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Electrospray Ionization 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: The potential for sorption and possible degradation of components in oil sands processed water (OSPW) by the use of synthetically engineered co-polymers is receiving growing attention. Recent research has highlighted the sorption of total oil sands naphthenic acid fraction components (NAFCs) by β-cyclodextrin (β-CD) co-polymers. The incorporation of β-CD within co-polymer frameworks represents a novel modular approach with significant potential for controlled tuning of the textural mesoporosity of the sorbents. Herein, we report the Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) characterization of aqueous samples containing oil sands NAFCs following sorption with a range of cyclodextrin-based co-polymers. 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. Variable sorption of NAFCs was observed according to the cross-linking density of the co-polymer framework and the nature of the cross-linker unit. Furthermore, the sorption of the NAFCs by the co-polymers was not affected by other parameters, such as metal ions, salinity, and non-oil sands acid fractions present in OSPW. The observation of molecular selective sorption in co-polymer materials containing β-CD represents an important contribution toward the development of sorbent materials for the controlled removal of oil sands acids in aquatic environments. The FT-ICR MS measurements also contribute further to the understanding of the thermodynamic sorption mechanism of such materials.

■ INTRODUCTION

The Canadian oil sands bitumen reserves in northern Alberta are projected to be 1.7 trillion barrels, with 173 billion barrels deemed to be cost-effectively recoverable.[1] A modification of the Clark caustic hot water method is used to extract surface mineable bitumen from the oil sands mixture.[2] The extraction process requires significant water consumption, i.e., ~3 barrels of water per 1 barrel of oil produced.[3] Because the Canadian government has enforced the oil sands industry to operate under a zero discharge policy, the oil sands processed water (OSPW) is preserved on-site in tailing ponds and settling basins that, as of March 2009, totaled around 130 km[2].[4]

The increased oil sands mining activities in the Fort McMurray region of Alberta, Canada, have seen a scrutiny of growing concern on the impact of water quality, as well as effects on the health of aquatic biota.[5,6] The oil sands acids [commonly referred to as naphthenic acids (NAs)][7−12] are of great concern because of their aquatic toxicity, mobility, and fate in aquatic environments.[8,13−15] The primary toxic molecular species are yet to be identified for the naphthenic acid fraction components (NAFCs) of OSPW, mainly owing to their complexity. Similarly, there is a knowledge gap regarding the interactions of the complex mixture of oil sands acids with

materials for remediation of aquatic environments via a sorption-based approach.

Although NAs are defined as carboxylic acids, which include one or more saturated ring structures, the definition appears to be broadening in the recent literature to include the range of organic acids found in the acid-extractable fraction of OSPW.[9,10,12,16] Generally, NAFCs consist of oil sands acid-extractable organics with aromatic functional groups and nitrogen and sulfur atoms, in conjunction with unsaturated groups.[12,16−19] Most of the components of oil sands acids contained in OSPW are resolved only by ultrahigh-resolution mass spectrometry.[20−22] The ultrahigh resolution (400 000 resolving power at m/z 250) for the characterization of OSPW in the presence of high background interferences, in comparison to low-resolution mass spectrometry (unit mass resolution), offers advantages that are well-described in the literature.[9,10,12,23,24] For example, low-resolution mass spec-

Scheme 1. Molecular Structure of the Diisocyanate Cross-linker Monomers (Scaffolds) with Variable Molecular Size for the Design of Co-polymer Sorbent Materials: (I) 1,6-Hexamethylene Diisocyanate (HDI), (II) 4,4′-Dicyclohexylmethane Diisocyanate (CDI), (III) 4,4′-Diphenylmethane Diisocyanate (MDI), and (IV) 1,4-Phenylene Diisocyanate (PDI)
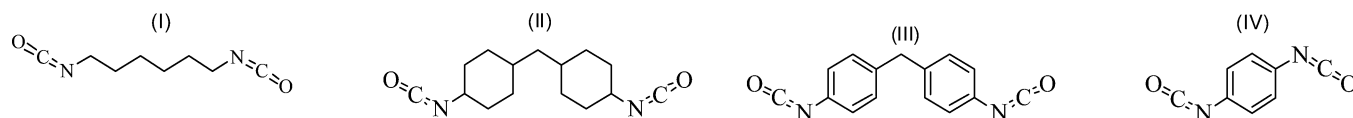
trometry of OSPW can result in erroneous identification of components as classical NAs. Furthermore, matrix interference can also lead to false negatives in environmental samples.

The potential for sorption and possible degradation of components in the OSPW by the use of synthetically engineered co-polymers is receiving growing attention as part of improved tailings management. For example, recent research has highlighted the sorption of total oil sands NAs by the use of a suite of β-cyclodextrin (β-CD) co-polymers.[25,26] The incorporation of β-CD within co-polymer sorbents represents a novel modular approach with significant potential for controlled tuning of the textural mesoporosity and sorption properties.[27,28] β-CD co-polymers represent an innovative series of materials for the development of "smart" or "functional" porous sorbents with improved solid-phase extraction (SPE) and molecular recognition properties because of their unique host–guest properties.[29−31] Carbohydrate-based co-polymers containing cyclodextrins (CDs) are of interest, in part, because of their ability to form stable inclusion complexes in aqueous solution.[30] The inclusion properties of β-CD co-polymers are largely determined by the surface area, pore structure, and site accessibility of inclusion sites within the co-polymer framework.

