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

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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

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 were analyzed over a pH interval using heptane as the oil phase and 3.5wt.% 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 nonionized 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.

Keywords
Equilibrium partitioning
Interfacial tension
Interfacial interaction
Partition ratio
Distribution ratio

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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 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 ($x \geq 3$)[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. Figure 1 depicts some of the equilibria encountered when considering acids and bases in oil water systems.

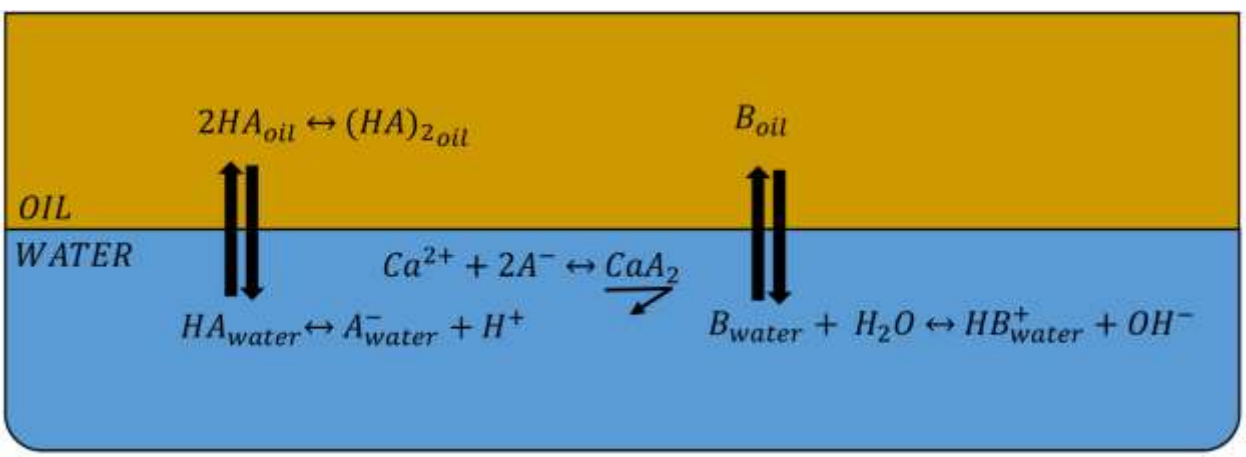


Figure 1 Schematic illustration of the acid and base equilibria that occurs in oil water systems. Depicted are dimerization of acids in oil phase, partitioning of acid between oil and water phase, dissociation of acid in water phase, metal soap precipitation in the water phase or at the interface, partitioning of the base between the oil and water phase and protonation of the base in the water phase.

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 saltwater systems over a pH range from 3-11. 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 and vice versa. They concluded that salinity has modest impact on partition and

distribution ratios compared to the high impact of temperature and pH. Their model also includes some interesting predictions of how the inclusion of a sulphur/nitrogen atom or changing a ring from aromatic to non-aromatic would change the behavior of an otherwise similar naphthenic acid.

In this study, the equilibrium partitioning of acids and bases with lower and higher molecular weight will be considered over the pH range. The goal is to determine the partitioning ratio for model acids and bases and obtain insight into how molecular weight influences the behavior of these compounds in two phase systems.

2.3. Modelling partition ratio with pH

In an oil-water system, the acids and bases in the system would partition themselves between the phases through the following equilibria.

$$HA_w \leftrightarrow HA_o \tag{1}$$

$$B_w \leftrightarrow B_o \tag{2}$$

These equilibria can be described by the following partition constants

$$K_{wo,HA} = \frac{[HA]_w}{[HA]_o} \tag{3}$$

$$K_{wo,B} = \frac{[B]_w}{[B]_o} \tag{4}$$

where $[HA]_w$ and $[B]_w$ represents the acid and base concentration in the water phase, $[HA]_o$ and $[B]_o$ represents the acid and base concentration in the oil phase, $K_{wo,HA}$ represents the partition constant of the acid and $K_{wo,B}$ represents the partition constant of the base. This partition constant is independent of concentration, but varies with temperature and pressure. Concentrations were used instead of activities as activity coefficients were assumed to be equal to 1 due to low concentrations. The carboxylic group makes the acids prone to associate into dimers in the oil phase [43]. Goodman [43] reported dimer association constants for C_8-C_{14} fatty acids in heptane to be 10^3-10^4, showing the dimer to be a stable and predominant form in the organic over a wide range of concentrations. Dimers form in the oil phase through the following equilibria

$$2HA \leftrightarrow (HA)_2 \tag{5}$$

where $(HA)_2$ is the dimer. The article by Havre, Sjöblom and Vindstad [14] stays true to the IUPAC definition [44] of the partition constant where only the monomer in each of the two phases is considered, but the article does not account for dimers in the mass balance. Equilibria like dimers give rise to numerous definitions of partition coefficient and similar terms reported in the literature [38, 41, 45, 46]. Mukerjee [47] studied dimerization of fatty acid anions in the water phase. They showed that the formation of trimers and higher aggregates are negligible compared to dimers and that the dimerization constant increase with increasing alkyl chain length, up until palmitate. Dimers of amines are also mentioned in the literature, this time in the water phase [41]. Unaccounted equilibria like dimerization, micellation and hydration can make the measured partition constant K_{wo} concentration dependent, which is why consideration should be given to what species of the compound are measured by the chosen method of analysis [45].

Scherrer and Howard [48] defined a partition ratio P_{wo} (then called partition coefficient) by the amount of nonionized compound in each phase which seems to be interpreted as the following equation.

$$P_{wo} = \frac{[HA]_w}{[HA]_{o,tot}} = \frac{[HA]_w}{[HA]_o + 2[(HA)_2]_o} \tag{6}$$

$$P_{wo} = \frac{[B]_w}{[B]_{o,tot}} \tag{7}$$

The partition ratio term is not independent of concentration, as the ratio of the two monomers in each phase would be, but it can be a more practical term due to ease of measurement. Spildo and Høiland [45] showed that the partition ratio of 4-heptylbenzoic acid did not vary much with concentration at acidic pH.

Scherrer and Howard [48] also defined a distribution ratio D_{wo} (then called distribution coefficient) which accounts for all forms of the compound in each phase.

$$D_{wo} = \frac{[HA]_{w,tot}}{[HA]_{o,tot}} = \frac{[HA]_w + [A^-]_w}{[HA]_o + 2[(HA)_2]_o} \tag{8}$$

This term can be useful when the compound can dissociate in water. For monoprotic acids and bases the term can be linked to the partition ratio by the following equations.

$$log(D_{wo,acids}) = log(P_{wo,acids}) - log\left(\frac{1}{1+10^{pH-pKa}}\right) \quad (9)$$

$$log(D_{wo,bases}) = log(P_{wo,bases}) - log\left(\frac{1}{1+10^{pKa-pH}}\right) \quad (10)$$

Equation (9) and (10) can be used to calculate the pH at which a phase shift would occur, if the pK_a and P_{wo} of the compound is known by setting the left side term to zero.

