure of asphaltene experience conjugative and steric effects which can result in the broad downfield shoulder at ca. 52 ppm. Methoxy group rotation of aryl and alkyl esters is commonly a facile process, e.g. an enthalpy of activation of 27 kJ mol^{-1} for methyl acetate and 21 kJ mol^{-1} for solid methyl salicylate [42]. Also, relaxation of the entire ester group around C–O and C–C bonds in either the liquid or solid states is exemplified by enthalpies of activation of ca. $26\text{--}36 \text{ kJ mol}^{-1}$, as for polyalkylmethacrylate polymers [42]. Furthermore, the methoxy group rotational barrier, ca. $10\text{--}15 \text{ kJ mol}^{-1}$, in ethers is appreciably lower than in esters [43]. Therefore, relaxation effects alone do not account for the difference in width of the alkyl and aryl ester and ether ^{13}C NMR peaks at 50–65 ppm. It is likely that electronic effects from the variety of aromatic structures are responsible for the range of chemical shifts of the different aryl methyl esters and ethers. Derivatization of free fatty acids, for example, would produce esters whose motional frequencies for segmental relaxations correspond to short picosecond correlation times resulting in narrow linewidths. In contrast, the molecular tumbling and diffusion of large asphaltene molecules and units are long correlation time, short T_2 value processes, with broad linewidths. On the foregoing basis the derivatization of alcohols would produce narrow peaks at ca. 58–59 ppm owing to the short correlation times for rotations around C–C and C–O bonds. The lack of *n*-alkyl methyl ether peaks implies that alcohols are absent or very minor components of AOSA. The $^{13}\text{CH}_3\text{OR}$ NMR peak, though, has been produced in experiments involving the reduction of methyl ester asphalts with lithium aluminum hydride or sodium borohydride [38].

Chemical exchange, e.g. monomer $\rightleftharpoons$ aggregate equilibria can also affect lineshapes. In a previous publication we reported the self-diffusion coefficients of AOSA in

Fig. 3. Carbon-13 NMR spectrum of AOSA treated with HCl (aq) and then phase transfer methylated with TBAH (aq) in THF. Inset: methoxy resonances.

deuteriochloroform solutions to correspond to large particle weights and molecular association complexes [21]. Other factors which can broaden nuclear magnetic resonances include paramagnetic species such as iron and mineral inclusions, and colloidal particles and water-in-oil emulsions, which can generate bulk diamagnetic susceptibility effects. The latter may be problematic in high resolution spectroscopy, especially if bound or encapsulated water occurs in bituminous materials. Indeed, dielectric measurements [44] on AOSA reveal loss maxima at 10^4 – 10^6 Hz and 200–231 K with an activation energy of 58 kJ mol^{-1} . The dielectric peaks of untreated AOSA, as well as those of O-methylated AOSA, AOSA in parowax, and trifluoroacetylated AOSA in parowax overlap with a higher frequency and temperature absorption. These dielectric dispersions and parameters are similar to those of water as an adsorbed phase and as moisture in the glassy media *o*-terphenyl, bis[*m*-(*m*-phenoxyphenoxy)phenyl] ether, and polyalkylmethacrylates [42].

Information on molecular structures can also be gleaned from the NMR lineshapes, which generally are more symmetric for the downfield band than the middle one which is skewed on its lowfield side (Figs. 1–5). Clearly, the upfield band is comprised of overlapping peaks at ca. 51.0–51.5 ppm from methyl esters of aliphatic carboxylic acids and at 52–53 ppm from aromatic methyl esters. The phenolic methyl ether resonances centered at ca. 55 ppm consist of an upfield resonance band corresponding to

Fig. 4. Carbon-13 NMR spectra of phase transfer methylated AOSA; (a) with TBAH in chloroform; LB = 0 Hz; (inset: methoxy resonance portion with a linebroadening factor of LB = 4.0 Hz); and (b) with TBAH in dichloromethane.

monohydroxyl structures and a downfield component, XOCH_3 at 56 ppm, from dihydroxyl (resorcinol) type functionalities [39,45,46], as in low temperature oxidized AOSA where the peaks are pronounced [21]. Partial resolution of the overlapping methoxy resonances is feasible by applying calculated Lorentzian lineshapes (Eqs. (1) and (3)) to the spectra (Fig. 1), as previously utilized for the oxidized material [21]. Areas under the component methoxy resonance peaks give the following relative percentages of phase transfer methylated (in THF) oxygen: RCOOCH_3 (19–29%); ϕCOOCH_3 (10–15%); ϕOCH_3 (16–22%); XOCH_3 (0.05–0.07%); and $\phi'\text{OCH}_3$ (36–41%) (Table 1). On average, OH groups account for ca. 62% of the methylated sites and outnumber COOH by about 3:2.