The ability to engineer the structure of the CD-based co-polymers facilitates the tuning of the textural properties and inclusion site accessibility because the latter is critical when the co-polymer sorption involves molecular recognition through the formation of well-defined host–guest inclusion complexes.[32] We use this property of β-CD-based co-polymers in the present study to systematically vary the sorbent structure by a judicious choice of cross-linking agent, according to the type of co-monomer units outlined in Scheme 1.

OSPW contains thousands of oil sands acids, many of which are resolved only by ultrahigh-resolution mass spectrometry. The differences in the composition of OSPW because of sorption with engineered polymer materials may be masked by interferences;[10,20,21] therefore, we report here the Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) characterization of aqueous samples containing oil sands NAFCs following sorption with a range of CD-containing co-polymers. The work builds on earlier low-resolution mass spectrometry studies of the sorption properties of urethane co-polymer materials reported by Mohamed et al.[25−27,32−34] and Wilson et al.[28] The use of ultrahigh resolution for the characterization of the sorption properties of the engineered polymers with FT-ICR MS is expected to increase our understanding of the molecular recognition properties of compound classes. This instrumentation capability was not possible in earlier low-resolution mass spectrometry investigations. Specifically, we demonstrate new insights gained for the molecular recognition of NAs, along with sulfur and nitrogen heteroatomic compound classes in aqueous solutions, that contribute to the development of novel co-polymers as SPE materials. The high-resolution electrospray ionization–

mass spectrometry (ESI−MS) measurements are also shown to improve the understanding of the thermodynamic sorption mechanism of such materials.

■ EXPERIMENTAL SECTION

Synthesis. The β-CD-based co-polymers were synthesized according to a previously reported procedure.[27] The nomenclature of the co-polymers is described in accordance with the type of diisocyanate (*cf.* Scheme 1) and the relative co-monomer mole ratio (β-CD/diisocyanate linker). For example, the 1:3 β-CD/HDI co-polymer designation is referred to as HX (X = 3), in which the molar quantity of β-CD in this designation is taken to be unity relative to 3 mol of HDI. CX, MX, and PX denote CDI, MDI, and PDI, respectively.

Sorption. The differences in the sorption properties of the co-polymers were investigated for two sets of conditions: (i) sorption to the engineered polymers of oil sands extracted NAs spiked in deionized water and (ii) sorption to the engineered polymers of oil sands extracted NAs from actual OSPW. The sorption properties of in condition ii is expected to be affected by other parameters, such as metal ions, salinity, and non-oil sands acids present in actual OSPW. A volume of 5 L of OSPW was centrifuged in batches to remove suspended particles. A total of 1 L of OSPW was mixed with 100 mg of the respective co-polymers and then stirred for 3 days to ensure that equilibrium was achieved. The mixture was centrifuged again after sorption to leave a clear supernatant solution. Specifically, characterization was performed for four samples: (i) OSPW before sorption, (ii) OSPW after sorption with C1, (iii) OSPW after sorption with M1, and (iv) OSPW after sorption with P1. For the sorption of NAFCs only to the engineered polymers, oil sands NAFCs at concentrations ranging between 10 and 100 ppm were spiked in deionized water and the following mixtures of co-polymers were investigated: (v) three samples of H1, H2, and H3, (vi) three samples of C1, C2, and C3, (vii) three samples of M1, M2, and M3, (viii) three samples of P1, P2, and P3, and (ix) NAs of known concentration without the co-polymers. The adopted sorption protocol was according to a previously reported procedure.[25]

ESI−MS. Following the sorption of the OSPW or NAFCs to the engineered co-polymers, the water extracts in acetonitrile/methanol solvents were characterized by negative-ion ESI−MS according to a previously reported procedure.[25]

Ultrahigh-Resolution FT-ICR MS. Samples were analyzed with a custom-built FT-ICR mass spectrometer equipped with a 9.4 T horizontal 220 mm bore diameter superconducting solenoid magnet.[35] A total of 10 μL of NH$_4$OH (2% in methanol) was added to each 1 mL of sample solution to ensure efficient deprotonation for negative-ion electrospray analysis.[10,20,21]

Sample solutions were infused via a microelectrospray source[20,21] (50 μm inner diameter fused silica emitter) at 400 nL/min by a syringe pump. Typical conditions for negative-ion formation were as follows: emitter voltage, −2.0 kV; tube lens, −350 V; and heated metal capillary current, 4 A. Negative ions were accumulated in an external linear octopole ion trap[36] for 0.1−5 s and transferred by radio-frequency (rf)-only octopoles to a 10 cm diameter, 30 cm long open cylindrical Penning ion trap. Octopoles were operated at 2.0 MHz and 120 V$_{p−p}$ rf amplitude. Broadband frequency sweep (chirp) dipolar excitation (70−641 kHz at 50 Hz/μs sweep rate and 190 V$_{p−p}$ amplitude) was followed by direct-mode image current detection to yield 4 Mword time-domain data sets. Time-domain data sets were co-added (100 acquisitions), Hanning-apodized, and zero-filled once

before fast Fourier transformation and magnitude calculation. Frequency was converted to mass-to-charge ratio (m/z) by means of the quadrupolar electric trapping potential approximation[37,38] to generate mass spectra. A modular ICR data station (PREDATOR)[39] facilitated instrument control, data acquisition, and data analysis.