Standal, Blokhus, Haavik, Skauge and Barth [46] compared the distribution ratios of an acid (1-Naphtoic acid), a phenol (5-Indanol) and a base (Quinoline), and showed how they varied with pH. They found that the phase transfer occurred at the pK_a for all three compounds, which differs with the results from other authors [14, 48]. They also found that the unprotonated base had a higher affinity for the oil phase than both the phenol and the acid due to the lower polarity.

In the water phase, the acids and bases can also deprotonate/protonate to form their conjugate bases and acids through the following equilibria.

$$HA_w \leftrightarrow A^-{}_w + H^+ \quad (11)$$

$$HB^+{}_w \leftrightarrow B_w + H^+ \quad (12)$$

These can be described by the following dissociation constants.

$$K_{a,HA} = \frac{[A^-]_w[H^+]}{[HA]_w} \quad (13)$$

$$K_{a,HB^+} = \frac{[H^+][B]_w}{[HB^+]_w} \quad (14)$$

By introducing some new terms, the following mass balances can be applied to the system,

$$[HA]_{o,init}\,V_o = [HA]_{w,tot}V_w + [HA]_{o,tot}V_o \quad (15)$$

$$[B]_{o,init}\,V_o = [B]_{w,tot}V_w + [B]_oV_o \quad (16)$$

where $[HA]_{o,init}$ and $[B]_{o,init}$ represents the initial concentration of acid and base in the oil phase, and $[HA]_{w,tot}$ and $[B]_{w,tot}$ represents the sum of dissociated and undissociated acids and base in the water phase. The terms V_o and V_w denote the volume of the oil and water phase.

The equation sets consisting of Equations (6, 13, 15) for acids and Equations (7, 14, 16) for bases can be combined to form an expression for the total acid or base content in the water phase as presented below.

$$[HA]_{w,tot} = \frac{[HA]_{o,init}}{\frac{[H^+]}{P_{wo,acid}(K_{a,HA}+[H^+])}+\frac{V_w}{V_o}} \tag{17}$$

$$[B]_{w,tot} = \frac{[B]_{o,init}}{\frac{[K_{a,HB^+}]}{P_{wo,base}(K_{a,HB^+}+[H^+])}+\frac{V_w}{V_o}} \tag{18}$$

It is assumed that the protonated base HB^+ and deprotonated acid A^- are completely insoluble in oil phase.

If the water phase contains divalent cations like calcium, other phenomena can occur, like precipitation of metal naphthenates [49] or solvating metal naphthenates in the crude oil [50]. Spildo and Høiland [45] found that the distribution ratio was greatly affected by calcium in their studies on 4-heptylbenzoic acid. The problems related to naphthenate deposits [27] led to increased research effort for mapping the behavior of naphthenic acids in systems with divalent cations [51-54].

The solubility product constant for divalent cations with monoprotic naphthenic acids can be expressed by the following equation.

$$K_{S,MA_2} = [M^{2+}]\,[A^-]^2 \tag{19}$$

This can be combined with Equation (6) and (12) to make the following expressions for the acid concentration in oil and water at the solubility limit.

$$[HA]_{w,tot} = \sqrt{\frac{K_{S,MA_2}}{[M^{2+}]}}\left(1+\frac{[H^+]}{K_{a,HA}}\right) \tag{20}$$

$$[HA]_o = \sqrt{\frac{K_{S,MA_2}}{[M^{2+}]}}\left(\frac{[H^+]}{P_{wo}K_{a,HA}}\right) \tag{21}$$

The equations with solubility products are only valid for systems with precipitate.

2.4. Interfacial tensions of naphthenic acids and bases

Organic acids and bases can have an amphiphilic nature which allows them to adsorb and desorb at the oil-water interface and lower the interfacial tension. If the adsorption rate is larger than the desorption, then the interfacial tension decreases over time until the desorption rate matches the adsorption rate and the interfacial tension is at equilibrium [55]. Crude oil can contain both surface active acids and bases as shown by Buckley, Takamura and Morrow [56]. They demonstrated that the interfacial charge changed from negative to positive at low pH, indicating both acidic and basic species at the interface. Interfacial tension in oil water systems with an organic acid has been reported to decrease with pH [14, 57, 58], go through a minimum [59, 60] or remain constant [45, 46].

Rudin and Wasan [59] and [60] found that the interfacial tension of oleic and octanoic acid went through a minimum upon increasing the pH. The minimum occurred at the point where the acid had equal distribution in both phases and it was theorized to be a synergetic effect between ionized and non-ionized acids at the interface. Interfacial tension of naphthenic acids has been studied by multiple authors [14, 46]. As with organic acids, the interfacial tension of organic bases depend on pH [61]. Lord, Demond and Hayes [41] studied the interfacial tension of dodecylamine over various pH values and found that the interfacial tension first started to decrease well below the pK_a of the compound. Likewise, Cratin [57] showed that the interfacial tension for stearic acid continued to decrease at pH values much higher than the pK_a of the acid. The pH at the interface was shown to be related to the bulk phase pH through the following equation [14, 57].

$$pH_{int} = pH_{bulk} + \frac{e\psi}{2.3kT} \tag{22}$$

where pH_{int} is the pH at the interface, pH_{bulk} is the pH in the bulk phase, e is the electronic charge, ψ is the interfacial potential, k is the Boltzmann constant and T is the temperature. The interfacial pK_a of the acids studied by Cratin [57] and Joos [62] were calculated to be 3-5 pH values above the bulk phase pK_a, which explains why the interfacial tension continues to decrease well above the bulk phase pK_a of the acid. Much of the previously mentioned work builds on Danielli [58] who used the Donnan equilibrium to relate the interfacial pH to the bulk phase pH in his work on oleic and palmitic acid. They found that the difference between bulk pH and

interfacial pH increased with bulk phase pH for acids and decreased with salinity. For organic bases it was shown by using experimental data on hexadecylamine from Peters [63] that the difference between interfacial pH and bulk pH decreased with increasing bulk pH as one would expect. Spildo and Høiland [45] demonstrated the salinity dependence of the interfacial pH vs the bulk pH when they showed that the interfacial tension in an oil-water system with 4-heptylbenozoic acid remained unchanged at increasing pH for distilled water.

Standal, Blokhus, Haavik, Skauge and Barth [46] compared the interfacial tension over pH for acid (1-Naphtoic acid), a phenol (5-Indanol) and a base (Quinoline) of similar structure. Their results show the interfacial tension of the system with the acid to be unaffected by pH, while the system with the phenol shows a decrease of interfacial tension as the pH reaches the pK_a. The system with the base exhibits a drop in interfacial tension around pH 6, which according to the authors, show that the unprotonated base is more interfacially active than the protonated base. It should however be mentioned that none of these molecules include a hydrophobic tail.

