energy&fuels Article
pubs.acs.org/EF

Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Characterization of Tunable Carbohydrate-Based Materials for Sorption of Oil Sands Naphthenic Acids

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ABSTRACT: Synthetically engineered copolymers are receiving growing attention for sorption and possible degradation of components in oil sands processed water (OSPW). β-Cyclodextrin (β-CD) copolymers, for example, have been shown in recent studies of electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to adsorb oil sands naphthenic acid fraction components (NAFCs). Herein, we report complementary results for atmospheric pressure photoionization (APPI) for characterization of NAFCs in OSPW samples following sorption with cyclodextrin-based copolymers. The materials investigated were β-CD-cross-linked with three different types of diisocyanates, namely, (i) 4,4′-dicyclohexylmethane diisocyanate, (ii) 4,4′-diphenylmethane diisocyanate, and (iii) 1,4-phenylene diisocyanate. The APPI studies revealed variable sorption for a complementary range of NAFCs with compound classes not detected by ESI. For example, sorption was observed for new classes of NAFCs: HC, N_1O_1, N_1O_2, N_1O_3, N_1O_4, N_1O_5, N_2O_1, N_2O_2, and N_2O_3, from OSPW in accordance with the nature of the cross-linker unit of the copolymer and the structure of the NAFCs. Sorption of NAFCs in general was more pronounced for β-CD copolymers cross-linked with 4,4′-dicyclohexylmethane diisocyanate, particularly for the O_2 class that was amenable to negative-ion APPI detection. In contrast to the 75% attenuation of O_2 species observed for sorption to the copolymer cross-linked with 4,4′-dicyclohexylmethane diisocyanate, little or no sorption was observed for the O_2 series with positive-ion APPI. The O_2 series is presumably mixtures of classical naphthenic acids and dihydroxy components with a range of different structures. The complementary nature of the APPI and the prior ESI results contribute further to the quality and understanding of the sorption mechanism of the copolymers.

■ INTRODUCTION

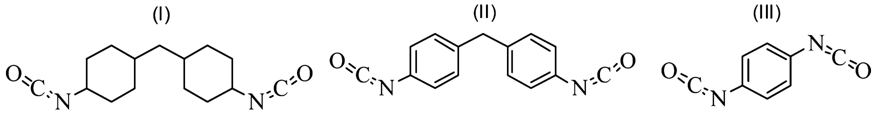
The bitumen in the Athabsca oil sands reserves of northern Alberta, Canada, is the third largest in the world, with 173 billion barrels deemed to be cost-effectively recoverable.[1] Surface mineable bitumen is extracted from the oil sands mixture by means of a modification of the Clark caustic hot water method.[2] The extraction process is water-intensive, and although much of the process water is recycled, there is a net consumption of 2−3 barrels of water per barrel of oil produced.[3] The oil sands industry operates under a zero discharge policy, and thus, the oil sands processed water (OSPW) is retained on site in vast tailing ponds and settling basins.[2,4]

There is growing attention and monitoring of oil sands mining activities in the Fort McMurray region of Alberta, Canada. For example, a new federal−provincial initiative was recently launched to monitor possible impacts on water quality as well as possible effects on the health of aquatic biota.[5−7] Among the components of concern are the oil sands acids [or naphthenic acids (NAs)][8−14] because of their aquatic toxicity, mobility, and fate in aquatic environments.[9,15,16] The oil sands acids in the OSPW are complex mixtures, and to date, the primary toxic molecular species are yet to be identified. The term naphthenic acid fraction component (NAFC) or acid-extractable fraction is thus used to reflect the complexity of the oil sands acids. Historically, NAs are defined as carboxylic acids including one or more saturated rings. However, the definition appears to be broadening in the recent literature to include the range of NAFCs found in the acid-extractable fraction of OSPW.[11−13,17] The NAFCs consist of the classical naphthenic acids, along with other components with aromatic functional groups and nitrogen and sulfur atoms, in conjunction with unsaturated groups.[13,17−23] The application of ultrahigh-

