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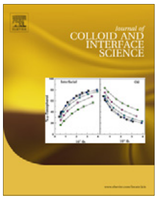

Colloidal properties of single component naphthenic acids and complex naphthenic acid mixtures

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Dedicated to honour the numerous contributions and distinguished scientific career of Professor Ronald E. Verrall at the University of Saskatchewan

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ABSTRACT

Tensiometry was used to provide estimates of the critical micelle concentration (cmc) values for three sources of naphthenic acids (NAs) and three examples of single component NAs (**S1**–**S3**) in aqueous solution at pH 10.5 and 295 K. Two commercially available mixtures of NAs and an industrially derived mixture of NAs obtained from Alberta oil sands process water (OSPW) were investigated. The three examples of single component NAs ($\mathbf{C_nH_{2n+z}O_2}$) were chosen with variable *z*-series to represent chemical structures with 0–2 rings, as follows: 2-hexyldecanoic acid (*z* = 0; **S1**), *trans*-4-pentylcyclohexanecarboxylic acid (*z* = −2; **S2**) and dicyclohexylacetic acid (*z* = −4; **S3**). The estimated cmc values for **S1** (35.6 μM), **S2** (0.545 mM), and **S3** (4.71 mM) vary over a wide range according to their relative lipophile characteristics of each carboxylate anion. The cmc values for the three complex mixtures of NAs were evaluated. Two disctinct cmc values were observed (second listed in brackets) as follows: *Commercial sample 1*; 50.9 μM (109 μM), *Commercial sample 2*; 22.3 μM (52.2 μM), and Alberta derived OSPW; 154 μM (417 μM). These results provide strong support favouring two general classes of NAs in the mixtures investigated with distinct cmc values. We propose that the two groups may be linked to a recalcitrant fraction with a relatively large range of cmc values (52.2–417 μM) and a readily biodegradable fraction with a relatively low range of cmc values (22.3–154 μM) depending on the source of NAs in a given mixture.

1. Introduction

The western Canadian oil sands industry in Northern Alberta uses a caustic warm water (i.e. The Clark Caustic Extraction Process) to recover oil-laden bitumen during processing from the sand and clay fractions [1] Bitumen from the surface mined oil sands may undergo emulsion formation due to the presence of elevated levels of colloidal materials with variable surface activity, hereafter referred to as naphthenic acids (NAs). The resulting oil sands process water (OSPW) is highly saline and contains a complex mixture of NAs, as illustrated in Scheme 1 [2,3]. NAs are defined as carboxylic acids which include one or more saturated ring structures, although the definition has become more generally used to describe the range of organic acids found within oil sands [4] (*cf.* Scheme 1). The broader definition includes oil sands acid extractable organics with aromatic functional groups, nitrogen and sulphur atoms, along with unsaturated groups (chemical structures not shown) [4–6]. For demonstration of the colloidal properties described herein, emphasis is given to components with the structural formulae $C_nH_{2n+z}O_2$ [7–11], where “*z*” is referred to as the “hydrogen deficiency”, and is zero or a negative even-integer value. More than one isomer will exist for a given *z*-homolog, and the carboxylic acid group is usually bonded or attached to a side chain, rather than directly to the cycloaliphatic ring [7,8]. The molecular weights differ by 14 mass units (CH_2) between *n*-series and by two mass units (H_2) between *z*-series [12]. However, in view of the broader definition adopted for NAs, recent attention has been given to related acid extractable organics containing single or multiple heteroatoms (e.g., O_1, O_3, O_4, O_2S, and O_3S species) [4–6]. The latter species are also known to occur in the water soluble fraction of petroleum crude oil acids where salting-out effects have been reported in sea water [13]. NAs are present primarily as their sodium naphthenate salts in oils sands process water (OSPW), and have greater solubility than the corresponding acid form of NAs. The former have industrial applications such as detergents and fungicides for wood preservatives [10,14,15].

NAs are considered to be a class of biological markers, closely linked to the maturity and the biodegradation level of the oil fields [5]. The composition, concentration, and colloidal properties of NAs depend on the source of oil [6–10]. The formation of colloids in OSPW is linked, in part, to the presence of ionized NAs with variable surface activity as the lipophilic surface area varies [16]. As well, Headley and coworkers reported that OSPW contain N- and