An important feature to consider is the variation of the degree of O-methylation with solvent dielectric constant (ϵ_0) (Table 1). Aliphatic carboxyls display greater sensitivity to reaction conditions, as reflected in the 2–4-fold increase in f_i in the sequence 0.04, 0.06, 0.11 ± 0.02 , 0.16 with an increase in solvent ϵ_0 (at 25 °C) in the order 2.4, 4.8, 7.4, 9.1 for toluene, chloroform, THF, and dichloromethane, respectively. In contrast, the degree of hydroxyl methylation changes slightly with increase of solvent polarity (Table 1).

Fig. 5. Carbon-13 NMR methoxy resonances of AOSA which was O-methylated with: (a) tetra-*n*-butylammonium hydroxide (aq) (1.0 ml)/dichloromethane; (b) tetra-*n*-butylammonium hydroxide (aq) (1.0 ml)/THF; and (c) sodium hydroxide (aq)/THF.

Notable is the research of Speight who observed a decrease from 2695 to 1380 in the MW of an Athabasca asphaltene fraction with an increase in dielectric constant of the solvent from ca. 2.3 (benzene) to 12.3 (pyridine) [19]. Ionic and dipolar interactions are affected by the dielectric permittivity of the medium. Hence, intermolecular forces responsible for aggregation diminish in high ϵ_0 solvents, thereby exposing core groups to the solvent and methylating agents. Ionogenic reactions, which generate anions of hydroxyl and carboxyl groups depend on the extent of solvation, delocalization of charge, and electric field effects from proximal dipolar groups [47,48]. Carboxyl groups thus have enhanced dissociation in high dielectric constant media, especially aprotic solvents, and increased nucleophilicity of the anion in S_N2 reactions with iodomethane. Ordinarily, the reactivity of acidic functionalities is directly proportional to the pK_a and inversely proportional to the dielectric constant of the solvent. Phenols and alcohols are less acidic than carboxyl groups, so their dissociation is not appreciably influenced by changes in solvent polarity though their anions are more basic and reactive to $^{13}\text{CH}_3\text{I}$. There is little effect of ϵ_0 on the dissociation of protonated bases, $\text{BH}^+ \rightleftharpoons \text{B} + \text{H}^+$, owing to no change in the total charge. In addition,

there are greater steric effects on the pK_a of COOH than OH because of the size difference. Charge crowding is a factor, which can partially inhibit methylation of proximal hydroxyl groups, and may explain some of the increase of O-methylation with repeat reaction on the same sample. For example, $pK_1 = 9.37$ and $pK_2 = 13.7$ for catechol at 20 °C [49]. Generally, pK_a values follow the trend COOH (3–5), phenols (8–10), alcohols (13–16), and active methylenes (≤ 23) [50,51]. Statistical factors should also be considered when a polybasic acid has n groups each of which has an equal probability of losing a proton. The observed pK_a would then be less by $\log(n)$ than the pK_a of a closely related monobasic acid [50]. Other factors which influence acidity are the spatial distribution and conformation of adjacent polar and ionized groups [48]. For example, humic acids have a Gaussian distribution of pK_a values from structural, statistical, and electronic effects, e.g. 0–13 for β -dicarbonyls, enols, and alcohols [48]. Active methylenes, as in fluorenes, indoles, etc. are sufficiently acidic when treated with base to yield anions [51].

Ionization of tetra-*n*-butylammonium hydroxide is affected by the dielectric constant of the solvent and as with other short-chain quaternary alkylammonium salts some of the physical properties of its solutions display concentration dependence owing to self-association [52]. In deuteriochloroform, TBAH has ^{13}C NMR peaks at ca. 13, 19, 23, and 58 ppm. TBAH is difficult to remove from the asphaltene reaction mixture, even after numerous aqueous extractions, because of its solubility in polar and apolar media. Residual base cannot only induce structural changes in asphaltene, but also modulate the shape of the ^{13}C NMR band at 58–60 ppm. TBAH undergoes slow thermal decomposition and hydrolysis reactions resulting in methylatable products containing NCH_3 , $^+\text{NCH}_3$, and OCH_3 groups, as discussed later. When sodium hydroxide is used as the base catalyst, then O-methylation products are again observed at 50–65 ppm (Figs. 2 and 5). However, the methoxy peaks are diminished in intensity and there is little or no methylation of aromatic carboxyls, perhaps owing to hydrolysis of methyl esters (Table 1). Aliphatic esters are more resistant to hydrolysis than their sterically unhindered aromatic analogues. Demetallation of AOSA, with aqueous hydrochloric acid to remove metal cations bound to carboxyl groups, does not inhibit methyl esterification. Also, there is no appreciable electrophilic reaction of HCl with olefinic groups to yield alcohols, as evidenced by the absence of a peak at ca. 58 ppm (Fig. 3).