Experiments were also conducted to confirm that dimers, if formed, were dissociated to their monomers. Trapped ions were irradiated for 200 ms with a high-intensity Synrad (Mukilteo, WA) CW CO_2 laser (λ = 10.6 μm) operating at 40 W. To increase the efficiency of irradiation of an ion cloud in the ICR cell, the initial laser beam diameter (3.5 mm) was expanded to 9 mm by a Synrad beam expander (Mukilteo, WA). The concentrations of the analytes were diluted as necessary to avoid dimer formation. FT-ICR mass spectra were internally calibrated with respect to a high-abundance homologous alkylation series of ions each containing two oxygen atoms, as previously described.[20,21] 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 values to facilitate identification of homologous alkylation series. Peak assignments were performed by Kendrick mass defect analysis.[40] In summary, molecular formulas were assigned to peaks of lowest m/z value for each Kendrick mass defect (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 less than 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 of various NAFCs was anticipated to occur for the co-polymers examined in the current investigation. Selective sorption was expected on the basis of the earlier work by Mohamed et al., in which a relationship was observed between inclusion site accessibility and the structure of the co-polymer materials with variable cross-link density.[25,32,34] Furthermore, Wilson et al.[28] demonstrated a solvent-mediated swelling behavior of such materials by means of solid−solution and solid−gas methods. What was not established, however, was whether or not high-resolution mass spectrometry characterization could reveal the level of selectivity of sorption for compound classes within the OSPW and NAFCs for the different co-polymers and what insights could be gained for the understanding of the thermodynamic sorption mechanism for such materials.

As illustrated in Figure 1, a wide range of compound classes was observed in the negative ESI FT-ICR mass spectra. At best, the data shown here are considered semi-quantitative because the response factors of the components are not known and are subject to ion-suppression and matrix effects. The range of O_x and OS_y species is similar to the range of compound classes observed earlier for OSPW and oil sands environmental samples.[7,21,41] Interestingly, the distribution of compound classes was, in general, the same whether or not the OSPW was treated with the engineered polymers. An exception was observed for M1, for which dramatic differences in the distribution are observed specifically for the O_2 class of compounds. A relative reduction of ~50% was observed for the O_2 class of compounds. The latter is presumably the classical NAs but could also be dihydroxy polar compounds with the same empirical formula. The OSPW contains not only NAFCs but also metal ions, salts, and non-oil sands acids. Thus,
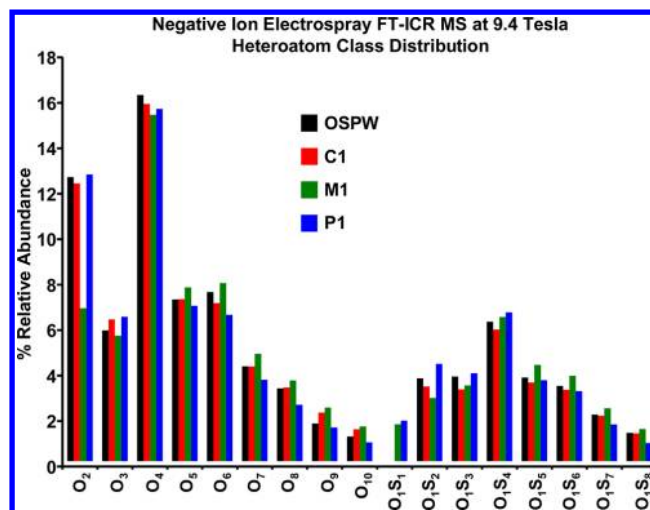

Figure 1. Negative-ion elestrospray 9.4 T FT-ICR MS heteroatom class distributions for OSPW treated with engineered polymers C1, M1, and P1. The relative standard deviation based on triplicate runs of the same sample was less than 10% of the measured values.

sorption of the NAFCs (that are amenable to detection by negative-ion electrospray FT-ICR MS) from OSPW thus appears to be non-selective for the engineered co-polymers C1 and P1. However, there is molecular recognition for the engineered polymer M1 for the O_2 class of compounds.

The components in the O_2 class form two distinct families with double bond equivalents (DBE is the number of rings plus double bonds involving carbon) $\approx$ 4 (non-aromatic components or possibly an aromatic six-membered ring with two hydroxyl groups) and DBE $\approx$ 8 (possibly aromatic components), with a carbon number range of 12−18. As illustrated in Figure 2, both groups are adsorbed with little or no discrimination by the engineered polymers C1, M1, and P1 from OSPW.