Acids and bases can react through proton transfer in solution to form ammonium carboxylate complexes, resulting in an 1:1 complex or in the case of acid excess, 3:1 complexes as demonstrated with fatty acids and amines by Saeten, Sjoblom and Gestblom [64]. Surface properties of these complexes have also been studied [65-67] and found that the surface activity of the mixtures are greater than that of the individual components due to the strong interaction between the oppositely charged head groups. It is also reported that the ratio is usually of an equimolar nature and that the complex interactions decrease with ionic strength. Ebeltoft, Sjoeblom, Saeten and Olofsson [67] compared the compression stabilities of Langmuir films made up of one of two acids (Stearic acid and Arachidic acid) combined with one of three amines (butyl, hexyl and octyl). They found that stearic acid was only able to make a stable film with octylamine, whereas arachidic acid could make stable films with the two smaller amines. Complexes of fatty acids and fatty amines have been observed to drastically change the properties of emulsions [64]. Spildo, Blokhus and Andersson [68] studied the interfacial interactions between octanoic acid and octylamine to find that the interfacial tension was significantly lower when both acid and base were present at the interface, compared to either compound alone. The effect was shown to be greatest for equimolar mixtures. The synergetic effect was only observed when the pH of the system was such that both species were ionized.

Experimenting with amines and carboxylic acids in oil-water systems, Peters [63] mentions the appearance of a tension buffering effect, which keeps the interfacial tension around the same value over a large range of different bulk pH values.

This article aims to assess how relevant acids and bases partition between the oil phase and the water phase. The influence of chain length of acids and bases will be determined. The partition ratio P_{wo} will be evaluated at the pH where no ionized acid or base is present in the water phase. Equations (17) and (18) will be used to obtain the dissociation constant pK_a of the acid or base that gives the model the best fit. The effect of divalent cations on the partitioning behavior of the acids will be evaluated to observe if the partitioning changes in the presence of calcium. The interfacial tension of single components and mixtures of organic acids and anilines will be analyzed to observe possible acid base interactions. Bases present in crude oil are pyridine-derivatives. However, long chain pyridines are not commercially available. Consequently, we have chosen to use aniline-derivatives as the base components due to its pK_a being like the pK_a of pyridine. The choice is not a perfect one. However, we think this is better than using amine-derivatives as frequently seen in the literature. Dimerization of bases will not be considered in this study. Dimerization of carboxylates in the aqueous phase will not be considered either, based on the dimerization constants from Mukerjee [47]. Partitioning of metal soaps into the oil phase can occur, but this has not been included into the model. Data obtained through these studies will be used as a basis for subsequent studies into the kinetics of acid and base partitioning and modelling through dissipative particle dynamics (DPD).

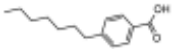
3. Materials and methods

3.1. Chemicals

The chemicals used as model acids and bases for crude oil acids and bases of different molecular weight are listed in Table 1, along with their abbreviations. The compounds were used without further purification. Compounds with an aromatic

ring were chosen to be measured with Ultraviolet (UV) spectroscopy. Heptane was obtained from Sigma Aldrich, >99% purity.

Table 1. Chemicals used as model acids and bases, their properties, structure, supplier and quality.

Name	Molecular mass (g/mol)	Chemical structure	Supplier	Purity
Phenylacetic acid (PAA)	136		Sigma	99%
4-heptyl benzoic acid (4HBA)	220		VWR	99%
4-ethylaniline (4EA)	121		Sigma	98%
4-decylaniline (4DA)	233		Sigma	97%

3.2. Equilibrium partitioning

Heptane solutions with the following concentrations were prepared: 1 mM 4HBA, 10 mM PAA, 10 mM 4EA and 10 mM 4DA. 3.5wt.% NaCl aqueous solutions were prepared with ultra-pure water (MilliQ resistivity of 18.2 Ω millipore), adjusted with 0.1 M NaOH or 0.1 M HCl solutions which also contained 3.5wt.% NaCl. Equal volumes of oil and water phase (between 10 and 15 mL) were shaken at 200 rpm for 24 h. Complete phase separation was often obtained within minutes; centrifugation was used when necessary. The pH was measured before and after. The equilibrium concentrations of both phases were determined by UV spectroscopy. When some concentrations fell below the detection limit of the UV spectroscopy, a larger volume (100 mL or 400 mL of each phase) was shaken before the water phase was removed. The pH of the water phase was adjusted before a smaller volume of pure heptane was added to the water phase and shaken over night to extract acids or bases from the water phase. The heptane phase was then evaporated to increase the concentration before UV analysis. The water phase in the high-volume experiment with low pH for the high molecular weight base (4DA) was adjusted to high pH before extraction. The water phase in the experiments with calcium contained 3.5wt.% NaCl and 10 mM $CaCl_2$. The pH of the solutions was adjusted with 0.1 M HCl solution with 3.5wt.% NaCl and 10 mM $CaCl_2$ or 0.1 M NaOH solution with 3.5wt.% NaCl.

3.3. UV spectroscopy

Calibration standards of the acids and bases in both phases were used to create calibration curves for quantification. A water phase adjusted to pH 12 was necessary to dissolve the high molecular weight acid 4HBA in the water phase. A calibration curve for the high molecular weight base 4DA in water could not be obtained due to limited solubility of this compound. The UV-vis recording spectrophotometer was of the type SHIMADZU UV-2401PC. It should be noted that the UV spectra are sensitive to pH of the aqueous phase. Adjusting the pH to lower than 2 in case of bases or higher than 12 in case of acid assures complete ionization in the aqueous solution to analyze ensured consistent absorption spectra.

3.4. Interfacial tension studies

Interfacial tension measurements were performed using a Du Noüy ring connected to a KSV Sigma 70 tensiometer. Heptane was used as the oil phase and the water phase was made up of 3.5wt.% NaCl and the aqueous buffers listed in Table 2.

Table 2 List of different aqueous buffers prepared [69]

pH	Buffers
2	0.01 M HCl
4	0.1 M CH_3COOH adjusted with NaOH
6	0.2 M KH_2PO_4 adjusted with NaOH
8.5	0.05 M Borax adjusted with HCl
10	0.05 M Borax adjusted with NaOH

Single compound experiments had heptane solutions with 1 mM of a single acid or single base.

Multi compound experiments had heptane solutions containing either 1 mM of each acid, 1 mM of each base or 1 mM of each acid and each base.

15 mL of buffer was added to the glass vessel and its surface tension was measured to check the absence of surface active impurities. 15 mL of oil phase was added

carefully to the glass vessel with the ring submerged under the aqueous surface. The interfacial tension was then measured for 6 hours. Over the course of the experiment the acids and bases in the oil phase would partition themselves between the phases depending on the pH. Evaporation of heptane was limited by covering the samples. pH was measured before and after the experiment and no variation of pH was observed.