It is significant that PTM reactions in toluene, THF, chloroform, or dichloromethane produce similar $^{13}\text{CH}_3\text{O}$ NMR spectral patterns at 50–65 ppm (Figs. 1–5). This suggests that THF is not the cause of the upfield band attributable to carboxyl methyl esters. THF has carbon-13 NMR peaks at 26 and 68 ppm. Also, the fact that methylation with NaOH in THF generates a peak at 51 ppm (Fig. 5) supports the view that the resonance is from intrinsic carboxylic acids and not from N-methylation of TBAH.

Table 2

Elemental analysis (wt%), atomic ratio, and aromaticity factor (f_a) values of AOSA samples (AT, asphaltene treated with aqueous hydrochloric acid; PTM, phase transfer methylated with TBAH (aq) in THF or toluene)

	C (%)	H (%)	N (%)	S (%)	O (%) ^a	H:C	N:C	S:C	O:C	f_a ^b
Asphaltene	79.41	7.82	1.20	–	–	1.18	0.013	–	–	0.48
Dried asphaltene ^c	78.28	7.78	1.12	8.11	4.71	1.19	0.012	0.039	0.045	0.52
AT–AOSA	79.49	7.96	1.14	8.35	3.06	1.20	0.012	0.039	0.029	
AOSA sludge	61.95	9.48	2.75	4.61	21.21	1.84	0.038	0.028	0.257	
AT–AOSA sludge	62.32	6.57	1.07	–	–	1.27	0.015	–	–	
PTM(THF) AOSA	78.59	7.87	1.13	9.02	3.39	1.20	0.012	0.043	0.032	
PTM(ϕ CH ₃) AOSA	79.08	8.34	1.26	–	–	1.27	0.014	–	–	

^a By difference.

^b From carbon-13 NMR.

^c Dried in vacuo at 80 °C for 7 days.

Within experimental error the degree of O-methylation displays slight variation with the amount (0.3–2.0 ml) of TBAH and [¹³C]-iodomethane added to the reaction mixture (Table 1). Methyl esters, however, can be hydrolyzed with excess TBAH. Therefore, an equilibrium or competition for [–]OH among PTM and hydrolysis reactions exists. Hydrolyzable groups in pretreated AOSA are likely to be of the Ar/RCOOAr type rather than Ar/RCOOR esters. In the presence of hydroxide and water the latter would produce alcohols whose methyl ether derivatives are notably absent indicating that the $-(O)C-O-R$ moiety is uncommon. Other functionalities, e.g. acid anhydrides, lactones, lactams, and amides, etc. could also contribute to the methoxy spectral pattern following hydrolysis and PTM reaction.

Factors to consider in analysis of the PTMs are side-reactions which can compete with the substrate for iodomethane, thereby complicating the NMR spectra. Prime among the secondary reactions are: (i) the decomposition of TBAH; and (ii) the oxidation of THF. TBAH undergoes a slow hydrolysis to produce butanol and tributylamine which can be methylated with ¹³CH₃I. Methylbutyl ether, though, is sufficiently volatile to be removed during drying and tri-*n*-butylmethylammonium iodide should be extractable with water. Pyrolysis of TBAH gives tributylamine, butene, and water via hydro-trialkylamine elimination. Butene can undergo further reaction with water and acid to form 1,2-dihydroxybutane which subsequently can be methylated resulting in a methyl ether peak at ca. 58–59 ppm. Reaction (ii) generates α -hydroperoxide tetrahydrofuran, γ -butyrolactone, and α -hydroxytetrahydrofuran. The latter can then be O-methylated into α -methoxytetrahydrofuran. In addition, THF is known to form several aging products, namely, α -oxotetrahydrofuran, butyraldehyde, 4-hydroxybutyraldehyde, butyric acid, 4-hydroxybutyric acid, and 4-hydroxyperbutyric acid [53]. The last four compounds can form methyl ethers and esters that are sufficiently volatile to be removed during the drying process. In addition, it is feasible that THF could react with methyl iodide to produce some oxonium salt, 1-methyltetrahydrofuran oxonium iodide. Unless

peroxide byproducts of THF are removed they are likely to oxidize asphaltene [53].

Some spectra have extra peaks at 47–49, 52–53, 58.2, and 62.5 ppm (Fig. 2). The peak at 62.5 ppm disappears after the sample is rigorously extracted with warm water on a mechanical shaker, which is characteristic of a polar compound. DEPT NMR reveals the 52–53 ppm peak to be CH₂. Any methanol produced by the reaction of iodomethane with hydroxide ions would have a NMR peak in the range ca. 47–49 ppm. When aqueous TBAH is thermally decomposed in air at ca. 70 °C for several hours, then ¹³C NMR peaks appear at 13.9, 20.7, 29.4, and 54.0 ppm in deuteriochloroform solution. Reactions of TBAH with chloroform to form reactive dichlorocarbene, and of CH₃I with basic nitrogen to yield methyl ammonium iodide salts are also possible.