Molecular recognition is evident for sorption of NAFCs in either the presence or absence of salts, metals, and other co-contaminants. For example, Figures 3 and 4 illustrate that there
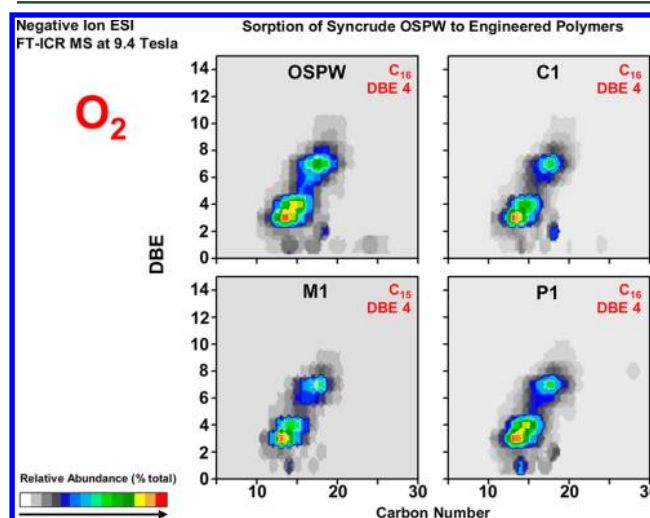

Figure 2. Negative-ion electrospray 9.4 T FT-ICR MS isoabundance-contoured DBE versus carbon number plots for the O_2 class ions from OSPW treated with engineered polymers C1, M1, and P1. The red text detail the highest magnitude peaks of the class.
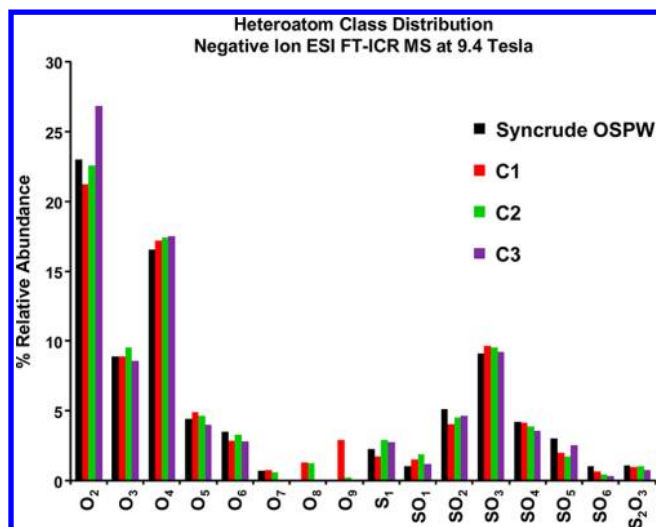
Figure 3. Negative-ion electrospray 9.4 T FT-ICR MS heteroatom class distributions for OSPW treated with engineered polymers C1, C2, and C3. The relative standard deviation based on triplicate runs of the same sample was less than 10% of the measured values.
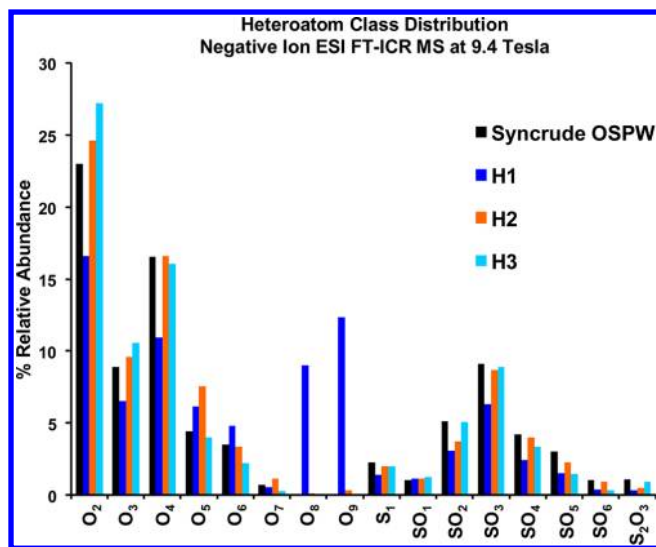

Figure 4. Negative-ion electrospray 9.4 T FT-ICR MS heteroatom class distributions for OSPW treated with engineered polymers H1, H2, and H3. The relative standard deviation based on triplicate runs of the same sample was less than 10% of the measured values.

is preferential sorption of a range of compound classes depending upon the cross-link density and type of linker used in the synthesis of the engineered polymer.

As illustrated in Figure 3, selective sorption is most evident for the O_2 class of compounds for C3 engineered polymers. For the C3 engineered polymer, there is a ~17% increase in the relative amounts of the O_2 class following sorption compared to the non-treated control. Some components, such as the O_8 and O_9 compound classes, are released from the engineered co-polymers C1 and C2 compared to the control and warrant a follow-up study to assess their aquatic toxicity.