4. Results and Discussion

4.1. Equilibrium partitioning of the low molecular weight model acid.

The equilibrium partitioning of phenylacetic acid (PAA) between heptane and 3.5wt.% NaCl water as a function of equilibrium pH is presented in Figure 2. PAA shows a high affinity for the water phase even at low pH levels and fully partition into the water phase when the pH reaches around 4.5. The partition ratio P_{wo} was calculated from the lowest pH experiments where the acid was assumed to be fully protonated in the water phase and was found to be 7.8. The pK_a was fitted to Equation (17) and was found to be 3.2, which is much lower than the reported value of 4.3 [70]. Benzoic acid is reported to have a pK_a of 4.2 and acids with the carboxyl group farther away from the aromatic ring like phenylacetic acid would be expected to have a higher pK_a [70]. However, the uncertainty associated to the pK_a value is high because the concentration of PAA in water changes by only 10% over the pH range. Consequently, the fitting of the data points with Equation (17) is difficult.

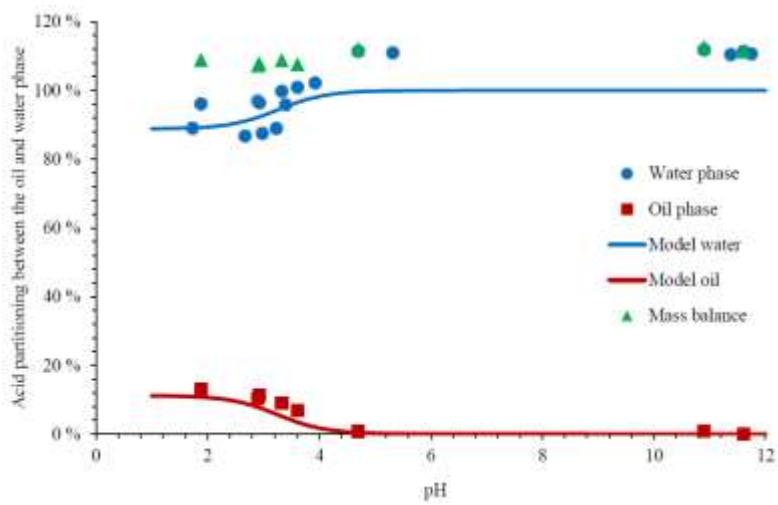


Figure 2 Equilibrium partitioning of the low molecular weight acid, Phenylacetic acid (PAA) in a heptane and aqueous phase (3.5wt.% NaCl) over a range of equilibrium pH values. Initial concentration in heptane was 10 mM, data fitted by Equation (17).

4.2. Equilibrium partitioning of the high molecular weight model acid.

The equilibrium partitioning of 4-heptylbenzoic acid (4HBA) in heptane and 3.5wt.% NaCl water as a function of equilibrium pH is shown in Figure 3. The larger acid, 4-heptylbenzoic acid, has a low affinity for the water phase at lower pH values before a complete phase transfer to heptane around pH 8 as seen in Figure 3 . The acid was first studied at the same initial concentration as the rest of the model compounds (10mM), but was diluted due to the formation of an inseparable viscous mixture at high pH levels. Spildo and Høiland [45] also encountered this problem at pH values around 8, using 1.5 mM initial concentration, 42% water cut. They noted that the problem only occurred for water containing NaCl and not with the distilled water. To measure the water concentration at low pH levels, high volume experiments with initial acid concentration of 10 mM were conducted. From the low pH experiments the partition ratio P_{wo} was calculated to be 3.7×10^{-4}. By fitting the data to Equation (17) the pK_a of 4.6 was calculated, which is somewhat lower than the pK_a of 5-6 for naphthenic acids reported by [20], although acids with an aromatic ring would be expected to have a lower pK_a. Havre, Sjöblom and Vindstad [14] obtained similar values for 4HBA with a pK_a to be 5 and the P_{wo} to be 1.2×10^{-4}, although they mention that the pK_a found was unexpectedly high and that other equilibria might have interfered. There is a discrepancy between the concentration profile predicted by Equation (17) and the measured values. This might be caused by other equilibria not accounted for in the mass balance like dimerization, hydration, micelle formation. With the obtained values P_{wo} and pK_a the distribution ratio from Scherrer and Howard [48] (Equation (9)) predicts a phase transfer around pH 8.03 which corresponds perfectly with the observed behavior. Since the maximum concentration of acid in the aqueous phase equals the initial concentration in the oil phase, the sodium naphthenate soap does not partition into the oil phase at any measurable level.

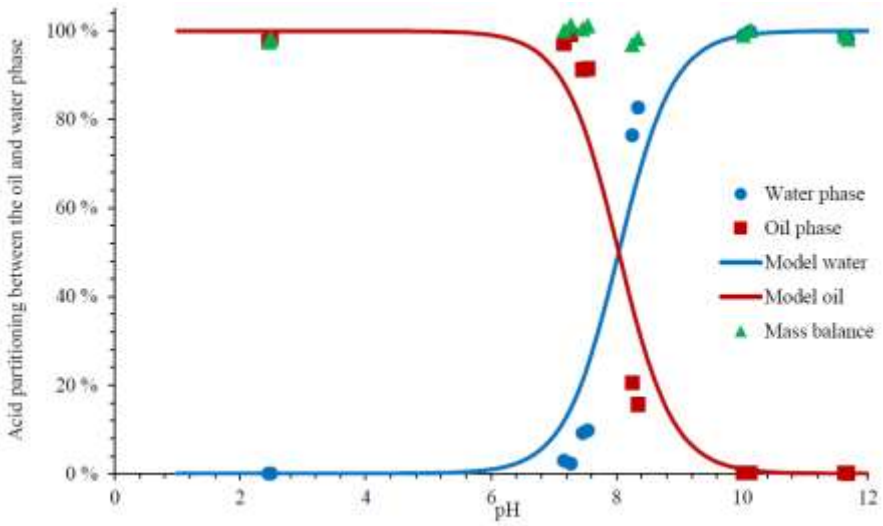


Figure 3 Equilibrium partitioning of the high molecular weight acid, 4-heptylbenzoic acid (4HBA), in heptane and aqueous phase (3.5wt.% NaCl) over a range of equilibrium pH values. The initial concentration in the oil phase was 1 mM. The data was fitted by Equation (17).

4.3. Equilibrium partitioning of the low molecular weight model base

The equilibrium partitioning of 4-ethylaniline (4EA) in heptane and 3.5% NaCl water as a function of equilibrium pH is shown in Figure 4. 4-ethylaniline is solely water soluble at low pH values, before it partially partitions into the oil phase around pH 4. At higher pH levels, around 10% of the base remains in the water phase irrespective of pH. The P_{wo} was calculated at high pH to be 0.099 and the pK_a was calculated with Equation (18) to be 5.1. This matches literature values for n-ethylaniline [71]. With the obtained P_{wo} and pK_a, the distribution ratio (Equation (10)) indicate a phase transfer at pH 4.15, from mostly water soluble at low pH to mostly oil soluble at high pH, which fits well with the observed values. The incomplete phase transfer is likely due to the increased affinity of aromatic rings towards the aqueous phase.