Special Issue: 14th International Conference on Petroleum Phase Behavior and Fouling

Received: August 16, 2013
Revised: October 29, 2013
Published: October 30, 2013

Scheme 1. Molecular Structure of the Diisocyanate Cross-Linker Units (Scaffolds) with Variable Molecular Size for the Design of Copolymer Sorbent Materials: (I) 4,4′-Dicyclohexylmethane Diisocyanate, (II) 4,4′-Diphenylmethane Diisocyanate, and (III) 1,4-Phenylene Diisocyanate (Adapted from Headley et al.[34])



resolution mass spectrometry (400 000 mass resolving power at m/z 250) has played an integral role in the characterization of OSPW and has changed the way in which NAFCs are now studied in environmental samples. For example, it is well-established that methods based on low-resolution mass spectrometry may not resolve high background interferences and can lead to misidentification of NAFCs.[11−13,24,25]

As part of ongoing research and development of technologies for improved tailings management, there is growing attention to explore the potential for sorption and possible degradation of NAFCs in the OSPW using synthetically engineered copolymers. Recent research has highlighted the use of a suite of β-cyclodextrin (β-CD) copolymers for sorption of total oil sands NAs.[26−28] β-CD is particularly well-suited for incorporation within copolymer sorbents and offers the potential for controlled tuning of the textural mesoporosity and sorption properties.[29,30] Furthermore, such copolymers containing cyclodextrins (CDs) are known to form stable inclusion complexes with guest molecules, such as carboxylic acids in the presence of water.[29,31,31] The inclusion properties of β-CD copolymers are known to be a function of the surface area, pore structure, and site accessibility of inclusion sites within the copolymer framework.[30,32]

The tuning of the textural properties and inclusion site accessibility is facilitated by the ability to engineer the structure of the CD-based copolymers. We use this property of β-CD-based copolymers in the present study by cross-linking with three types of diisocyanate agents, as outlined in Scheme 1. The strategy builds on the work of Mohamed et al.,[25,27] in which the copolymer sorption involves molecular recognition through the formation of well-defined host−guest inclusion complexes.[33,34]

The difference in the composition of OSPW and sorption-processed OSPW may be masked by interferences.[12,21,22] However, many of the interferences can be resolved by ultrahigh-resolution mass spectrometry. For example, in a recent study employing electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), β-CD copolymers were shown to adsorb a wide range of NAFCs. Herein, we report complementary results for atmospheric pressure photoionization (APPI) characterization of NAFCs in OSPW samples, following sorption with a range of similar cyclodextrin-based copolymers. Protonated species and radical cations are typically observed when APPI is used as the ionization method. The use of APPI ultrahigh-resolution FT-ICR MS to characterize the sorption properties of the engineered polymers is expected to reveal new classes of components sorbed or released by the copolymers that were not revealed in prior work. Thus, it is anticipated that the new studies will increase our understanding of the molecular recognition properties of compound classes. Specifically, we demonstrate new insights gained for the molecular recognition of new classes of NAFCs in accordance with the nature of the cross-linker unit. The high-resolution APPI-MS measurements are also shown to improve the understanding of the sorption mechanism of such materials with respect to the different structures of the O_2 heteroatom series from NAFCs.

■ EXPERIMENTAL SECTION

Synthesis. The β-CD-based copolymers were synthesized according to a previously reported procedure[29] using three types of diisocyanates shown in Scheme 1. β-CD was cross-linked with a given diisocyanate at a 1:1 mol ratio to form copolymers C1, M1, and P1 using 4,4′-dicyclohexylmethane diisocyanate, 4,4′-diphenylmethane diisocyanate, and 1,4-phenylene diisocyanate, respectively.

