

Stability and interactions in mixed monolayers of fatty acid derivatives on Artificial Sea Water



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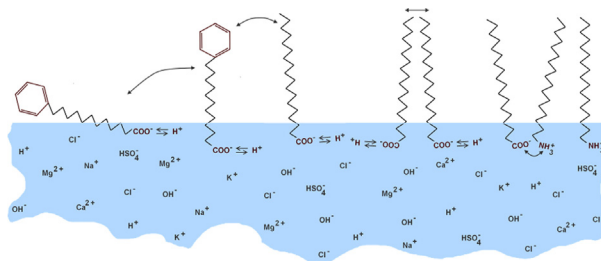
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HIGHLIGHTS

- Mixtures of stearic acid and stearyl amine at air/water interfaces show area contraction.
- Higher salinity of the sub-phase leads to stronger contraction and more stable mixed layers.
- Most stable mixtures are obtained for equal amounts of SA and SAM.
- Interfacial 12-phenyl dodecanoic acid (PDA) dissolves into the sub-phase at pH 7.
- Mixtures of SA and PDA show ideal mixing (weak interactions) at pH 3.

GRAPHICAL ABSTRACT

Schematic representation of possible interactions between SA, SAM and PDA molecules at the air–liquid interface. The possible interactions include the followings: hydrophobic interactions between hydrocarbon and phenylated hydrocarbon chains, interactions between charged head groups, and interactions between charged head groups and counter-ions present in the sub-phase.



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ABSTRACT

We studied the formation and stability of fatty acid and derivatives films on aqueous sub-phases by means of Langmuir trough experiments. Films were prepared from pure stearic acid (SA), stearyl amine (SAM) and 12-phenyldodecanoic acid (PDA), and from binary systems of SA with either SAM or PDA. For the aqueous sub-phase, multicomponent salt solutions ('Artificial Sea Water') at various concentrations (c_{ASW} , 0–100%) and pH values (3–7) were explored. SAM and SA differ most strongly at pH 7, where they can dissociate into oppositely charged species. For SA:SAM mixtures at this pH, pressure-area isotherms indicate mixing on a molecular scale. Increase of salt concentration from 0.05 to 0.5 M causes significant contraction of the layer, which is ascribed to (enhanced) electrostatic attractions between the head-groups. Relaxation experiments with these films indicate that dissolution of SAM into the sub-phase is suppressed by SA. The most stable films are formed at $x_{SA} = 0.5$, in agreement with the calculated excess free energy of mixing. PDA is much less amphiphilic than SA. (Meta-) stable mixed films of SA and PDA are formed only at high salt concentration and low pH, where the solubility of PDA into the sub-phase is the lowest. Under these conditions, SA appears to have a stabilizing effect, which is however not strong enough to prevent expulsion of PDA from interface. Isobars of SA:PDA films corroborate this picture. The weak interactions between SA and PDA are confirmed by the excess free energies of mixing, which are close to those of ideal mixtures.

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1. Introduction

Interfacial layers of amphiphilic hydrocarbons play a crucial role in enhanced oil recovery (EOR) [1–4]. These hydrocarbons naturally occur in adsorbed or chemically bonded states on rock surface [5–7], and in a dissolved state in crude oil [8–11]. When either the rock or the oil is brought into contact with an aqueous phase, new interfaces are created, providing opportunities for the amphiphiles to accumulate there. As a result, the deposited layers can desorb from the rock and disintegrate, therewith changing the wettability of the rock. In parallel, the adsorption of the amphiphiles at the oil/water interface can also lower the interfacial tension, with consequences for the manner in which the oil and aqueous phases co-exist at rest and in flow [11–15]. Although these adsorption-related key phenomena in EOR are well-known [16–20], questions still remain at the mechanistic level.

One important category hereof concerns the role of the water composition: how does the coexistence of different ions (especially the mono- and divalent cations) affect the integrity of adsorbed layers? It is known from studies in the field and in the lab that pH [21–29], overall salinity [3,21,30–32] (and sometimes even the presence of specific ions [22,23,28,33–41]) can strongly influence the ad- or desorption of amphiphilic species from interfaces with solid (S), oil (O) and air (A). Charge interactions play an important role, but it is not always clear how. The dissociation of the amphiphilic molecules is often governed by acid-base equilibria, but these equilibria can be shifted due to the electrical potential of the interface [25,42–48]. Polar solid substrates (like silica or mica) generally contribute to this potential via the dissociation of surface groups (e.g. [49–54]). For air or oil ‘substrates’ the potential is entirely set by the adsorption of the (charged) amphiphiles themselves.