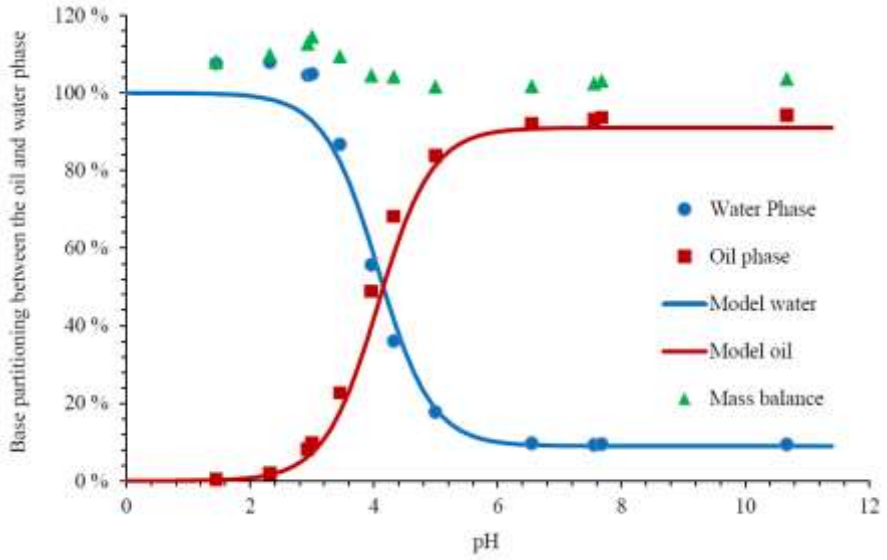


Figure 4 Equilibrium partitioning of the low molecular weight base 4-ethylaniline(4EA) in heptane and aqueous phase (3.5wt.% NaCl) given as a function of equilibrium pH. Initial concentration in heptane was 10 mM and the data was fitted with Equation (18).

4.4. Equilibrium partitioning of the high molecular weight model base

The equilibrium partitioning of 4-decylaniline (4DA) in heptane and 3.5wt.% NaCl water as a function of equilibrium pH is shown in Figure 5. The high molecular weight base 4DA did not partition into the water phase, even at low pH levels which in turn meant no water phase calibration curve could be obtained. No UV signal was registered from the water phases after the equilibrium studies. High volume (100 mL of each phase) experiments at high pH (pH 12) and low pH (pH 2) followed by heptane extraction showed that the 4DA has comparable partitioning into the water phase at both high and low pH, albeit, slightly higher for the low pH experiments as would be expected. From the high volume, high pH equilibrium experiments, the P_{wo} was calculated to be 7.8×10^{-4}. The pK_a could not be found through Equation (18) because of the low solubility of this compound in the aqueous phase.

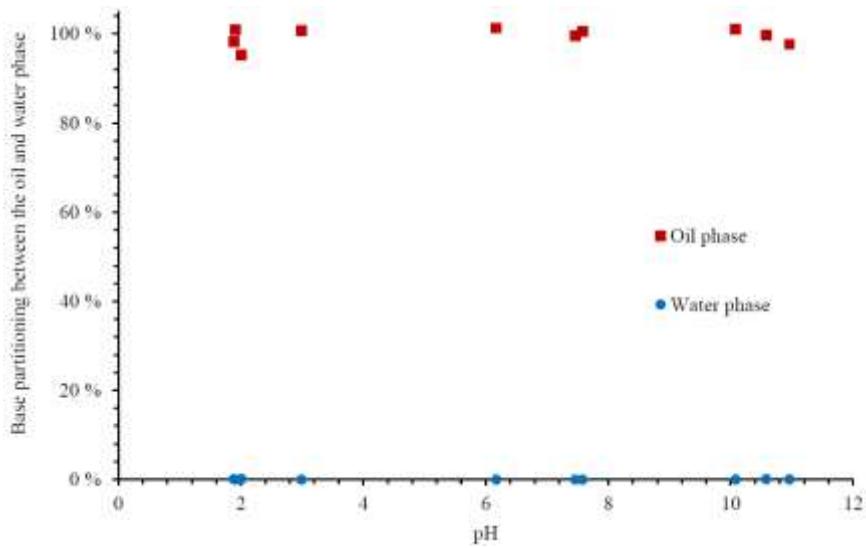


Figure 5 Partitioning of high molecular weight base 4-decylaniline(4DA) in heptane and aqueous phase over equilibrium pH (3.5wt.% NaCl). Initial concentration was 10 mM in heptane.

4.5. Comparison of P_{wo} and pK_a

Table 3 presents the P_{wo} and pK_a of the 2 model acids and 2 model bases studied in the equilibrium partitioning experiments. From the table, it can be noted that acids are more soluble than bases of equivalent molecular weight. The pK_a of the acids and bases are also similar. A good fit can be obtained with Equations (17) and (18), but it seems the influence of other equilibria can be seen in Figure 3 with 4HBA. It should be pointed out again that the partition ratio, by the way it is defined, is concentration dependent to some degree if dimerization takes place in the oil phase. However, it is used as a constant when Equations (17) and (18) are used to find the pK_a.

Table 3 Partition ratio and dissociation constants for naphthenic acid model compounds

Model compound	Initial concentration	P_{wo}	pK_a
PAA	10 mM	7.8	3.2
4HBA	1 mM*	3.7×10^{-4}	4.6
4EA	10 mM	9.85×10^{-2}	5.1
4DA	10 mM	7.8×10^{-4}	-

* The P_{wo} for 4HBA was found by using 10 mM as initial concentration due to the low absorbance in UV in oil phase obtained by using 1 mM.

4.6. Partitioning of the low molecular weight acid in presence of calcium

The influence of calcium on the partition of phenylacetic acid (PAA) can be observed in Figure 6. The addition of 10 mM $CaCl_2$ to the aqueous phase does not seem to affect the partitioning of the low molecular weight acid in the heptane water system at any pH, and the curve in Figure 6 is indeed very similar to the curve without calcium from Figure 2. From the low pH equilibrium concentrations, the P_{wo} was calculated to be 4.56 and by fitting the data to Equation (17) the pK_a was calculated to be 2.19. The uncertainties related to the calculated pK_a is discussed in the previous section regarding this acid.