Sorption. The sorption properties of the copolymers were studied using APPI spectra obtained for the (i) absence of engineered polymers in oil-sands-extracted NAFCs spiked in deionized water and (ii) sorption to the engineered polymers of oil sands NAFCs extracted from OSPW. The oil sands NAFC investigated here was a dichloromethane extract from OSPW at pH 2. The sorption in part ii is affected by other co-contaminants, such as metal ions and non-oil sands acids, and the salinity of the OSPW. Centrifugation of batches of 5 L OSPW was used to remove suspended particles. A total of 100 mg of the respective copolymers was mixed with 1 L of OSPW. The resulting mixture was stirred for 3 days to establish equilibrium conditions. After sorption, the mixture was centrifuged once more to give a clear solution. A previously reported procedure[26] was used for characterization of four samples: (i) OSPW prior to sorption, (ii) OSPW following sorption to C1, (iii) OSPW following sorption to M1, and (iv) OSPW following sorption to P1.

Ultrahigh-Resolution APPI FT-ICR MS. Upon completion of the sorption experiments, acetonitrile/methanol extracts of the water were studied by positive- and negative-ion APPI FT-ICR MS. An APPI source (Thermo Fisher Scientific, Waltham, MA) was connected to a custom-built 9.4 T FT-ICR mass spectrometer[35] equipped with a Predator data station.[36] The analyte was vaporized orthogonally to the heated metal capillary inlet and the krypton ultraviolet (UV) lamp (λ = 124 nm). The nebulizing unit was heated to 325−350 °C with nitrogen as the sheath gas at 500 kPa. The auxiliary gas port was plugged. Sample solutions in toluene/methanol (1:1) were introduced to the ion source at a rate of 50 μL min^{-1}, via a syringe pump.

An external linear octopole ion trap[37,38] was used to accumulate ions for 0.1−5 s. Ions were transferred by radio frequency (rf)-only octopoles to a seven-section open cylindrical analyzer cell.[39] Octopoles were operated at 2.0 MHz and 220 V_{p-p} rf amplitude. The dipolar excitation broadband frequency sweep (chirp) was 72−710 kHz at 50 Hz/μs sweep rate and 190 V_{p-p} amplitude. Direct-mode detection of the image current was used to yield eight Mword time-domain data sets. The time domain data sets were processed and frequency-converted to mass-to-charge ratio (m/z) as previously described.[40,41]

Sample extracts were diluted as required to limit the formation of dimers. A high-abundance homologous alkylation series was used for internal calibration of FT-ICR mass spectra as previously reported.[21,22] As per the ESI FT-ICR studies of the copolymers,[34] further data reduction was conducted as follows: The m/z values (for singly charged ions) of 145−900 Da with relative abundance greater than 6 times the standard deviation of the baseline noise were exported to a spreadsheet. Measured masses were converted from the International Union of Pure and Applied Chemistry (IUPAC) mass scale to the Kendrick mass scale and sorted according to Kendrick mass defect (KMD) values to facilitate identification of the homologous alkylation series. Peak assignments were performed by KMD analysis.[42] In summary, molecular formulas were assigned to peaks of lowest m/z value for each KMD series. Peaks of higher m/z ratio for the same

KMD value were assigned by adding multiples of CH_2 to the molecular formula. Calculations were limited to formulas containing at most 100 ^{12}C, 2 ^{13}C, 200 ^{1}H, 5 ^{14}N, 10 ^{16}O, 3 ^{32}S, and 1 ^{34}S. If more than one possible formula was generated for a specific mass, one or more could almost always be confirmed or eliminated by the presence/absence of a corresponding ion containing ^{13}C, ^{18}O, or ^{34}S.

■ RESULTS AND DISCUSSION

Selective sorption was anticipated to be revealed for a new series of NAFCs that are amenable to detection by APPI in the current investigation compared to those observed by ESI in prior work. Selective sorption was expected on the basis of differences in the inclusion site accessibility and structure of the copolymer materials.[26,32,33,30] Likewise, the application of different modes of ionization (negative- versus positive-ion APPI) was also anticipated to reveal differences in sorption for NAFCs in the same series but with different structures.