Molecular recognition of various NAFC classes is clearly evident for the H1, H2, and H3 series of engineered polymers, as illustrated in Figure 4. Selective sorption is observed for the O_x classes, where x = 1−9, and also measurable for the S_sO_o classes. For example, for the H1 polymer, there is a relative

~25−35% reduction in the distribution of the O_2, O_3, and O_4 compound classes with similar reductions in the SO_x compound classes for x = 1−6. Some highly oxygenated species in the O_8 and O_9 compound classes are released by the H1 polymer compared to the control and warrant a follow-up study to assess their aquatic toxicity. Further development of the polymers for molecular recognition should thus center on the H1−H3 series of co-polymers.

For a given compound class, it was not clear whether or not there was molecular recognition based on the distribution of DBE, as illustrated for the O_2 class in Figure 5. Further investigation employing complementary ionization methods, such as atmospheric pressure photoionization (APPI), may shed light on other components, including less polar NAFCs, which are not accessed by ESI.

The observed molecular recognition according to compound class is attributed to the formation of host−guest inclusion complexes. The stability of the host−guest complexes depends upon the chemical structure of the NAFC and its relative concentration, the carbon number, the nature of the SO_x compound class, and the type of co-polymer. These parameters strongly influence the relative hydrophile−lipophile properties of the guest molecule, thereby affecting the complex stability. The extent to which molecular selective sorption occurs in the case of CD co-polymer materials is consistent with the findings of earlier work reported by Mohamed et al.[25,34] Those authors observed variable sorption of NAFCs according to the cross-link density of the co-polymer and the nature of the cross-linker unit. The earlier work provided evidence for selective sorption based on differences in the sorption of the z series of classical NAs. Because the earlier work used low-resolution mass spectrometry, it was not possible to measure or resolve compound classes or indeed report on the selective sorption of non-classical NAs and other polar components present in the OSPW according to their respective compound classes. The observation of molecular selective adsorption in co-polymer materials containing β-CD represents an important contribution toward the development of SPE materials. The ability to selectively adsorb specific compound classes of NAFCs, such as the O_x and SO_x compound classes, is important in environmental chemistry and toxicological studies that aim to further understand the fate and transport of NAs in OSPW.

Thermodynamic Sorption Mechanism of Co-polymer Materials. According to Figure 1, the greatest attenuation is observed for M1 with the O_2 series of NAs. This result may be understood in terms of the rigid framework of this co-polymer, its relatively high inclusion accessibility, and the apolar framework. There is a good *size-fit* compatibility with the O_2 series, thereby resulting in the greatest uptake of this component class for the M1 polymer. The higher molecular weight components for the higher O series and other higher molecular weight components do not afford proper *size-fit* matching between the host framework and this fraction of NAs. As evident in Figures 1, 3, and 4, however, the relative abundances for certain compound class series are higher in the presence of co-polymers relative to OSPW. Although the reasons for this observation are not established, it is likely that either (a) the component classes in question are leached from the polymers (as in the case of O_8 and O_9 classes for the H1 polymer) or (b) there is matrix suppression and ion enhancement of some components in the presence of the co-polymers. Notwithstanding these uncertainties, the attenuation (~50%) for the O_2 compound class for the M1 polymer
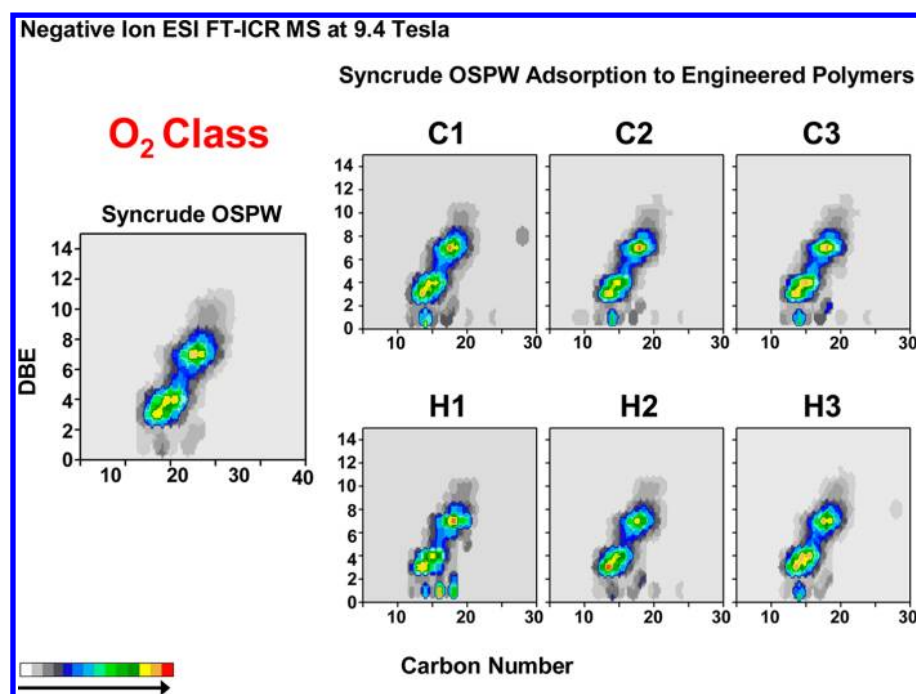
Figure 5. Negative-ion electrospray 9.4 T FT-ICR MS isoabundance-contoured DBE versus carbon number plots for the O_2 class ions from OSPW treated with engineered polymers C1−C3 and H1−H3.

appears to be real and well outside the 10% relative standard deviation (RSD) experimental precision of the measurements.