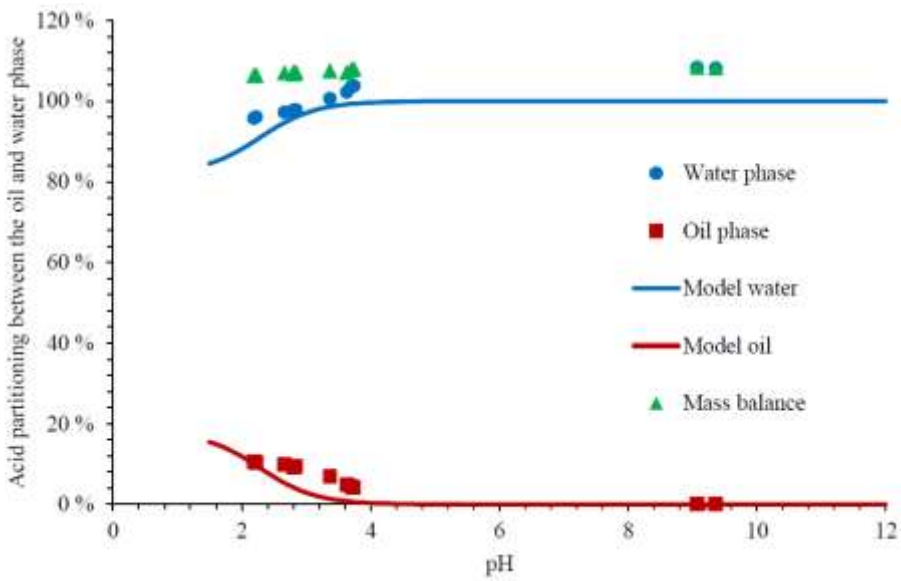


Figure 6 Partitioning of the low molecular weight acid(PAA) in heptane and aqueous phase over equilibrium pH (3.5wt.% NaCl and 10 mM $CaCl_2$). The initial concentration in heptane was 10 mM and the data is fitted with Equation (17).

4.7. Partitioning of the high molecular weight acid in the presence of calcium

Figure 7 show how 4-heptylbenzoic acid (4HBA) partition between heptane and water over equilibrium pH when divalent cations like calcium are present. When the pH was below pH 6.8, the mass balance from the measurement of the oil and water phase added up to 100%. However, when the pH was higher than 6.8, the mass balance did not add up and 4HBA started to form precipitate of calcium naphthenate. This precipitate would place itself at the interface and the amount was observed to increase with the equilibrium pH, mirroring the increasing amount of missing mass from the mass balance. Comparing the curves in Figure 3 and Figure 7 it can be seen

that with 10 mM of calcium present in the system, 4HBA transfers phase from oil to water at a lower pH (0.5) than when the system only contained sodium ions. Spildo and Høiland [45] reported stable emulsion formation at pH values over 7 upon adding calcium to their partitioning studies of 4HBA. No such stable emulsions were formed in these experiments, although it should be mentioned that the systems used are somewhat different, particularly regarding calcium concentration (10 x more). As seen in Figure 7, the concentrations of 4HBA in the water and oil phase are well-fitted by Equations (20) and (21) when pH > 6.8, where precipitates start to form. The K_s was calculated from Equations (19) and (21) to be between 1.5 and $2x10^{-10}$.

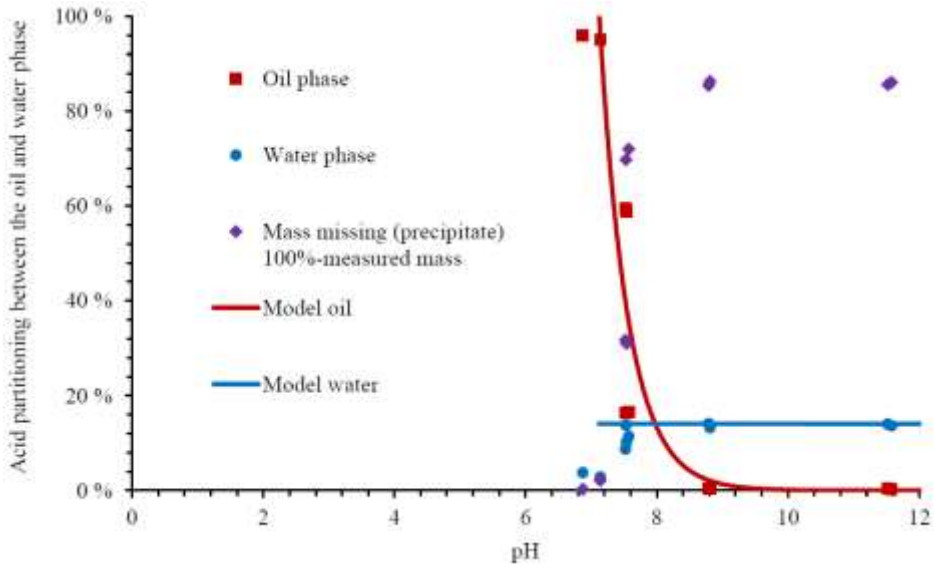


Figure 7 Partitioning of the high molecular weight acid 4-heptylbenzoic acid in heptane and aqueous phase over equilibrium pH (3.5wt.% NaCl and 10 mM $CaCl_2$). Precipitation of calcium naphthenate particles occurs. Equations (20) and (21) were used to fit the water and oil phase concentration at pH > 6.8.

4.8. Interfacial tension analysis

Before measuring the interfacial tension of solutions with acids and bases, the interfacial tension between heptane and MQ water was measured to be 51 mN/m, and it did not change significantly for the buffer solutions. The interfacial tension for the single acids and bases considered in this study are shown for various pH values in Figure 8. It can be observed that only the long chain acid 4HBA and base 4DA presents interfacial activity at high and low pH. The low molecular weight acid PAA and low molecular weight base 4EA, show no interfacial activity at the pH values explored here. This might be expected due to the short hydrophobic part of

these molecules. The system with the high molecular weight acid (4HBA) decreases slowly towards pH 6 before a noticeable drop between pH 6 and 8.5 followed by a small decrease towards pH 10. This interfacial tension change at higher pH than bulk phase pK_a is in accordance with the interfacial pK_a theories previously mentioned [57, 58]. The high molecular weight base 4DA only becomes interfacially active between pH 4 and 2. In a separate experiment it has been observed that the interfacial tension for 4DA at pH 0.5 goes towards 6 mN/m.