In the following discussion both the protonated species and the radical cations are illustrated in the respective figures. As illustrated in Figures 1 and 2, wide ranges of compound classes were observed in both the negative- and positive-ion APPI FT-ICR mass spectra. The data are considered semi-quantitative because the components have unknown response factors and are subject to matrix effects and ion suppression. The APPI studies revealed variable sorption for a complementary range of NAFCs exhibiting compound classes not detected by ESI.[10,22,34,43] For example, sorption was observed for new NAFC classes: HC, N_1O_1, N_1O_2, N_1O_3, N_1O_4, N_1O_5, N_2O_1, N_2O_2, and N_2O_3, from OSPW in accordance with the nature of the cross-linker unit. The range of species observed is similar to those reported by Barrow et al., for APPI studies of non-treated OSPW.[10]

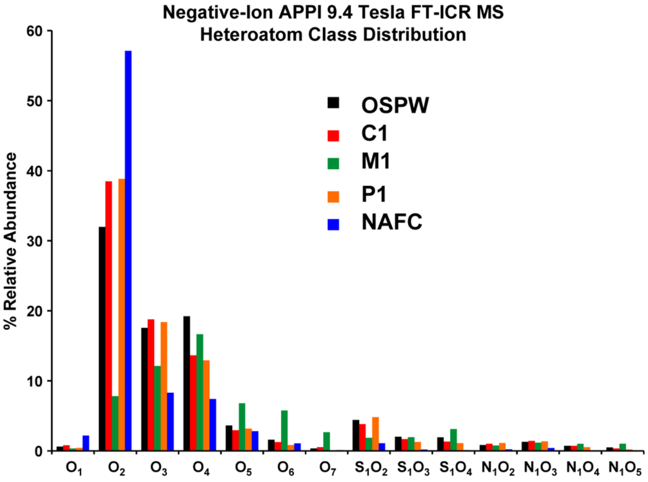


Figure 1. Negative-ion APPI 9.4 T FT-ICR MS heteroatom class distribution for untreated OSPW, along with OSPW treated with engineered polymers C1, M1, and P1, and untreated NAFCs. The relative standard deviation based on triplicate runs of the same sample was less than 10% of the measured values.

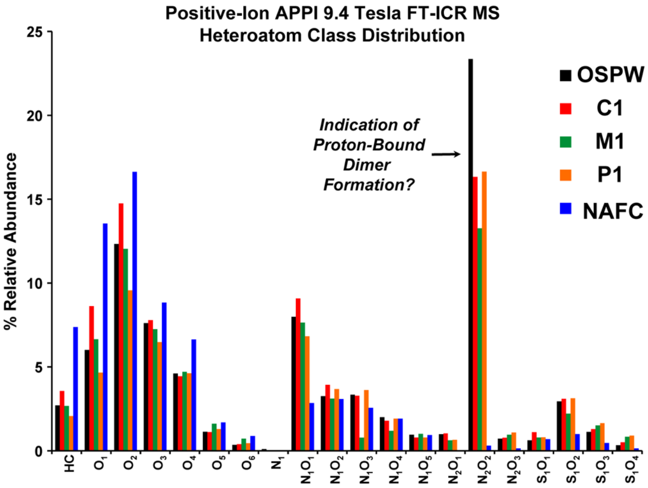


Figure 2. Positive-ion APPI 9.4 T FT-ICR MS heteroatom class distribution for untreated OSPW, along with OSPW treated with engineered polymers C1, M1, and P1, and untreated NAFCs. The relative standard deviation based on triplicate runs of the same sample was less than 10% of the measured values.

In prior negative-ion ESI characterization of the sorption of NAFCs to engineered polymers,[34] the distribution of compound classes was generally the same whether or not the OSPW was treated with polymers. An exception was reported for M1, for which a 50% reduction was observed for members of the O_2 compound class. The latter were presumed to be classical NAs and possibly dihydroxy polar compounds with similar molecular formula. The sorption of the NAFCs from OSPW (that are amenable to detection by APPI but not by negative-ion ESI FT-ICR MS) is shown below to be selective for all of the engineered copolymers investigated, depending upon the component class of interest and whether or not the detection is by negative or positive ions.