Elemental analysis of dried AOSA renders values of 78.3% C, 7.8% H, 1.1% N, 8.1% S, and 4.7% O (by difference) (Table 2). The weight percent oxygen from elemental analyses of several samples is ca. 3–5% (Table 2) with literature values being in the range $3.2 \pm 0.9\%$ [1,6,17,19–21]. Spectroscopic and chemical investigations on Athabasca bitumen fractions reveal a variety of oxygen containing groups, e.g. ketones, esters, ethers, amides, sulf-oxides, and sulfones, etc. [1,6,54]. Therefore, ≤ 3 wt% of the oxygen must be in the hydroxyl and carboxyl groups. Likewise, the atomic ratio shows about 3–4.5 oxygen atoms per 100 carbon atoms. Moreover, from Table 2 the S:C and N:C ratios are fairly consistent at 4 sulfur and 1.3 ± 0.1 nitrogen atoms per 100 carbons. Collectively, the data in Table 2 along with observed number average MWs of 2648 [20] and 2750 amu [17] for AOSA yield average molecular formulae in the range $C_{172.6-182.0}H_{206.0-218.9}N_{2.1-2.2}S_{6.7-7.7}O_{5.0-8.1}$, i.e. less than 8 OH and COOH. These results are confirmed from comparison of the elemental content of pretreated and PTM derivatized asphaltenes (Table 2). No substantial incorporation of labelled ¹³CH₃ was observed, i.e. few labile oxygenic functional groups. However, the isotopically enhanced carbon-13 NMR spectra are sensitive to slight changes at the molecular level, and reveal at least three different

Fig. 6. DEPT 135° carbon-13 NMR spectrum showing CH and CH₃ with positive intensities and CH₂ resonances as negative signals of phase transfer methylated (with TBAH (aq) (2.0 ml) in THF) AOSA. Chemical shift assignments (●) are for carbon atoms in typical hydrocarbon moieties (a, 14.1 ppm; b, 19.7 ppm; c, 32.7 ppm; d, 22.7 ppm; e, 29.7 ppm; f, 31.9 ppm; g, 37.4 ppm. Observed values are relative to TMS for AOSA in CDCl₃).

OH/COOH type groups spread over various sites. Consequently, the OH and COOH groups must be attached to different moieties of a polyaryllalkyl molecular structure.

The methoxy nature of the multiple resonances at 50–65 ppm is verified from ¹³C NMR DEPT experiments. A 135° sorting pulse nulls quaternary carbons generates CH and CH₃ resonances with positive intensity and CH₂ as negative peaks. Assignment of the alkyl resonances is simplified using DEPT as: CH in the range 25–60 ppm; CH₃ at 10–24 ppm; CH₂ at 21–45 ppm; and OCH₃ at 50–65 ppm as in Fig. 6 [41,55]. The experiment also reveals that the broad unresolved band of overlapping resonances at ca. 10–28 ppm can be accounted for by methyl carbons attached to a variety of benzenoid, fused alicyclic, and heteroatom moieties as well as the terminal CH₃ of *n*-ethyl and *n*-propyl groups [21,41,46,55–57]. Accordingly, the region upfield of peak (a) in Fig. 6 can be assigned to α-CH₃ of aromatic and hydroaromatic (tetralin, etc.) systems shielded by two adjacent rings or groups; alkyl methyl thioethers; and methyl on *trans*-decalin systems [6,55,57]. The weak resonance below ca. 14 ppm attests that the foregoing types of methyl (e.g. ethyl, 9- or 10-methyl anthracene, alkyl-*S*-methyl) are scarce in AOSA and are fewer in number than α-CH₃ on naphthenic, hydroaromatic and heterocyclic groups, and α-CH₃ shielded by one adjacent ring or group, whose resonances occur between

peaks (a) and (d) in Fig. 6. Spectral intensity between peaks (d) and (e) in Fig. 6 can be attributed, at least in part, to methyls on tertiary carbon (e.g. 2,2-diphenylpropane) and N-CH₃ in indole and pyrrolidine systems [46,58,59]. Indeed, the DEPT 135° spectrum supports the concept that N-, S- and C-methylations occur concomitantly with PTM O-methylation of AOSA. Aromatic carbon atoms bonded to the oxygens of phenols and arylalkyl ethers typically resonate in the region 145–160 ppm [46,56]. From Figs. 1–4 there are few such groups although there is some intensity in this region of the spectrum. Application of Eq. (4) to a weak broad band centered at 152 ppm yields a calculated integral which correlates to ca. 3% of the total aromatic carbons, and for a total of 172–182 carbon atoms of which 48–52% (Table 2) are aromatic, this translates into 2–3 C_{Ar}-O groups.