With regard to the results in Figures 3 and 4, the co-polymers (H1−H3 and C1−C3) contain aliphatic linker units. The behavior of such materials is different relative to M1 because of their propensity to undergo greater swelling in aqueous solution. Therefore, the accessibility of the inclusion sites in the framework differs significantly for co-polymers with aliphatic versus aromatic linker units, as evidenced by Figures 3 and 4 and in accordance with the variable sorptive uptake if one compares H1−H3 versus C1−C3. In general, the inclusion site accessibility decreases as the cross-link density increases, and the swelling decreases at greater cross-link density. The variation in relative abundance of NAs (%) correlates with the variation in the cross-link density for a given cross-linker (HDI versus CDI; Scheme 1). A quantitative correlation between *size fit* of the various NAFCs and the binding sites within the co-polymer is beyond the scope of the present work and requires verification through molecular modeling.

Further insight on the thermodynamics of the sorption of the polymers relates to the FT-ICR MS of the systems in the presence of salts and additives with the observed changes in molecular recognition. The observation of variable uptake in aqueous solution in the presence and absence of additives (e.g., electrolytes) is well-known for the host−guest chemistry of CDs. The Gibbs energy of complex formation is a function of several variables, one of which is hydration. It follows that the apparent binding constant (K_{app}) is given by eq 1

$$K_{app} = K_{actual} \, a_w{}^p \tag{1}$$

where p refers to the stoichiometric amount of water released through the association of an apolar guest and the CD host because of inclusion complex formation.[42] The variation in uptake of the fractions of NAs in solutions containing additives versus no additives is consistent with complexation phenomena involving hydrophobic effects.[43] However, little or no

measurable differences were observed in the sorption properties of the co-polymers for the two sets of conditions investigated, namely, (i) sorption to the engineered polymers of oil sands extracted NAs spiked in deionized water and (ii) sorption to the engineered polymers of oil sands extracted NAs from actual OSPW. Because metal ions, salts, and non-oil sands acids are present in OSPW, these parameters do not appear to affect the sorption properties of the engineered polymers.

CONCLUSION

The application of ultrahigh-resolution FT-ICR MS reveals molecular recognition of sorption of NAFCs compound classes to co-polymers, which was not evident in earlier work based on low-resolution mass spectrometry. Variable sorption of NAFCs was observed according to the cross-linking density of the co-polymer and the nature of the cross-linker unit. Furthermore, the sorption of the NAFCs to the co-polymers was not generally affected by other parameters, such as metal ions, salinity, and non-oil sands acids, present in OSPW. The observation of molecular selective sorption in co-polymer materials containing β-CD represents an important contribution toward the development of sorbent materials for removal of oil sands acids in aquatic environments. The FT-ICR MS measurements also contribute further to the understanding of the thermodynamic sorption mechanism in such materials.

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Notes
The authors declare no competing financial interest.

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■ **REFERENCES**

(1) Burrowes, A.; Marsh, R.; Evans, C.; Teare, M.; Ramos, S.; Rahnama, F.; Kirsch, M.-A.; Philp, L.; Stenson, J.; Yemane, M.; Horne, J. V.; Fong, J.; Sankey, G.; Harrison, P. *Alberta's Energy Reserves 2008 and Supply/Demand Outlook 2009–2018*; Energy Resources Conservation Board, Government of Alberta: Calgary, Alberta, Canada, 2009; p 220.

(2) Schramm, L. L.; Stasiuk, E. N.; MacKinnon, M. Surfactants in Athabasca oil sands extraction and tailing process. In *Surfactants: Fundamentals and Applications in the Petroleum Industry*; Schramm, L. L., Ed.; Cambridge University Press: Cambridge, U.K., 2000; pp 365–430.

(3) Schindler, D. W.; Donahue, W. F. An impending water crisis in Canada's western prairie provinces. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103* (19), 7210–7216.

(4) Han, X.; MacKinnon, M. D.; Martin, J. W. Estimating the in situ biodegradation of naphthenic acids in oil sands process waters by HPLC/HRMS. *Chemosphere* **2009**, *76* (1), 63–70.

(5) Baird, D.; Banic, C.; Bickerton, G.; Burn, D.; Dillon, P.; Droppo, I.; Dubé, M.; Hazewinkel, R.; Hewitt, M.; Kelly, E.; Lindeman, D.; Marriott, P.; McCauley, E.; McEachern, P.; Muir, D.; Munkittrick, K.; Noton, L.; Prowse, T.; Rasmussen, J.; Smol, J. *Lower Athabasca Water Quality Monitoring Program. Phase 1. Athabasca River Mainstem and Major Tributaries*; Wrona, F. J., di Cenzo, P., Eds.; Environment Canada: Ottawa, Ontario, Canada, 2011; p 97.