A similar trend was observed in the current APPI studies, with M1 also showing the most evidence of selective sorption among compound classes. However, as illustrated in Figure 1, APPI reveals a more pronounced reduction in the O_2 species than for the negative-ion characterization of OSPW treated with the M1 polymer (32% reduced compared to 8%). The level of O_2 species in the corresponding NAFC extract was 57% under negative-ion APPI. These differences in relative-ion abundances may reflect (i) differences in the ionization efficiency for negative-ion ESI and APPI, along with (ii) possible differences in ionization efficiencies for the classical NA species versus the dihydroxy components. The level of molecular recognition for the engineered polymer M1 is thus pronounced for the O_2 class of compounds ionized by negative-ion ESI or negative-ion APPI. The molecular recognition for the O_2 species observed with positive-ion APPI, as illustrated in Figure 2, is not pronounced, exhibiting similar relative ion abundance as for the untreated OSPW of ~13%. Thus, the O_2 class ions likely differ in structure depending upon the mode of APPI ionization, consistent with Pereira et al.'s similar negative- and positive-ion ESI characterization of OSPW.[44] The O_2 classes of structures therefore appear to include carboxylic acids and dihydroxy components, such as, for example, estradiol and isomers. The use of authentic standards along with MS/MS studies of such components would aide in the confirmation of these structures.

The positive-ion APPI FT-ICR MS data (see Figure 2) reveal the sorption of many new compound classes not observed in earlier work: HC, N_1O_1, N_1O_2, N_1O_3, N_1O_4, N_1O_5, N_2O_1, N_2O_2, and N_2O_3. The N_2O_2 class could be a proton-bound dimer of N_1O_1, although attempts were made to minimize dimer formation by running the samples at low concentration. The levels of the N_2O_2 class in the NAFC are relatively low compared to the OSPW and treated OSPW, providing further indication that those components are likely proton-bound dimers. There is also evidence for desorption of O_5, O_6, O_7, and S_1O_4 species for the M1 polymer, as seen in Figure 1. Those component classes are relatively minor components in the OSPW and the NAFC extract and, thus, likely originate from the polymer material. Further studies are thus warranted to determine whether or not the desorption of the compound classes affects the toxicity of the treated OSPW.

As observed in the ESI studies and confirmed here, the components in the O_2 class form two distinct families with double bond equivalents (DBE = number of rings plus double bonds involving carbon) ≈ 4 (i.e., non-aromatic components or possibly an aromatic six-membered ring with two hydroxyl substiuents) and DBE ≈ 8 (possibly aromatic components), with a carbon number range of 10−20. As illustrated in Figures 3 and 4, however, APPI characterization complements the prior ESI findings. For example, there is a marked difference in isoabundance-contoured DBE versus carbon number plots for the O_2 class ions from the NAFC sample compared to all other samples (non-treated OSPW and OSPW treated with engineered polymers C1, M1, and P1). There is evidence of possible enrichment of the higher DBE components relative to the lower DBE components for the NAFCs relative to the other samples. As shown in Figure 4, this enrichment is more evident in the positive-ion APPI data, in which the carbon number range narrows to 12−15. The NAFC sample was extracted from OSPW with dichloromethane. The observed differences in the isoabundance-contoured DBE versus carbon number plots are thus attributed to solvent effects.[45] Likewise, solvent effects were evident for the positive-ion APPI of the N_1O_1 species (data not shown for brevity). The magnitude of the solvent effect relative to sorption of the respective compound classes to the engineered polymers was not anticipated and highlights the importance of an appropriate calibration standard for characterization of the OSPW. Standards obtained by solvent extraction will not be identical to the mixture of NAFCs in the original OSPW. The environmental relevance of solvent effects in monitoring of NAFCs is discussed further in a recent study employing negative-ion ESI Orbitrap FTMS,[45] with reference to an earlier investigation employing negative-ion ESI FT-ICR MS.[24]