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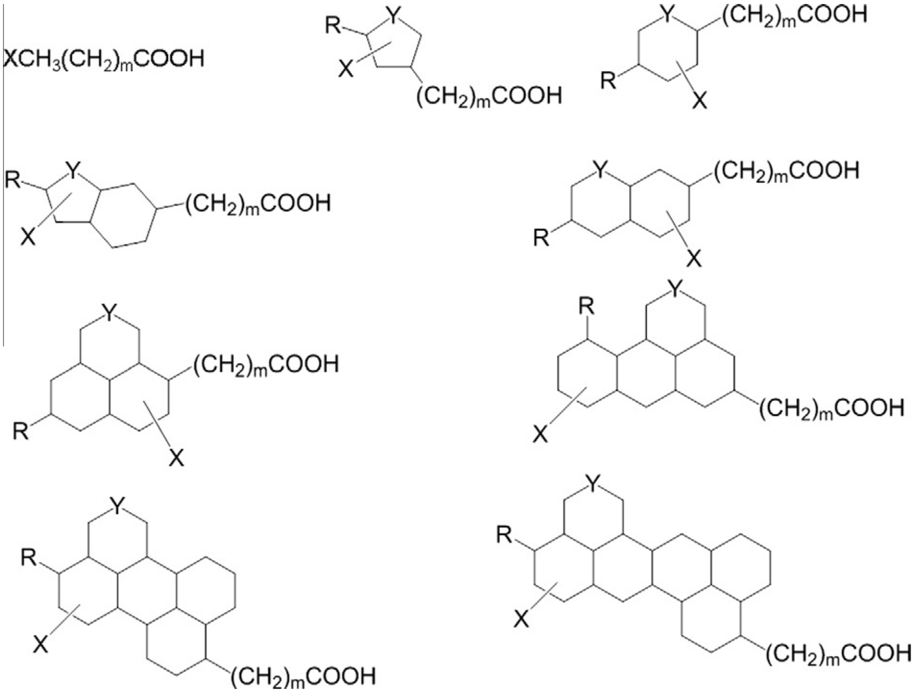

Scheme 1. Representative structures of naphthenic acid fraction components (NAFC) in OSPW. *R* = alkyl group, *X* = COOH, R, OH, SO_x, NO_x, SH and *Y* = C, S, N. Ring structures may not be fully saturated.

S-species according to preliminary results for high resolution MS [17]. This supports the fact that OSPW samples might display colloidal behaviour.

The presence of NAs in petroleum has led to environmental, health and industrial concerns because NAs are known to be toxic to aquatic organisms, algae, and mammals [10–14], evidenced by their endocrine-disrupting properties. The toxicology of the various single component and mixtures of NAs are poorly understood [15,18]. The Government of Canada has issued a zero discharge policy, in part, due to the limited understanding of the toxicity of NAs. The long-term storage of OSPW in large on-site settling ponds is problematic due the potential for accidental release of NAs into aquatic environments [19]. The concentrations of NAs in OSPW were reported in the range 40–120 ppm and are suspected to be principal toxic components in the complex mixture [1,19,20].

NAs are considered as conventional colloidal materials since they are amphiphilic in nature resulting from the polar carboxylic acid/carboxylate group(s) and the hydrocarbon fragment represents the lipophilic domain of the molecule. Notwithstanding the presence of heteroatoms (e.g., S and N), the variable structure of NAs in accordance with the variation of the *n*- and *z*-series likely results in wide-ranging surface-active behavior. In addition to the intrinsic toxicity of NAs, their presence in OSPW may augment the transport and bioavailability of other environmental contaminants [21–24]. Thus, the molecular structure and relative fractions of NAs are key factors in understanding their physicochemical properties and relative toxicity [25] Frank et al. [26] predicted an increased toxic potency for NAs containing fewer carbon rings using an ECOSAR model. Frank et al. [26] also reported that NAs with linear groupings of carbon rings had a greater predicted toxic potency than NAs containing multiple carbon rings in a clustered grouping. The size and structure of the NAs are suggested as controlling parameters in prediciting the toxicity of OSPW. Likewise, the size and structure of the respective NAs are hypothesized in this investigation to be controlling factors in determining the value of the cmc. If this hypothesis is valid, the presence of rings will increase the cmc (i.e. reduces lipophilicity) value of a structural isomer with a similar number of C atoms.

In general, the lipid membrane is anticipated to be a key site of interaction for colloidal materials because cellular function and transport may be disrupted by membrane lyses, membrane permeability, and membrane exchange processes [27–29]. Exchange of lipid membrane components or solubilization of colloidal materials is well described by the partition coefficient between the aqueous and bilayer membrane phase. Thus, an important parameter for colloidal materials is the critical micelle concentration (cmc). Ahlstrom et al. [30] highlighted the relationship between toxicity of surfactant compounds and their cmc values, as evidenced by the association of cell membranes with pre-micellar complexes. Generally, toxicity is observed in the vicinity of the cmc of colloidal materials [31–33]. We hypothesize that since size and structure are both controlling parameters for the toxicity of NAs and also controlling factors for micelle formation, there will be at least two distinct cmc values for NAs in OSPW and commercial NA mixtures. The lower cmc value for a given mixture would correspond to components which are more readily biodegradable, where the higher of the two cmc values would correspond to components that are more recalcitrant. The objective of this study is to test this hypothesis by evaluation and measurement of the cmc values for a series of single component and mixtures of NAs. The results of this study will further contribute to the development of improved quantitative structure–activity relationships (QSAR) [26,34–38] for a readily measurable physicochemical parameter (i.e. cmc) and its relationship to toxicity of single component and mixtures of NAs.

2. Experimental section

2.1. Materials

2-Hexyldecanoic acid (**S1**), *trans*-4-pentylcyclohexanecarboxylic acid (**S2**) and dicyclohexylacetic acid (**S3**) and Fluka (*commercial*