(6) Dowdeswell, L.; Dillon, P.; Ghoshal, S.; Miall, A.; Rasmussen, J.; Smol, J. P. *A Foundation for the Future: Building an Environmental Monitoring System for the Oil Sands—A Report Submitted to the Minister of the Environment*; Environment Canada: Ottawa, Ontario, Canada, 2010; p 49.

(7) Barrow, M. P.; Witt, M.; Headley, J. V.; Peru, K. M. Athabasca oil sands process water: Characterization by atmospheric pressure photoionization and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2010**, *82* (9), 3727–3735.

(8) Headley, J. V.; McMartin, D. W. A review of the occurrence and fate of naphthenic acids in aquatic environments. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2004**, *39* (8), 1989–2010.

(9) Headley, J. V.; Peru, K. M.; Barrow, M. P. Mass spectrometric characterization of naphthenic acids in environmental samples: A review. *Mass Spectrom. Rev.* **2009**, *28* (1), 121–134.

(10) Headley, J. V.; Peru, K. M.; Armstrong, S. A.; Han, X.; Martin, J. W.; Mapolelo, M. M.; Smith, D. F.; Rogers, R. P.; Marshall, A. G. Aquatic plant-derived changes in oil sands naphthenic acid signatures determined by low-, high- and ultrahigh-resolution mass spectrometry. *Rapid Commun. Mass Spectrom.* **2009**, *23* (4), 515–522.

(11) Frank, R. A.; Fischer, K.; Kavanagh, R.; Burnison, B. K.; Arsenault, G.; Headley, J. V.; Peru, K. M.; Kraak, G. V. D.; Solomon, K. R. Effect of carboxylic acid content on the acute toxicity of oil sands naphthenic acids. *Environ. Sci. Technol.* **2008**, *43* (2), 266–271.

(12) Grewer, D. M.; Young, R. F.; Whittal, R. M.; Fedorak, P. M. Naphthenic acids and other acid-extractables in water samples from Alberta: What is being measured? *Sci. Total Environ.* **2010**, *408* (23), 5997–6010.

(13) Barrow, M. P.; McDonnell, L. A.; Feng, X.; Walker, J.; Derrick, P. J. Determination of the nature of naphthenic acids present in crude oils using nanospray Fourier transform ion cyclotron resonance mass spectrometry: The continued battle against corrosion. *Anal. Chem.* **2003**, *75* (4), 860–866.

(14) Barrow, M. P.; Headley, J. V.; Peru, K. M.; Derrick, P. J. Fourier transform ion cyclotron resonance mass spectrometry of principal components in oilsands naphthenic acids. *J. Chromatogr., A* **2004**, *1058* (1–2), 51–59.

(15) Smith, B. E.; Rowland, S. J. A derivatisation and liquid chromatography/electrospray ionisation multistage mass spectrometry method for the characterisation of naphthenic acids. *Rapid Commun. Mass Spectrom.* **2008**, *22* (23), 3909–3927.

(16) Headley, J. V.; Barrow, M. P.; Peru, K. M.; Derrick, P. J. Salting-out effects on the characterization of naphthenic acids from Athabasca oil sands using electrospray ionization. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2011**, *46* (8), 844–854.

(17) Headley, J. V.; Peru, K. M.; Janfada, A.; Fahlman, B.; Gu, C.; Hassan, S. Characterization of oil sands acids in plant tissue using Orbitrap ultra-high resolution mass spectrometry with electrospray ionization. *Rapid Commun. Mass Spectrom.* **2011**, *25* (3), 459–462.

(18) Kavanagh, R. J.; Burnison, B. K.; Frank, R. A.; Solomon, K. R.; Van Der Kraak, G. Detecting oil sands process-affected waters in the Alberta oil sands region using synchronous fluorescence spectroscopy. *Chemosphere* **2009**, *76* (1), 120–126.

(19) Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M. Screening of oil sands naphthenic acids by UV–vis absorption and fluorescence emission spectrophotometry. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2008**, *43* (14), 1700–1705.

(20) Headley, J. V.; Peru, K. M.; Mishra, S.; Meda, V.; Dalai, A. K.; McMartin, D. W.; Mapolelo, M. M.; Rodgers, R. P.; Marshall, A. G. Characterization of oil sands naphthenic acids treated with ultraviolet and microwave radiation by negative ion electrospray Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Commun. Mass Spectrom.* **2010**, *24* (21), 3121–3126.

(21) Headley, J. V.; Armstrong, S. A.; Peru, K. M.; Mikula, R. J.; Germida, J. J.; Mapolelo, M. M.; Rodgers, R. P.; Marshall, A. G. Ultrahigh-resolution mass spectrometry of simulated runoff from treated oil sands mature fine tailings. *Rapid Commun. Mass Spectrom.* **2010**, *24* (16), 2400–2406.