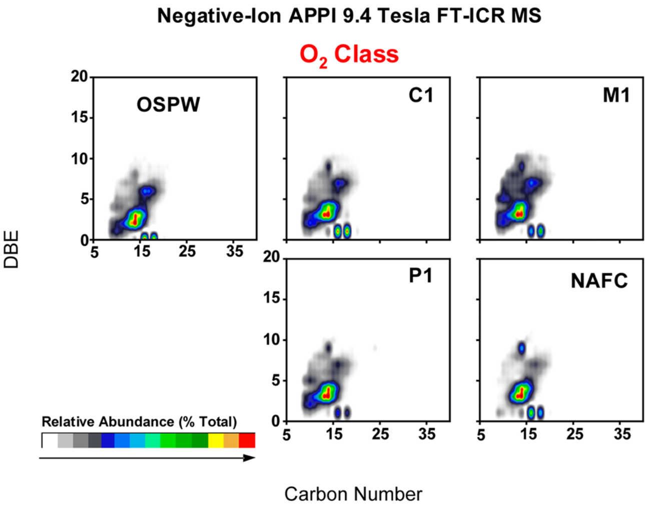


Figure 3. Negative-ion APPI 9.4 T FT-ICR MS isoabundance-contoured DBE versus carbon number plots for the O_2 class ions from non-treated OSPW and OSPW treated with engineered polymers C1, M1, and P1. For comparison, the corresponding plot is given for NAFCs extracted from OSPW using dichloromethane.

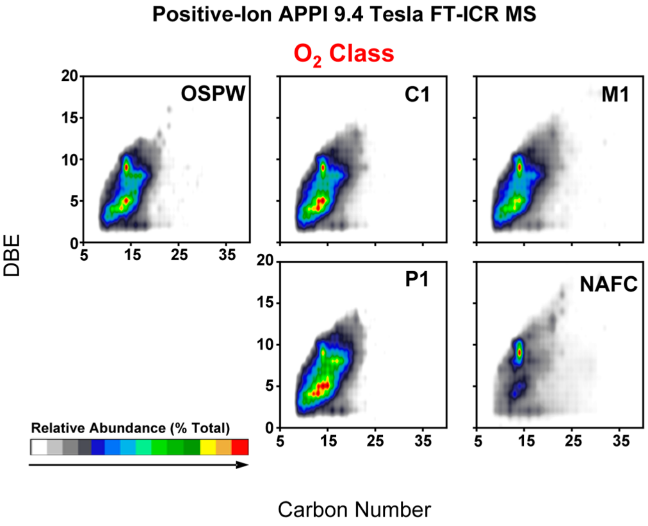


Figure 4. Positive-ion APPI 9.4 T FT-ICR MS isoabundance-contoured DBE versus carbon number plots for the O_2 class ions from non-treated OSPW and OSPW treated with engineered polymers C1, M1, and P1. For comparison, the corresponding plot is given for NAFCs extracted from OSPW using dichloromethane.

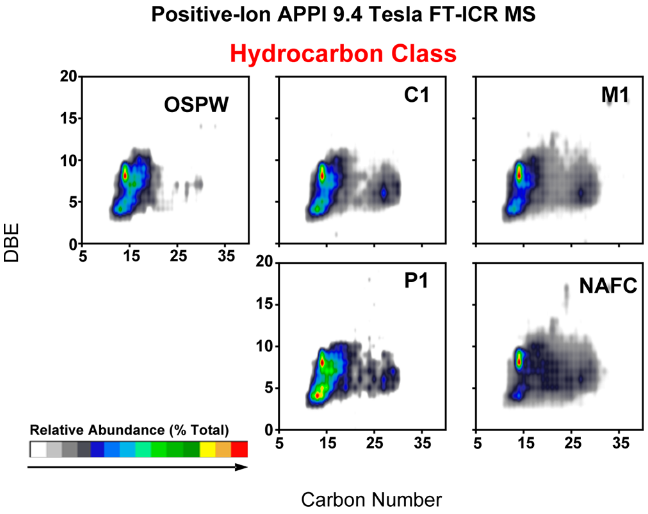


Figure 5. Positive-ion APPI 9.4 T FT-ICR MS isoabundance-contoured DBE versus carbon number plots for the HC class ions from non-treated OSPW and OSPW treated with engineered polymers C1, M1, and P1. For comparison, the corresponding plot is given for NAFCs extracted from OSPW using dichloromethane.