In this paper we focus on air/water interfaces. This arguably more ‘simple’ system (compared to solid–water interfaces) allows focusing on the interactions of the amphiphilic molecules: (i) amongst themselves at the interface and (ii) with the ionic species in the sub-phase. The pH and salinity of the water will simultaneously influence both types of interactions. Previous studies with single component acidic amphiphiles (fatty acids) have addressed the effect of the hydrocarbon tail length, head group dissociation and counter-ion condensation on the 2D phase behaviour [25,42,44,55–75]. In a recent study, using (dilutions of) Artificial Sea Water, we found that the hydrophobic interactions between the tails dominate at low pH and low (but finite) salinity, leading to the formation of 3D solid phase. However, when the pH and/or the salinity is raised, charge interactions between the head-groups lead to suppression of this phase separation, and to an increased resistance against compression [29,76].

A second important category of questions concerns the coexistence of different types of amphiphilic molecules in crude oil (and hence also at interfaces). How do these different species interact, and how does this translate to the overall phase behaviour and mechanical properties of the interfacial layer? This type of question has hardly been addressed in the literature so far, although it is well known that crude oil contains a variety of amphiphilic components [8,77], and that the interfacial behaviour of amphiphilic mixtures can vary significantly, including synergistic or non-synergistic effects (e.g. [78–81]) affecting mechanical properties (stability) of the interfacial films (e.g. [82]). We address this issue in our present work, focusing at air/water interfaces and varying the aqueous composition. Here, we restrict ourselves to binary mixtures of amphiphiles. Inspired by the distinctions that can be made between the types of amphiphiles occurring in crude oil, we consider two mixtures.

In the first mixture, the difference between the two molecules lies entirely in the type of head-group, being carboxylic acid for

one, and amine for the other. The hydrophobic tail is an octadecyl chain. Individually, both stearic acid (SA) [29,62–64,83–85] and stearyl amine (SAm) [76,86–90] are relatively well characterised regarding their interfacial behaviour, but on their mixtures only few studies have been undertaken [78,91]. At (near-) neutral pH both molecules show partial dissociation, leading to oppositely charged head-groups. While this could lead to the formation of a molecularly mixed phase [78], also segregated phases of SA and SAm have been found [91], indicating meta-stable behaviour. An interesting question is how the strength of the attraction between the head-groups of interfacial SA and SAm compares to the interactions of these groups with the counter-ions in the aqueous sub-layer. Varying the salt concentration should provide a suitable way to study the relative importance of these interactions.

In the second mixture the head-group is carboxylic acid for both amphiphiles, but the hydrophobic tail is different: one has an octadecyl chain (SA) while the other one contains an aromatic group. By choosing 12-phenyldodecanoic acid (PDA), the number of carbon atoms is kept the same. SA and PDA could be regarded as simplistic representations of the naphthenate and asphaltene fractions in crude oil (we remark that this would be in the context of interfacial behaviour only, and that other model representations of crude oil fractions by single molecules have been proposed [92–95]). Despite having the same functional group and the same number of C-atoms in the tail, the interfacial behaviours of SA and PDA might be very different. The ability of PDA to form stable monolayers is expectedly governed by the properties of the hydrocarbon chain (rather than the functional group). Since the phenyl group of PDA is more ‘bulky’ than the octadecyl chain of SA, the interactions between the hydrophobic chains are expected to be less attractive for the PDA. Besides that, the amphiphilic character of PDA should be less strong since the phenyl group is more polar than the octadecyl group. While the behaviour of PDA at A/W interfaces has never been studied (as far as we know), some findings were published on phenylated fatty acids containing diacetyl groups. Yoshioka [96] reported that on water sub-phases at pH 6.8, the stability of monolayers of such molecules increases with number of CH₂-groups separating the phenyl and diacetyl groups. As there is no diacetyl group in PDA, the molecules having the largest separation between the phenyl group and diacetyl group might offer the closest resemblance in behavior. The behavior of PDA:SA mixtures is more difficult to predict: the dissimilarities between PDA and SA might result in interfacial phase separation, but molecular mixing is also conceivable.

To study these interfacial phenomena, we performed experiments on a Langmuir trough. Isotherms were analysed for extracting information about the interactions between adsorbed species, both via the signature of the entire π -A curve, and via the specific molecular areas and pressures at which transitions are found. Moreover, they were also analysed for the excess free energy of mixing, as a function of the mixing ratio (and the salinity of the aqueous sub-layer). Isobars were measured to quantify the loss rate of material at selected values of the surface pressure. The dependence of these rates on the amphiphile mixing ratio and the sub-layer salinity were analysed to infer about which component is expelled from the layer, and what the mechanism might be. This work can be considered as a follow-up on a study in which we studied the interfacial behaviour of pure SA on a variety of Artificial Sea Water sub-phases [29].

In this paper, we will present clear indications that in SA:SAm mixtures, charge-induced contraction can take place, provided that the pH is near neutral, and that the amphiphiles are mixed at the molecular level. We will also show that in SA-PDA mixtures the interactions between the two amphiphiles are rather weak.

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