(22) Martin, J. W.; Han, X.; Peru, K. M.; Headley, J. V. Comparison of high- and low-resolution electrospray ionization mass spectrometry for the analysis of naphthenic acid mixtures in oil sands process water. *Rapid Commun. Mass Spectrom.* **2008**, *22* (12), 1919–1924.

(23) Headley, J. V.; Peru, K. M.; Barrow, M. P.; Derrick, P. J. Characterization of naphthenic acids from Athabasca oil sands using electrospray ionization: The significant influence of solvents. *Anal. Chem.* **2007**, *79* (16), 6222–6229.

(24) Barrow, M. P.; Headley, J. V.; Peru, K. M.; Derrick, P. J. Data visualization for the characterization of naphthenic acids within petroleum samples. *Energy Fuels* **2009**, *23* (5), 2592–2599.

(25) Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M. Sequestration of naphthenic acids from aqueous solution using β-cyclodextrin-based polyurethanes. *Phys. Chem. Chem. Phys.* **2011**, *13* (3), 1112–1122.

(26) Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M. Novel materials for environmental remediation of tailing pond waters containing naphthenic acids. *Process Saf. Environ. Prot.* **2008**, *86* (4), 237–243.

(27) Mohamed, M. H.; Wilson, L. D.; Headley, J. V. Design and characterization of novel β-cyclodextrin based copolymer materials. *Carbohydr. Res.* **2011**, *346* (2), 219–229.

(28) Wilson, L. D.; Mohamed, M. H.; Headley, J. V. Surface area and pore structure properties of urethane-based copolymers containing β-cyclodextrin. *J. Colloid Interface Sci.* **2011**, *357* (1), 215–222.

(29) Crini, G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **2005**, *30* (1), 38–70.

(30) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*, 2nd ed.; John Wiley and Sons, Ltd.: West Sussex, U.K., 2009; p 970.

(31) Yu, J. C.; Jiang, Z.-T.; Liu, H.-Y.; Yu, J.; Zhang, L. β-Cyclodextrin epichlorohydrin copolymer as a solid-phase extraction adsorbent for aromatic compounds in water samples. *Anal. Chim. Acta* **2003**, *477* (1), 93–101.

(32) Mohamed, M. H.; Wilson, L. D.; Headley, J. V. Estimation of the surface accessible inclusion sites of β-cyclodextrin based copolymer materials. *Carbohydr. Polym.* **2010**, *80* (1), 186−196.

(33) Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M. Electrospray ionization mass spectrometry studies of cyclodextrin−carboxylate ion inclusion complexes. *Rapid Commun. Mass Spectrom.* **2009**, *23* (23), 3703−3712.

(34) Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M. Investigation of the sorption properties of β-cyclodextrin-based polyurethanes with phenolic dyes and naphthenates. *J. Colloid Interface Sci.* **2011**, *356* (1), 217−226.

(35) Kaiser, N.; Quinn, J.; Blakney, G.; Hendrickson, C.; Marshall, A. A novel 9.4 T FT-ICR mass spectrometer with improved sensitivity, mass resolution, and mass range. *J. Am. Soc. Mass Spectrom.* **2011**, *22* (8), 1343−1351.

(36) Senko, M. W.; Hendrickson, C. L.; Emmett, M. R.; Shi, S. D. H.; Marshall, A. G. External accumulation of ions for enhanced electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *J. Am. Soc. Mass Spectrom.* **1997**, *8* (9), 970−976.

(37) Ledford, E. B.; Rempel, D. L.; Gross, M. L. Space charge effects in Fourier transform mass spectrometry. II. Mass calibration. *Anal. Chem.* **1984**, *56* (14), 2744−2748.

(38) Shi, S. D. H.; Drader, J. J.; Freitas, M. A.; Hendrickson, C. L.; Marshall, A. G. Comparison and interconversion of the two most common frequency-to-mass calibration functions for Fourier transform ion cyclotron resonance mass spectrometry. *Int. J. Mass Spectrom.* **2000**, *195−196*, 591−598.

(39) Blakney, G. T.; Hendrickson, C. L.; Marshall, A. G. Predator data station: A fast data acquisition system for advanced FT-ICR MS experiments. *Int. J. Mass Spectrom.* **2011**, *306* (2−3), 246−252.

(40) Hughey, C. A.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G.; Qian, K. Kendrick mass defect spectrum: A compact visual analysis for ultrahigh-resolution broadband mass spectra. *Anal. Chem.* **2001**, *73* (19), 4676−4681.

(41) Headley, J. V.; Barrow, M. P.; Peru, K. M.; Fahlman, B.; Frank, R. A.; Bickerton, G.; McMaster, M. E.; Parrott, J.; Hewitt, L. M. Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Commun. Mass Spectrom.* **2011**, *25* (13), 1899−1909.

(42) Gerasimowicz, W.; Wojcik, J. Azo dye−α-cyclodextrin adduct formation. *Bioorg. Chem.* **1982**, *11*, 420−427.

(43) Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M. A spectral displacement study of cyclodextrin/naphthenic acids inclusion complexes. *Can. J. Chem.* **2009**, *10*, 1747−1756.