Investigation of dissociation constants for individual and total naphthenic acids species using ultra performance liquid chromatography ion mobility time-of-flight mass spectrometry analysis

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HIGHLIGHTS

- UPLC-IM-TOFMS was able to identify O_yS−NAs from O_x−NAs.
- Dissociation constants were estimated for individual and total NA species from OSPW.
- The pK_a decreases with increasing n and −Z numbers for O_2, O_3, O_4, and O_2S species.
- The pK_a values were 3.3 for O_2, 4.4 for O_3, 7.3 for O_4, and 4.1 for O_2S species.
- The pK_a value was 3.9 for total NAs.

GRAPHICAL ABSTRACT
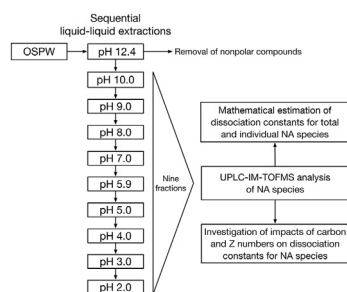
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ABSTRACT

Ultra-performance liquid chromatography ion mobility time-of-flight mass spectrometry (UPLC-IM-TOFMS) was utilized for the analysis of naphthenic acids (NAs) in fractions of pH-dependent sequential liquid-liquid extractions from oil sands process-affected water. Ion-mobility separation technique allowed the differentiation of O_yS−NAs ($2 \leq y \leq 4$) from O_x−NAs ($2 \leq x \leq 5$) via drift time versus retention time separations. The results indicated that the addition of S atom to the O_2−NA molecule led to a lower increase in the dissociation constant (pK_a) compared to that caused by the addition of O atom. Because additional O is present as −OH while the S atom is present as the C−S−C structure, the latter does not involve into the deprotonation process directly. The pK_a value decreased along with increasing carbon number and $|Z|$ number for O_2−, O_3−, O_4−, and O_2S−NA species, except for O_5−, O_3S−, and O_4S−NA species, each of which are comprised of chemical structures with distinct functional groups. A calculation model was developed to estimate pK_a values for individual and total NA species via nonlinear regression curve fitting, utilizing the relative abundances of detected NA species. pK_a values were calculated as 3.9 for total NAs, 3.3 for O_2−NAs, 4.4 for O_3−NAs, 7.3 for O_4−NAs, and 4.1 for O_2S−NAs. Knowledge of NAs pK_a is crucially important for the comprehensive understanding of their potential transformation route and toxicity as well as for the development of water remediation applications. Both

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the ion-mobility separation technique and the new calculation model could be widely applied for the investigation of other complicated pollutants present in water and wastewater.

1. Introduction

As a result of the bitumen extraction process by the oil sands industry in Northern Alberta (Canada), large amounts of oil sands process-affected water (OSPW) are generated and stored in tailings ponds (Schindler, 2014). Similar to other petroleum refinery and hydraulic fracturing wastewaters, OSPW contains abundant toxic persistent organic compounds, such as naphthenic acids (NAs), adversely affecting the environmental health (Hagen et al., 2012; Scarlett et al., 2013). NAs are a complex mixture of carboxylic acids with empirical formulas of $C_nH_{(2n+Z)}O_x$ or $C_nH_{(2n+Z)}O_yS$, where n is the carbon number ($7 \leq n \leq 26$), Z is zero or a negative even integer ($0 \leq |Z| \leq 18$) that specifies the hydrogen deficiency resulting from ring or unsaturated bonding formation, and x and y represent the number of oxygen atoms ($2 \leq x \leq 5$, and $2 \leq y \leq 4$) (Huang et al., 2016a). NA species have been reported to induce toxic effects to aquatic organisms through multiple modes of action, including narcosis, endocrine disruption, immunotoxicity, and carcinogenicity (Hagen et al., 2012; Scarlett et al., 2013; Wang et al., 2013b).

