Equilibrium partitioning of naphthenic acids and bases and their consequences on interfacial properties

Are Bertheussen[*], Sébastien Simon, Johan Sjöblom

Ugelstad Laboratory, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

HIGHLIGHTS

- Partitioning of acids and bases to determine water quality of produced water.
- Equilibrium partitioning of acids and bases vs pH, with or without calcium.
- No interfacial interactions were detected between acids and bases.

GRAPHICAL ABSTRACT
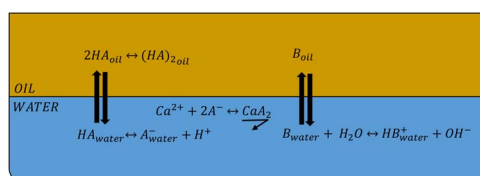
ARTICLE INFO

ABSTRACT

This article aims to create a model to accurately predict the equilibrium partitioning of naphthenic acids and basic crude oil components between the oil and water phase. The model was tested on 2 acids and 2 bases. After a review of the properties of crude oil acids and bases, the equilibrium partitioning of acids and bases with different molecular weight was analyzed over a pH interval using heptane as the oil phase and 3.5 wt.% NaCl as the water phase. Phenylacetic acid would represent the low molecular weight acid while 4-heptylbenzoic acid was chosen to represent the high molecular weight one. Likewise, 4-ethylaniline and 4-decylaniline were chosen as corresponding bases. The partitioning of the two acids and the low molecular weight base was successfully modelled by considering the acid dissociation constant pK_a in aqueous phase and the partition ratio P_{wo} of the non-ionized species between oil and aqueous phase. The high molecular weight base did not significantly partition into the aqueous phase at the pH range studied. The results show that acid species are more water soluble than basic species of similar molecular weight. In presence of calcium the partitioning of acids is successfully modelled by accounting for the precipitation of naphthenate soap with a solubility constant K_s. The kinetic interfacial tension between heptane and 3.5% NaCl aqueous buffer was also analyzed with oils that contained single compounds, two bases, two acids and all four components over a pH interval to identify any interfacial acid-base interactions. No significant interfacial interaction could be identified, mostly due to similar pK_a values.

1. Introduction

Crude oils have been produced for over one hundred years. The conventional oil resources are slowly running out [1] while energy demands continue to increase [2]. Development of demanding fields can become economically viable by implementing new technological solutions in areas like subsea production and processing [3,4]. One aspect of subsea processing entails liquid–liquid separation [1,3,5]. Three subsea liquid–liquid separators have been installed to date: Troll C, Tordis and Marlim; all of which were designed to inject (e.g. into a disposal reservoir) or reinject (e.g. into the production reservoir) the produced water [6]. Produced water is generated during the production of oil and gas [7] and it contains both dissolved and dispersed oil components [8]. Several oil companies have envisioned a futuristic scenario where an entire production and processing facility would operate on the seafloor, eliminating the need for topside processing all together [6,9,10]. To achieve export quality crude oil from such a facility, additional oil dehydration steps would be required. The water
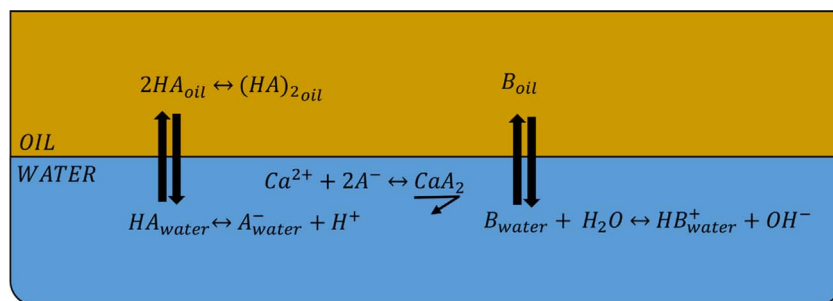
Fig. 1. Schematic illustration of the acid and base equilibria that occurs in oil water systems. Depicted are dimerization of acids in oil phase, partitioning of acid between oil and water phase, dissociation of acid in water phase, metal soap precipitation in the water phase or at the interface, partitioning of the base between the oil and water phase and protonation of the base in the water phase.

quality from these dehydration steps might require additional or different treatment to reach injection or discharge criteria. This paper will focus on the dissolved components in the produced water.

Production of biodegraded crude oil is increasing as reserves of conventional light oil are running low [11]. Biodegradation is known to lower the oil quality by, for example, decreasing the API gravity and increasing the total acid number (TAN) of the crude oil [12]. The total base number (TBN) has also been found to increase with biodegradation [13]. These acids and bases in crude oil will partition themselves between the oil and water phase or at the interface depending on parameters like molecular size, structure and pH [14,15]. This article will focus on the equilibrium partitioning of naphthenic acids and bases and the interfacial interactions between such compounds.

