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Elemental and spectroscopic characterization of fractions of an acidic extract of oil sands process water

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HIGHLIGHTS

- Methylated OSPW fractions examined by elemental analysis, UV and IR spectroscopy.
- Some examined by GCxGC–MS: one, containing most sulfur, also examined by GCxGC–SCD.
- Alicylic acids eluted with hexane: little S and no aromatics present.
- Mono- and possibly diaromatics eluted with ether/hexane: little S present.
- Major aromatic S carboxylic acids detected; accurate mass spectra reported.

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ABSTRACT

'Naphthenic acids' (NAs) in petroleum produced water and oil sands process water (OSPW), have been implicated in toxicological effects. However, many are not well characterized. A method for fractionation of NAs of an OSPW was used herein and a multi-method characterization of the fractions conducted.

The unfractionated OSPW acidic extract was characterized by elemental analysis, electrospray ionization-Orbitrap-mass spectrometry (ESI-MS), and an esterified extract by Fourier Transform infrared (FTIR) and ultraviolet–visible (UV) absorption spectroscopy and by comprehensive multidimensional gas chromatography–MS (GCxGC–MS). Methyl esters were fractionated by argentation solid phase extraction (Ag^+ SPE) and fractions eluting with: hexane; diethyl ether: hexane and diethyl ether, examined. Each was weighed, examined by elemental analysis, FTIR, UV, GC–MS and GCxGC–MS (both nominal and high resolution MS). The ether fraction, containing sulfur, was also examined by GCxGC–sulfur chemiluminescence detection (GCxGC–SCD).

The major ions detected by ESI-MS in the OSPW extract were assigned to alicyclic and aromatic 'O2' acids; sulfur was also present. Components recovered by Ag^+ SPE were also methyl esters of alicyclic and aromatic acids; these contained little sulfur or nitrogen. FTIR spectra showed that hydroxy acids and sulfoxides were absent or minor. UV spectra, along with the C/H ratio, further confirmed the aromaticity of the hexane:ether eluate.

The more minor ether eluate contained further aromatics and 1.5% sulfur. FTIR spectra indicated free carboxylic acids, in addition to esters. Four major sulfur compounds were detected by GCxGC–SCD. GCxGC–high resolution MS indicated these were methyl esters of C_{18} S-containing, diaromatics with $\geqslant C_3$ carboxylic acid side chains.

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1. Introduction

Some offshore produced water from petroleum production and acidic extracts of process water produced during the operations of the oil sands industries of Alberta, Canada are reported to be toxic to a variety of organisms (e.g. reviewed by Hrudey et al. (2010)). One class of compounds thought to be responsible for the toxic effects is the so-called 'classical' alicyclic naphthenic acids (NAs) containing only carbon, oxygen and hydrogen, but a number of other elements, notably sulfur and nitrogen, are present in organic compounds in oil sands process water (OSPW) extracts, for instance (e.g. Grewer et al., 2010), and probably also in petroleum produced waters. Ultra-high resolution mass spectrometry, following electrospray ionization (ESI-MS), has also indicated that a variety of SOx and NOx species are present in OSPW, though none have been identified (Barrow et al., 2010; Grewer et al., 2010; Headley et al., 2011). Recently a preliminary study (Jones et al., 2012) indicated that the proportion of aromatic acids in at least one OSPW extract, was also substantial (>30%). A further characterization of such extracts should therefore be valuable.

In the present study an unfractionated OSPW acidic extract was examined by a number of methods and the methyl esters then isolated and sub-fractionated by argentation solid phase extraction (Ag^+ SPE). Semi-quantified sub-fractions were examined by elemental analysis (CHNS), Fourier Transform infrared spectroscopy (FTIR), ultraviolet–visible absorption spectrophotometry (UV), gas chromatography-mass spectrometry (GC–MS) and GCxGC–MS (accurate and nominal mass MS). The ether fraction, containing most of the sulfur, was also examined by GCxGC with a sulfur chemiluminescence detector (i.e. GCxGC–SCD).

2. Methods

Authentic adamantane-1-carboxylic and adamantane-1,3-dicarboxylic acids for ESI-MS (Orbitrap) were obtained from commercial sources (Sigma, Dorset, UK). Diamantane-3-carboxylic and diamantane-1,6-dicarboxylic acids were gifts from Stanford and Prague universities. ESI-MS in the negative ion mode was conducted on triplicate solutions in methanol with a trace of ammonium hydroxide added to initiate ionization.

The OSPW was a subsample of ca 3000 L of oil sands tailings pond water collected from Syncrude Canada Ltd. West Endpit settling basin in Fort McMurray, Alberta, Canada in June 2005 (Frank et al., 2008). The subsequent treatment to isolate a concentrated NA (sodium salts) mixture has been described fully (Frank et al., 2006, 2008). A subsample (~30 mL) of this concentrate as received (pH 11–12) was acidified with hydrochloric acid to pH < 2 and extracted with ethyl acetate.

For ESI-MS of the OSPW, the solvent was removed and the residue dissolved in methanol. Before ESI-MS, the sample was treated with NaOH/water for examination in negative ion mode.