3.2. Analysis and derivatization of sludge fractions

An appreciable amount of sludge was collected from aqueous extraction of the organic phase of the O-methylation reactions. The original and derivatized asphaltenes were not pretreated to remove oil phase solids and hence reflect the chemistry of suspended and bitumen complexed inorganic components which have been retained and co-precipitated with asphaltene. Athabasca oil sands are complex, multiphase mixtures containing ~10 wt% water and ≤18 wt% bitumen, in a conglomerate of quartz sand, clays (e.g. kaolin composed of hydrous aluminum silicate (Al₂Si₂O₅(OH)₄) and other mineral fines possessing Fe (260 ppm), Ni (240 ppm), V (640 ppm), Ti, Zr, Al, Ca, Mg, and Mn [6,20]. Experimental evidence in favor of the presence of organomineral components comes from elemental analyses of the sludge and hydrochloric acid treated AOSA sludge fractions which yielded ca. 62% C, 8% H, 2% N, and 5% S (Table 2). The ca. 17% reduction in weight percent carbon, compared to whole asphaltene, can be explained by higher relative amounts of mineral matter. Some of the decrease in wt% S may be from loss of inorganic sulfur during the acid and aqueous treatments. Indeed, up to 50% of the sulfur in AOSA oil phase solids may be inorganic [6]. These CHNS values are similar to those of the insoluble fractions of adsorbed organic matter from Athabasca oil sand tailings [6].

A consequence of the hydro- and oleophilic character of the oil sands is that a variety of colloids can exist in situ and in the extracted fractions [60,61]. Although minerals and clays have hydrophilic properties, they can be partitioned into oleophilic media, such as toluene, owing to the adsorption of bitumen and organic molecules on ultrafine particles, some <200 μm in size [22,61]. Stabilization of the resultant sols and microemulsions can be actuated via net negative charges on the dispersed phase by substitution of Al³⁺ or Si⁴⁺ with lower valency isomorphous metal ions. Indeed, it has been shown from electrokinetic measurements that asphaltenes colloiddally stabilize clays in hydrocarbons

[61]. Additionally, the dissociation of acidic functional groups, such as OH and COOH of asphaltene adsorbed on clay/minerals can alter the net charge on the aluminosilicate lattice and impart negative charge on the particles. Changes induced by chemical derivatization can therefore effect the phase behavior and colloidal properties of AOSA suspensions.

O-methylation inhibits (AOSA-OH/COOH)/(AOSA-O⁻/COO⁻)-(metal ion)-clay interactions, subsequently decreasing the electrostatic and steric repulsions which stabilize clay dispersions in low polarity media leading to agglomeration in a hydrophilic sludge. Also, PTM alters AOSA-XH...O to AOSA-X...H type hydrogen bonds with water, i.e. enhanced intermolecular reactions of asphaltene as a base resulting in a different hydrophile-lipophile balance of AOSA and its emulsions, e.g. in the tailings ponds. The extra CH₃ groups from PTM at the reactive solvent exposed sites render AOSA slightly more lyophilic to toluene. When toluene solutions of PTM asphaltene are subjected to bulk hydration the distribution of hydrocarbon and polar groups plays an important role in sludge formation via the lowering of interfacial tension by AOSA and AOSA-clay/mineral complexes acting as surface active agents, as in the emulsification of water-oil mixtures by surfactants. Partial coverage of clay/mineral fines by bitumen gives the particles amphiphilic properties [22]. Hence, toluene-(Ar/R-AOSA-OH/COOH)-water; toluene-(Ar/R-AOSA-OH/COOH)-mineral-water, and simple oil-in-water and water-in-oil type emulsions can exist in the heterogeneous sludge layer.

Treatment of Athabasca asphaltene with hydrochloric acid resulted in enhanced sludge formation, as reported for crude petroleum in contact with acid [60]. This effect complies with a model where metal cations react with acids to make the clay more anionic. HCl also reacts with carbonates to lower the carbon and oxygen contents of AOSA via the evolution of carbon dioxide, and with salts of acids to regenerate carboxyls. Heavy metal salts of humic and possibly fatty acids may exist in AOSA [6]. Any lead, mercury, and silver ions would be precipitated as metal chlorides and metals more active than hydrogen would be oxidized. There is also the possibility of hydrolysis, cleavage of ethers to alcohols and alkyl halides, and electrophilic additions. These would intensify the polarity and hydrophilicity of the organic phase, and stabilize oil-in-water type emulsions. Consideration of mineral-asphaltene complexes is thus an important part of the chemistry of bituminous materials owing to their geological nature.