2. Structure and properties of acids and bases

2.1. Definition

The term "naphthenic acids" has become ambiguous as noted by Grewer, Young, Whittal and Fedorak [11]. Although the traditional definition is that of a carboxylic acids with a naphthene ring, it can apparently be used to describe all organic acids found in crude oil [16,17]. Naphthenic acids have a high diversity in size and structure [18] with an average molecular weight of 300–500 g/mol [19]. On a structural basis, they are often described by the isomer $C_nH_{2n+Z}O_2$. The n represents the number of carbon atoms while Z is a negative, even integer specifying the hydrogen deficiency [20,21]. Oxy-naphthenic acids with the general formula $C_nH_{2n+Z}O_x$ have also been introduced to describe naphthenic acids with added hydroxyl groups or multiple carboxylic groups (x ≥ 3)[22] like the ARN acid responsible for calcium naphthenate deposition [23,24]. Naphthenic acids can stabilize water in oil (W/O) and oil in water (O/W) emulsions depending on several conditions, especially pH [17,25], cause corrosion [26] or naphthenate deposits [27]. They have a detrimental effect on the environment and are toxic to a variety of aquatic organisms [28]. Although acidic crude oils are problematic, the naphthenic acids can also, through their dispersive properties, limit problems related to adhesion or sedimentation [29].

The basic components in crude oil are nitrogen compounds, especially pyridines and its homologues [30–32]. Amines are generally not present or at low concentration in crude oils [30]. However, they have been used to model crude oil bases as mentioned below. The nitrogen content in crude oil is generally around 0.1%-0.9%wt [33] and studies suggest that only 30%–50% of the nitrogen compounds are basic nitrogen compounds [33,34]. There are basic components in both the resin and asphaltene fractions of crude oil although some studies found the basic fraction of asphaltenes to be small compared to the basic fraction of resins [13,34]. Both Eftekhardadkhah, Kløcker, Trapnes, Gaweł and Øye [35] and Nenningsland, Simon and Sjöblom [36] found that basic crude oil species had lower surface affinity at low pH when they are protonated compared with acidic crude oil species at high pH when they are ionized.

2.2. Oil water partitioning

In oil water systems, acids and bases will partition between the oil and water phase, depending on parameters like pH, pressure, temperature and the hydrophilic-lipophilic balance (HLB) value of the compounds. Fig. 1 depicts some of the equilibria encountered when considering acids and bases in oil water systems.

Havre, Sjöblom and Vindstad [14] studied the partitioning of naphthenic acids using crude oil acids and commercial acids. The study found that naphthenic acids in crude oil water systems had a pK_a of 4.9, which is in the lower range of the 5–6 reported by Brient, Wessner and Doyle [20]. The study also found that the linear relationship between the logarithm of the partitioning constant and the number of carbons in the molecule, reported for low molecular weight fatty acids by Reinsel [37], is also valid for higher molecular weight naphthenic acids. Touhami, Hornof and Neale [38] presented a comprehensible partitioning diagram and set of equations, accounting most of the equilibria encountered for organic acid in oil water systems, even for the partitioning of naphthenate soap back into the oil phase.

Stanford, Kim, Klein, Smith, Rodgers and Marshall [39] analyzed the water solubility of nitrogen compounds in crude oils. They found that the basic water soluble fractions of the crude oil had a lower hydrogen to carbon ratio and more nitrogen compared to the molecular distribution of bases in the two crude oils, as would be expected due to lower hydrophobic part and higher polarity. Eftekhardadkhah, Kløcker, Trapnes, Gaweł and Øye [35] studied the effect of pH on the solubility of nitrogen compounds in produced water. By mixing 7 crude oils with water at different pH they found that nitrogen concentration in water decreased with increasing pH from 2 to 8 for 6 of the 7 crude oils tested. This trend is likely caused by pyridinic nitrogen compounds which ionize at low pH. The exception could be caused by the presence of zwitterionic compounds. Hutin, Argillier and Langevin [15] studied the mass transfer of acidic and basic species from the oil phase to the water phase. A model based on the equations from Havre, Sjöblom and Vindstad [14] and Hurtevent, Bourrel, Rousseau and Brocart [19] was fitted with initial pH and final pH measurement to obtain average partitioning constants for the acids and bases. With the obtained average partitioning constants, their model could to some degree predict the final pH of a crude oil water system based on TAN, TBN and the initial pH. In a subsequent study they also reported significantly higher mass transfer of bases from crude oil when the surfactant sodium dodecyl benzenesulfonate (SDBS) was present [40]. Lord, Demond and Hayes [41] measured the distribution of dodecylamine in xylene salt-water systems over a pH range from 3 to 11. Their results show that the base had a greater affinity for the oil phase at pH values over 6 and that although the pK_a for the base was 10.6 the interfacial tension did not start to change before lowering the pH to < 8. Celsie, Parnis and Mackay [42] used COSMO-RS solvation theory to model how salinity, temperature and pH would affect the naphthenic acid concentration in water for 55 representative naphthenic acids. The predicted partition ratios had adequate fits to experimental data. Their model showed that the partitioning tendency over increasing temperature was towards unity i.e. mainly oil soluble components became more water soluble