The remaining ethyl acetate extract was dried (nitrogen stream), esterified by heating with fresh BF_3/methanol complex (70 °C, >30 min), back extracted into hexane, dried and weighed. Approximately 80 mg of the resulting esterified fraction was sub-fractionated by argentation solid phase extraction as described previously (Jones et al., 2012), but repeated fifteen times on ~5 mg aliquots to obtain larger fractions which could then be weighed accurately. Briefly, Ag^+ SPE was conducted on the methylated OSPW extracts using 6 mL Discovery® Ag-Ion SPE cartridges (750 mg sorbent; Sigma–Aldrich, Dorset, UK). Cartridges were conditioned with hexane (3 × 5 mL). OSPW extracts in hexane were then loaded onto the cartridges which were subsequently eluted using hexane (3 × 5 mL), 95% hexane, 5% diethyl ether (4 × 5 mL) and finally 100% diethyl ether (5 mL). Fractions were collected and reduced to dryness under a steady stream of nitrogen at 40 °C.

High resolution MS accurate mass measurements of the unfractionated, non-esterified OSPW extract, were made as described previously (Rowland et al., 2011a) using a Thermofisher LTQ Orbitrap XL high resolution mass spectrometer. The mass range was m/z 120–2000; mass accuracy <3 ppm RMS with external calibration. For negative electrospray ionization the instrument was externally calibrated using sodium dodecyl sulfate and sodium taurocholate. For loop-injections a Thermo Scientific Surveyor MicroLC was used to provide solvent flow at 20 μL min^{-1} through a 2 μL sample loop. Solvents used were H_2O:MeOH (1:1). For nano-electrospray an Advion Triversa NanoMate was used to deliver samples diluted into MeOH ± 10% NH_4OAc or NaOH at a flow of approximately 0.25 μL min^{-1}.

Elemental analysis of the esters was determined using a CE Instruments (Thermo) elemental analyser model EA1110 running under software control. Samples were precisely weighed (typically 0.5–2.5 mg) using a Mettler UMT5 microbalance. The system response was calibrated to known calibration standards. The elemental composition of cysteine was examined periodically as an internal check.

Infrared spectroscopy of the esters was performed with a Bruker Optics Alpha FT-IR spectrometer.

UV spectra of solutions of the esters in dichloromethane were recorded on an Agilent/Hewlett Packard model 8453 (Agilent Technologies, Waldbronn, Germany), wavelength range 190–1100 nm, slit width 1 nm.

Esterified fractions were reconstituted in hexane (hexane and ether: hexane fractions) or dichloromethane (ether fraction) prior to analysis by GC–MS and GCxGC–MS and/or GCxGC–SCD. GC–MS and GCxGC–MS with nominal and accurate mass examinations of the esters were conducted as described previously (Rowland et al., 2011a; West et al., 2013). Briefly, for GC–MS, extracts were analyzed using an Agilent GC-MSD (Agilent Technologies, Wilmington, DE, USA). This comprised a 7890A gas chromatograph fitted with a 7683B Series autosampler and a 5975A quadrupole mass selective detector. The column was a HP-5MS fused silica capillary column (30 m × 0.25 mm i.d × 0.25 μm film thickness). The carrier gas was helium at a constant flow of 1.0 mL min^{-1}. A 1.0 μL sample was injected into a 300 °C splitless injector. The oven temperature was programmed from 40 to 300 at 10 °C min^{-1} and held for 10 min.

Briefly, nominal mass GCxGC–MS analyses were conducted using an Agilent 7890A gas chromatograph (Agilent Technologies, Wilmington, DE) fitted with a Zoex ZX2 GCxGC cryogenic modulator (Houston, TX, USA) interfaced with an Almsco BenchTOFdx™ time-of-flight mass spectrometer (Almsco International, Llantrisant, Wales, UK) operated in positive ion electron ionization mode and calibrated with perfluorotributylamine. The scan speed was 50 Hz. The first-dimension column was a 100% dimethyl polysiloxane 50 m × 0.25 mm × 0.40 μm VF1-MS (Varian, Palo Alto, USA), and the second-dimension column was a 50% phenyl polysilphenylene siloxane 1.5 m × 0.1 mm × 0.1 μm BPX50 (SGE, Melbourne, Australia). Helium was used as carrier gas and the flow was kept constant at 0.7 mL min^{-1}. Samples (1 μL) were injected at 280 °C splitless. The oven was programmed from 40 °C (hold for 1 min), then heated to 300 °C at 2 °C min^{-1} then at 10 °C min^{-1} to 320 °C (held for 10 min). The modulation period was 5 s. The transfer line temperature was 280 °C and ion source 300 °C. Data processing was conducted using GC Image™ v2.1 (Zoex, Houston, TX, USA).

Accurate mass GCxGC–MS was conducted (e.g. West et al., 2013) using an Agilent 7890A gas chromatograph fitted with a Zoex ZX1 thermal modulator interfaced with a Jeol AccuTOF GCv (Jeol Inc., USA) time of flight-mass spectrometer operated in positive ion mode. The scan speed was 25 Hz. The first-dimension column was a 100% dimethyl polysiloxane 10 m × 0.25 mm × 0.25 μm DB-1 (Agilent Technologies J & W, Wilmington, DE) and the