3.3. Fluorine-19 NMR spectroscopy of trifluoroacetylated asphaltene

Trifluoroacetylation (Eq. (6)) of AOSA and phase transfer methylated AOSA with trifluoroacetyl chloride generate broad bands of overlapping ¹⁹F NMR peaks at ca. -7

to -8 ppm (Fig. 7) [21]:

X = O, S, N, NH

The latter, as with repeat PTM derivatizations, suggests that perhaps not all hydroxyl groups are isotopically labeled by a single reaction with TBAH/THF and ¹³CH₃I [38]. Variances in the degree of derivatization from different reactions can be accounted for by the selectivity and reactivity of the derivatizing agents, as discussed in a previous publication [21]. Trifluoroacetyl chloride is more reactive than iodo-methane toward nucleophiles, owing to its carbonyl group and weak basicity of chloride, making it a better leaving group than is iodine from CH₃I. 2,6-Lutidine as base catalyst also enhances the S_N2 reaction with active heteroatom groups. A drawback of the trifluoroacetylation reaction is the facile hydrolysis of acyl chlorides into carboxylic acids and hydrochloric acid, which subsequently can catalyze the hydrolysis of esters, lactones, acid anhydrides, acetals, hemiacetals, etc. to generate carboxylic acids, alcohols, and phenols. Hemiacetals though are not hydrolyzable by bases in the PTM reaction. Reactivity of hydroxyls and carboxyls is also affected by solvent and steric factors, and the degree of ionization and solvation sphere of the nucleophile, which must be disrupted for reaction. Therefore, tightly solvated anions are less nucleophilic, e.g. COO⁻ in protic solvents. Dissolution of asphaltene can induce conformational changes, which make protected groups accessible for reaction with derivatizing molecules. Steric crowding diminishes the availability of nucleophilic RO⁻ or ArO⁻ sites to CH₃I or CF₃COCl. These factors vary with solvent dielectric constant and donor-acceptor interactions, so differences are anticipated among PTM in THF, dichloromethane and chloroform, and trifluoroacetylation in deuteriochloroform.

¹⁹F peak assignments are basically as discussed in an earlier paper on the effects of low temperature oxidation on AOSA [21]. Although precautions were taken to exclude moisture, remove excess reagents, and to neutralize the reaction mixture, peaks from residual trifluoroacetyl chloride at -7.9 ppm and trifluoroacetic acid at -8.4 ppm were detected (Fig. 7). Fluorine-19 NMR confirms the presence and polydispersity of hydroxyl functionalities, though hydrolysis products can contribute to the multiple resonances. From the work of Sleevi et al. on model compounds, primary alcohol derivative peaks would appear upfield of -7.8 ppm, e.g. 1-butanol and 1-octanol at -7.9 ppm, while benzyl alcohols are candidates for the -7.66 to -7.70 ppm region [26]. The downfield signals are in the range of trifluoroacetylated phenols, cresols, and catechols (-7.40 to -7.67 ppm) [26]. Therefore, at least 40% of the derivatized groups are phenolic with few amines and alkyl thiols (-8.08 to -8.33 ppm), albeit TFA thiophenol resonates at -7.50 ppm [26].

Fig. 7. Fluorine-19 NMR spectra of deuteriochloroform solutions of: (a) trifluoroacetylated phase transfer methylated AOSA (* trifluoroacetyl chloride); (b) solution purged with nitrogen and neutralized with potassium carbonate. Inset: trifluoroacetyl (TFA) resonances of derivatized AOSA.

3.4. Silicon-29 NMR spectroscopy of trimethylsilylated asphaltene

Trimethylsilylation (Eq. (7)) using HMDSN is a proven method for the derivatization of OH, SH, NH, and COOH groups of natural products and fossil fuels [2,27,29,30,62].

Although stable trimethylsilyl (TMS) ethers can be formed under mild conditions, hindered hydroxyls and secondary amines are less reactive [30]. Some drawbacks of the reaction are that HMDSN and TMS esters of carboxylic acids (^{29}Si NMR peaks at ca. 20–27 ppm) (Fig. 8) can be hydrolyzed in the presence of water and acid, resulting in

trimethylsilanol which can then form hexamethyldisiloxane. In fact, HCl is generated by trimethylchlorosilane used to catalyze the TMS reaction [28]. Precipitation of ammonium chloride and pyridinium hydrochloride in the CDCl_3 solution can subsequently contribute to line broadening of the NMR peaks.

Silicon-29 NMR spectra of trimethylsilylated AOSA reveal hydroxyl groups (Fig. 8). The peak at ca. 18 ppm is in the chemical shift range of phenol derivatives (ca. 16–21 ppm) [2,29,62], while the peak at 7.3 ppm is likely trimethylsilanol or hexamethyldisiloxane. A sequence of reference ^{29}Si NMR spectra (Fig. 8) were recorded to assist in the assignment of chemical shifts: (i) HMDSN in deuteriochloroform; (ii) trimethylchlorosilane was added; (iii) tetramethylsilane was next added as an internal standard set to 0 ppm; and (iv) finally trimethylsilylated AOSA was included in the mixture. Residual HMDSN produced a