Figure 5 reveals evidence of possible enrichment of the HC classes, with lower DBE values of ∼4 versus 8 for the P1 copolymer. These observations are entirely novel because the HC series was not observed in prior sorption studies with the copolymers, and thus, selected sorption of specific HC species could not be measured. The molecular recognition observed for the compound classes is attributed to the formation of stable host−guest inclusion complexes. The stability of the complexes is a function of (i) the chemical structure of the NAFC, (ii) its relative concentration, (iii) the number of carbons, (iv) the type of the compound class, and (iv) the cross-linking nature of the copolymer.[34] These parameters are known to strongly influence the relative hydrophile−lipophile properties of the guest molecule and, thus, control the stability of the complex.[26,32] The selectivity of the polymers to adsorb specific compound classes of NAFCs, such as the new classes revealed by the present APPI characterization, is important in studies of the fate and transport of oil sands components in aquatic environments.

Sorption Mechanism of Copolymer Materials. As illustrated in Figure 1, the greatest attenuation is observed for M1 with the O_2 and O_3 series of NAFCs that are amenable to detection by negative-ion APPI. This result agrees with the trends observed for negative-ion ESI characterization of the copolymers.[34] The latter was rationalized in terms of the rigid framework of this copolymer, the relatively high accessibility to inclusion sites, and the apolar framework. There appears to be a good size-fit compatibility with the negative ions in the O_2 series. This compatibility, in turn, results in the M1 polymer displaying the greatest uptake of the O_2 component class. As mentioned above, the opposite is true for the O_2 series accessed by positive-ion APPI. The size-fit matching between the host framework and this fraction of NAs is poor for the corresponding structures with molecular weights comparable to those observed by negative-ion APPI. As shown in Figures 1 and 2, certain compound class series have a higher relative abundances in the presence of copolymers than for OSPW. For example, the O_2 series observed by negative-ion APPI is greater for C1 and P1 than for the original OSPW. Likewise, the HC, O_1, and O_2 series observed by positive-ion APPI are more abundant for OSPW treated with the C1 polymer than the non-treated OSPW. These differences may be due in part to components leached from the polymers, along with possible matrix suppression and ion enhancement of some components in the presence of the copolymers. Notwithstanding these uncertainties, the ~75% attenuation for the O_2 compound class for the M1 polymer observed by negative-ion APPI, along with the earlier reported 50% attenuation observed for negative-ion ESI studies,[34] appears to be real and well outside the 10% relative standard deviation experimental precision of the measurements.

■ CONCLUSION

The application of ultrahigh-resolution APPI FT-ICR MS revealed molecular recognition of sorption of new NAFC compound classes by copolymers, which were not evident in earlier work. Variable sorption of the new NAFCs was observed according to the nature of the cross-linker unit of the copolymer. Furthermore, the sorption was linked closely to the structure of the NAFCs, as evident from differences observed for the O_2 series of components. For the M1 copolymer, there was a 75% attenuation compared to relatively 0% attenuation for the O_2 series based on negative- and positive-ion APPI. This difference in sorption observed is attributed to inclusion accessibility of the β-CD site in the copolymer framework based on the structure of the O_2 series components. The observation of molecular selectivity of sorption of the new NAFCs in copolymer materials containing β-CD represents an important contribution toward the development of sorbent materials for removal of oil sands acids in aquatic environments.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for financial support of this research, along with the Program of Energy and Research Development (PERD), National Science Foundation (NSF) Division of Materials Research through DMR-11-57490, the Florida State University Future Fuels Institute, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, and the State of Florida. Amy McKenna is thanked for valuable contributions in the preparation of a report of the processed FT-ICR MS data. Mohamed H. Mohamed acknowledges the NSERC for the award of a Visiting Fellowship in a Canadian Government Laboratory.

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