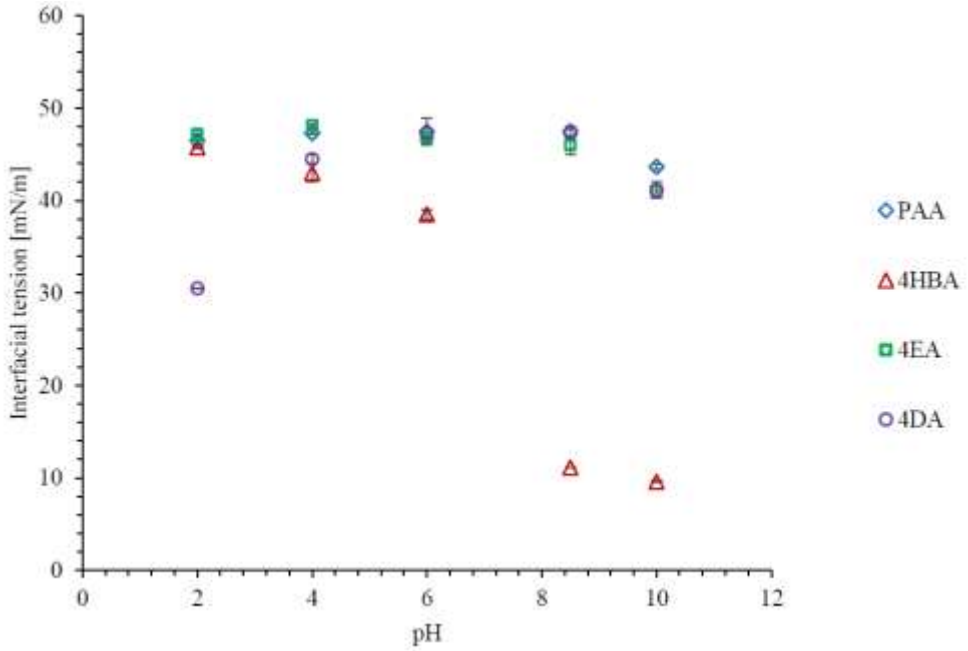


Figure 8 Interfacial tension of single components between heptane and aqueous buffers (3.5wt.% NaCl). The components were: Low molecular weight acid (PAA), high molecular weight acid (4HBA), low molecular weight base (4EA) and high molecular weight base (4DA). The initial concentration of each compound in heptane was 1 mM. Values were measured after 6 hours of equilibration. The pH was measured before and after to assure no change occurred. The values are the average of two measurements where the error bars represent the range of values

Figure 9 shows the dynamic interfacial tension of the high molecular weight acid 4HBA and gives some interesting insight into the phase transfer over the oil-water interface. A logarithmic plot of the interfacial tension data reveal that equilibrium is not completely reached after 6 hours. The values after 6 hours were reported as equilibrium values for practical reasons and are considered close to the equilibrium due to the slow variation of interfacial tension we see after 6 hours. For high pH experiments, the interfacial tension starts out at around 5 mN/m due to the fast adsorption of 4HBA at the interface, and then slowly increases towards equilibrium

as the 4HBA partitions into the aqueous phase, depleting the oil phase of acids. This is in accordance with the kinetic partitioning experiments by Spildo and Høiland [45] which show partitioning of 4HBA at pH 8 takes about 5 hours to reach equilibrium.

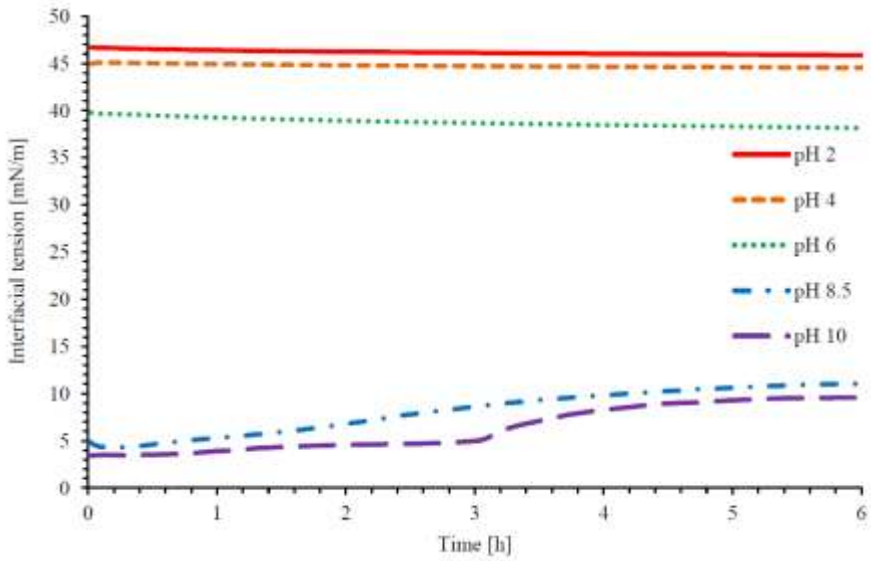


Figure 9 Dynamic interfacial tension curves for the high molecular weight acid 4HBA in oil phase over aqueous buffers of different pH values. The initial concentration in the oil phase was 1 mM.

4.9. Interfacial interactions

The interfacial tension between heptane and aqueous buffers was measured with oil phases containing 2 acids, 2 bases or all 4 components as shown in Figure 10. By comparing Figure 8 and Figure 10, the interfacial tensions of the mixtures are observed to be completely dominated by the high molecular weight acid and base at their respective active pH values. The interfacial tension of the mixture with 2 acids and 2 bases, is similar to the interfacial tension of the mixture with 2 bases at pH 2 and similar to the interfacial tension of the mixture with 2 acids at all other pH values considered. From these observations, it can be deduced that there are no interactions between acids and bases that would influence the interfacial tension. In their studies of crude oil bases, Nenningsland, Simon and Sjöblom [36] obtained a similar curve to the one seen in Figure 10 for the three mixtures of crude oil, extracted bases and non-basic crude oil.

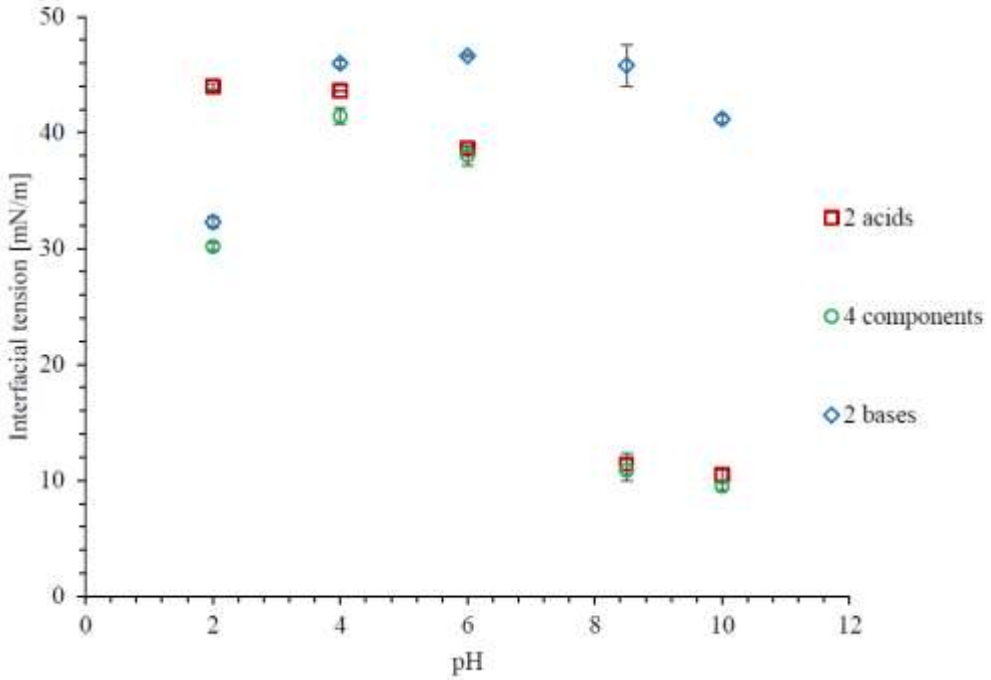


Figure 10 Interfacial tension between heptane and aqueous buffers (3.5wt.% NaCl) where the oil phase initially contained 2 acids, 2 bases or all 4 components. The heptane solution with 2 acids contained 1 mM PAA and 1 mM 4HBA, the solution with 2 bases contained 1 mM 4EA and 1 mM 4DA. The heptane solution with 4 components contained 1 mM of each acid and 1 mM of each base. The values are the average of two measurements where the error bars represent the range of values. Values measured after 6 hours of equilibration.