Fig. 8. Silicon-29 NMR spectra (relative to tetramethylsilane at 0 ppm) of deuteriochloroform solutions of: HMDSN; HMDSN plus trimethylchlorosilane; and trimethylsilylated AOSA (AOSA-TMS) (* indicates a peak which can be assigned to trimethylsilanol and/or hexamethyldisiloxane). The chemical shift ranges of trimethylsilyl (TMS) derivatives are shown.

signal at ca. 2.5 ppm and trimethylchlorosilane appeared at ca. 30.7 ppm. This experiment shows the absence of TMS alkyl ethers at <14 ppm [2,29] and supports the conclusion from carbon-13 NMR that alcohols are very minor components of AOSA. Primary and secondary amines typically resonate at higher fields (<12 ppm) [2], and thus are unreacted or negligible components of Athabasca asphaltene.

3.5. Average molecular structure of asphaltene

Athabasca asphaltene has a broad asymmetric distribution of MWs in the range ca. 10^2 – 2×10^4 amu [5,12,19]. Further complications arise from geochemical variances, which can alter the MWs of samples from different locations in oil or tar sands deposits. Typical number average values are in the range 1800–3600 amu [5,17,20] with 2648 amu [20] being cited for a sample similar to the one used in this study. Semi-quantitative analyses based on an average MW in the range 2648–2750 amu offer an upper limit of 5–8 oxygen atoms in hydroxyls and carboxyls (e.g. 4 OH and 2 COOH) from elemental analyses, whereas estimates of the number of introduced $^{13}\text{CH}_3$ from NMR integral ratios of methoxy to aromatic carbons, favor lower numbers of ca. 1–2 groups per average molecule. In the determination of an average molecular structure of Athabasca asphaltene, one route is to consider the ratios of the different atoms. For

example, H:C is 1.2 or 12 hydrogen atoms per 10 carbon atoms, thus the asphaltene molecules are highly unsaturated, as revealed by the aromaticity factor of 0.48–0.52 from carbon-13 NMR spectra (Table 2). Furthermore, the shape of the aromatic resonance at 115–155 ppm has higher intensity at 128 and 139 ppm attributable to carbons at the junction of two rings and alkyl-substituted (except methyl) aromatic rings, respectively. The average molecular structure is thus a highly fused polyaromatic molecule. Also, there are nearly equal numbers of oxygen and sulfur atoms in the ratio of one S or O per ca. 25 carbon atoms. These ratios allow for a first approximation molecular model of AOSA. In addition, there is ca. 1 heteroatom per 10 carbon atoms, so that dipolar interactions are likely to be important in determining the overall structure of asphaltene multimers. Based on a H:C atomic ratio of 12:10, a simple structure such as tetralin or phenylbutene provides units (MW = 132) for the model, i.e. ca. 20 per number average MW of 2648—therefore, an upper limit of ca. 20 benzene rings in AOSA. The smallest unit would contain $(\text{C}_{43.5}\text{H}_{52.75}\text{N}_{0.5}\text{S}_{1.75}\text{O}_{1.5})$, i.e. a tetramer of five condensed heteroatom substituted tetralin or phenylbutene structures. The alicyclic and butenyl moieties could be converted to other analogues to best fit the NMR data. One probable average molecule of AOSA is represented by structure I in Fig. 9. It includes data from the chemical derivatization/NMR experiments. The model yields the correct

Fig. 9. Hypothetical average molecular structures (I; MW $\cong$ 2767–2800 and II; MW $\cong$ 3746–3824 amu) of AOSA showing positions of carboxyl and hydroxyl groups (A unhindered and A' sterically hindered).

aromaticity factor, H:C and heteroatom:C ratios, and many of the observed carbon-13 NMR peaks. Note also that it has a ratio of 1.5 of sterically hindered to unhindered sites of OH substitution in compliance with the value of 1.6 ± 0.2 for PTM using TBAH (Table 1). In order to account for the variety of hydroxyl and carboxyl sites, there must be a polydispersity of MWs around ca. 2700 amu [17,20]. The tetramer of the unit of structure I has a MW of ca. 2767–2800 amu for empirical formulae $\text{C}_{184}\text{H}_{209-210}\text{N}_2\text{S}_{7-8}\text{O}_6$ with OH and COOH at different positions in different monomers and molecules to conform to the NMR model of a wide asymmetric distribution of these groups. Structure I has 32 places where OH, COOH, CH₃ and H can be interchanged. Overall in a single molecule there can be one unhindered hydroxyl at the A positions, one sterically hindered hydroxyl at the A' sites, one aliphatic carboxyl at A'', one aromatic carboxyl at A or A', seven methyls at the A''' sites, and 17 aromatic hydrogen atoms at the A and A' locations. On the fourth unit the sulfide can be replaced with a thiol group. Occasionally, an aliphatic or benzylic OH may appear in the structure, such as at sites A'' or A''', respectively, of some molecules, as evidenced from ^{19}F NMR spectra of trifluoroacetylated AOSA.