The structural information of O_x–NAs and O_yS–NAs have been investigated using high resolution mass spectrometry in the literature, indicating that the natural oxidation and degradation products of NAs contain only the –OH and –COOH groups that are involved in the deprotonation processes (Lengger et al., 2013; Wang et al., 2013a; West et al., 2014; Huang et al., 2015a). The functional group of the additional O atom in O_x–NAs would have a significant impact on the physical chemistry parameters, such as the dissociation constant (pK_a), which will influence the extraction process of NAs at various pH values as it has been reported previously (Havre et al., 2003; Huang et al., 2015b). For example, Havre et al. (2003) reported that the dissociation constant for total NAs from crude oil was 4.9 based on an investigation of oil/water-partitioning and interfacial behavior. Huang et al. (2015b) reported the dissociation constants for O_2–, O_3–, and O_4–NAs from OSPW as 3.5, 4.8, and 6.8 through the pH-dependent sequential liquid-liquid extractions and associated modeling estimation, which was developed considering both the liquid-liquid distribution equilibrium and the acid-base equilibrium in the water layer. Based on pK_a values of O_x–NAs, the presence of O_4–NAs should be predominantly (COOH)(OH)$_2$–NAs instead of (COOH)$_2$–NAs, because the latter one is more acidic with lower pK_a than O_2–NAs (Bruice, 2004). Beside O_x–NAs, the sulfur-containing NAs have been identified and characterized in a number of studies (West et al., 2014; Headley et al., 2016); however, the related dissociation constants have not been reported until date. In addition to reveal the structure information, the dissociation constant values for NA species are also useful for comprehensive understanding of their fate and transport in various wastewater treatment processes (Faust and Aly, 1998; Babic et al., 2007). For example, it has been demonstrated that pK_a has a significant impact on the ozone reaction rate with organic compounds (Hoigné and Bader, 1983).

Although the pK_a values for O_2–, O_3–, and O_4–NAs have been obtained previously, the insufficient mass accuracy (± 5 mDa) and resolution (40,000) in previous measurements have prevented the identification of O_yS–NAs from O_x–NAs (Huang et al., 2015b). Also, previous calculation model was established using the semi-

quantification results, which may raise concern about the reliability of modeling results that could be affected by the quantification errors. In our study, to identify and determine both O_x–NAs and O_yS–NAs species in fractions from the pH-dependent sequential liquid-liquid extractions, ultra performance liquid chromatography ion mobility time-of-flight mass spectrometry (UPLC-IM-TOFMS) with three-dimensional (3D) separation (drift time versus retention time versus mass) technique was applied for measurements (Huang et al., 2016a). Then, the mathematical model has been re-invented to estimate pK_a values for individual and total NA species based on the relative abundances of detected NA species instead of semi-quantification results used in previous work. This improvement not only prevented the modeling results to be affected by the quantification errors, but also greatly extended the application of the new modeling method to other compounds. In addition, the influence of carbon and Z numbers to the pK_a values were investigated for O_x–NAs and O_yS–NAs.

2. Experimental

2.1. Reagents and materials

Optima grade dichloromethane and cyclohexane (Fisher Scientific, ON) were used as the extraction solvents in this study. NaOH and H_2SO_4 (Sigma-Aldrich, ON) were used for solution pH adjustment. All the solvents (i.e., water, methanol and acetonitrile) used for instrumental analyses were purchased from Fisher Scientific (ON) and their purities were optima-grade. Anhydrous Na_2SO_4 used to remove trace water in the separated organic layers and myristic acid-1-^{13}C applied as the internal standard in the instrumental analyses were acquired from Sigma-Aldrich (ON).

2.2. Sample collection and preparation

OSPW was collected from a tailings pond in Fort McMurray, Canada, on September 2010 and was stored at 4 °C prior to use. We completed all experiment by January 2013 with original dataset archived. OSPW was stable under this storage condition given the natural degradation half-lives for OSPW NAs were reported as 13 years in the field (Han et al., 2009). This UPLC-IM-TOFMS dataset could not be processed, until related data mining analysis method was developed during 2014–2015 (Huang et al., 2015a, 2016a), allowing the extraction and identification of detected peaks from the UPLC-IM-TOFMS data format. The archived dataset (2013) was then processed to acquire chemical information that was subsequently applied to the new modeling calculations in this work.

Prior to the experiments, the OSPW was mixed uniformly using an electric paddle. A filtration step using a 0.45 μm nylon filter (Millipore, ON) was firstly used to remove the suspended solids from a 2-L sample. After filtration, the OSPW sample was alkalized to pH > 12.0 (measured as 12.4 in this step) by adding NaOH (2 M) dropwise, while stirring on an ice bath, to ensure dissociation of entire NAs into ions in the solution. At pH 12.4, the OSPW was extracted using the cyclohexane 900 mL to remove the nonpolar compounds that were not relevant to the investigation of NAs (Huang et al., 2015b). The aqueous layer was thereafter acidified to pH 10.0 with H_2SO_4 (1.8 M) on a continuous stirring ice bath, and