Table 4 presents a summary of the equilibrium interfacial tension study of the chosen acids and bases. The bases control interfacial tension at low pH. At pH 4 their contribution to interfacial tension is about equal, before the acids take control of the interfacial tension at pH 6 and above. The lack of interaction of acids and bases is most likely because the pH window, where both acid and base would both exist in the dissociated state, is much smaller for anilines and carboxylic acids than for the amines and carboxylic acids studied by previous authors. The synergetic effect of octylamine and octanoic acid occurred at pH 7 in the experiments by Spildo, Blokhus and Andersson [68]. Here, the pK_a of the amine and acid were respectively 4.8 and 10.6, indicating that the synergetic effect would occur at a pH where the distribution ratios for both species goes towards 1 (Equation (8)), i.e. the acid and base had almost equal solubility in both phases. In this respect, there might not exist a synergetic pH window where the aniline and organic acid can interact at the interface. These results also indicate that acid base complexes formed in the oil or water phase, if they exist, does not affect the interfacial tension. Moreover, since crude oil bases are mainly pyridine homologues, use of anilines with similar pK_a

would give a more accurate representation to phenomena in crude oil systems compared to amines which are not present in crude oil to any large extent.

Table 4 Summary of equilibrium interfacial tensions measured for heptane aqueous buffer (3.5wt.% NaCl) systems with 2 acids (1 mM of each acid), 2 bases (1 mM of each base) or 4 components (1 mM of each acid and 1 mM of each base) initially in the heptane phase.

pH	2 acids	4 components	2 bases
2	44 mN/m	30 mN/m	33 mN/m
4	43 mN/m	41 mN/m	46 mN/m
6	39 mN/m	37 mN/m	46 mN/m
8.3	12 mN/m	10 mN/m	44 mN/m
9.6	11 mN/m	10 mN/m	41 mN/m

4.10. Comparison of interfacial tension and partitioning

In Figure 11 the interfacial tension can be seen versus the total amount of 4HBA and corresponding carboxylate in the system. The biggest drop in interfacial tension with pH occurs between ca. 6 and 8, which corresponds to approximately the pH range at which 4HBA transfer from the oil phase to the water phase. The decrease of the interfacial tension is therefore correlated to the partition of the high molecular weight acid.

The situation is different in the case of the base 4DA. Indeed, the interfacial tension increases when the pH varies from 2 to 4 while the base stays in the oil phase as seen in Figure 5 and Figure 8. Consequently, such correlation between interfacial tension and partitioning does not exist for this compound at the pH range studied.

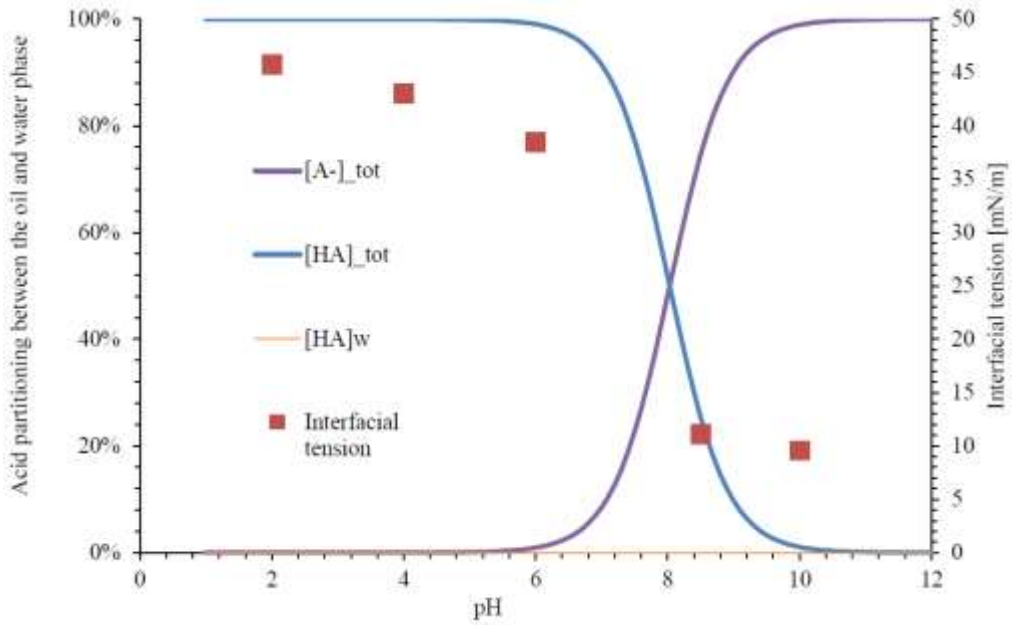


Figure 11 Summary graph showing the partitioning of the high molecular weight acid 4HBA (1 mM) and the interfacial tension at different pH values. The lines were calculated from Equation (17) and pK_a and P_{wo} reported in Table 3. Interfacial tension values measured after 6 hours of equilibration.

5. Conclusion

A simple system with model acids and bases in heptane was used to represent crude oil containing acidic and basic species. Low molecular weight acids like phenylacetic acid (PAA) would to a high degree partition in the water phase regardless of pH or cations present in the water phase. Larger acids like 4-heptylbenzoic acid (4HBA) would exist in the oil phase with moderate interfacial activity at low pH. At higher pH, the acid would be activated to accumulate at the interface and diffuse into the water phase. The high molecular weight acid is highly affected by higher valence cations like calcium and readily form calcium precipitate at higher pH values. Low molecular weight bases like 4-ethylaniline would exist in the water phase at low pH and partition into the oil phase at pH 4 and higher. The high molecular weight base did not partition to the water phase for any of the pH values explored in this article. Acids were observed to be much more soluble in water compared to bases of equal molecular weight. These results can be the basis for more studies into the kinetics of acid and base partitioning and dissipative particle dynamics (DPD) modelling.

No interfacial interactions between acids and bases could be indicated by interfacial tension studies. The reason for this is most likely the pH window in which both the acids and the base can exist in the dissociated state simultaneously. This pH window might not exist due to similar pK_a values. There is no indication of oil phase complexation between the studied acids and bases affecting the interface.

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