Refinement of the model includes proportionation of the different groups according to the observed values from PTM in THF (Table 1), i.e. $\phi'\text{OH}:(\phi\text{OH} + \text{XOH}):\phi\text{COOH}:\text{RCOOH} \approx 3:2:1:2$. Thus, there would be roughly twice as many aliphatic as aromatic carboxylic acids. Some of the A''(CH₂)₃ groups would be at the adjacent *para* position to

allow for about 6% of the O-methylated sites to be *meta* OH, i.e. resorcinols. Rarely, other functionalities, e.g. heteroatom groups and aromatic methyl are present at diverse sites including A, A' and A'''. A large number of configurational isomers of the average structure are also feasible. Isomerism of the polyaromatic and fused alicyclic structures would enhance the environmental dispersion of labile methine carbon atoms. These would intensify the broad underlying component of the aliphatic region as observed in some ^{13}C NMR spectra of phase transfer methylated AOSA, especially in toluene (Fig. 2). The model should also be compatible with structures, e.g. tertiary carbons, diaryl methylene and ether groups, which can generate additional hydroxyls and carboxyls upon low temperature oxidation [21].

Some indication of the variability of the model to MW increments is available from a structure of ca. 3800 amu, which is at the upper end of the commonly observed range of average values. The empirical formula then becomes $\text{C}_{248}\text{H}_{296}\text{N}_{3.04}\text{S}_{9.61}\text{O}_{11.2}$ and the ^{13}C NMR integral ratio of C(OCH₃) to C_{ar} once again yields the number of OH and COOH as 1–2 per average molecule. The resultant modifications lead to structure II in Fig. 9 wherein the number of feasible OH/COOH substitution sites is increased by 20 per molecule relative to structure I, yet allows for a total of eight OH/COOH groups to be maintained in the aforementioned 3:2:1:2 ratio. The extra oxygen atoms can be incorporated in one hydroxyl and one carboxyl, or in 3 hydroxyls, although they could also be part of nonacidic functionalities. In order

to account for 9–10 sulfur atoms, one or two SH group(s) can be substitutes at A, A' or A'''. If one of each type of acidic oxygen containing group, i.e. six oxygen atoms is present then the distribution can take the form 16A = OH, COOH, SH, 13H; 20A' = OH, SH, 18H; 12A'' = RCOOH, 11CH₃; 4A''' = 4H; and 4X = 3N, CH; with MW = 3746 amu for C₂₅₀H₂₈₅N₃S₁₀O₆. Alternatively, if all eight of the oxygen atoms are hydroxylic and carboxylic, then 16A = 2OH, COOH, SH, 12H; 20A' = 3OH, SH, 16H; 12A'' = 2RCOOH, 10CH₃; and 4A''' = 4H; 4X = 3N, CH; with MW = 3824 amu for C₂₅₀H₂₈₃N₃S₁₀O₁₁. Though a large number of positional permutations of acidic oxygenic functionalities exist, their quantification from combined elemental, and ¹³C, ¹⁹F and ²⁹Si NMR analyses reveals probable dipolar arrays. Evaluation of the resultant net molecular electric dipole moments is useful in understanding physico-chemical interactions in situ, during processing, and in the products of oil sand refining.

4. Conclusions

Nuclear magnetic resonance spectroscopy of chemically derivatized AOSA has allowed for the analysis of acidic oxygen containing functional groups (OH and COOH) to be included in an average molecular structure. Utilization of calculated lineshapes and integrals is a valuable method for the partial resolution of overlapping methoxy ¹³C NMR peaks in the determination of the relative proportions and degree of methylation of acidic sites. PTM, especially of alkylcarboxyls, varies with the catalyst/solvent combination and the dielectric constant of the dispersing medium. Unless carefully controlled the PTM reaction can synthesize by-products, which interfere with methoxy resonances and their interpretation. PTM and trifluoroacetylation reactions along with ¹³C and ¹⁹F NMR spectra, reveal a broad asymmetric distribution of hydroxyl and carboxyl sites, with alcohols as negligible though possible components from hydrolysis side-reactions. Phenols were also detected from silicon-29 NMR spectra of trimethylsilylated AOSA. There are ≤8 oxygen atoms in OH and COOH groups per average asphaltene molecule.

Asphaltene extracted from Athabasca oil sand bitumen contains a considerable amount of sludge material which is lower in carbon content than whole AOSA. This organically bound mineral fraction has hydrophilic characteristics. Emulsification of asphaltene via interactions with aqueous media is dependent on the donor-acceptor capabilities of the organic phase and hence its acidity. Quantification of the hydroxyl and carboxyl content is thus relevant to extraction and environmental problems concerning mineral bound asphaltene in oil sand tailings ponds.

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