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# Model compounds for $C_{80}$ isoprenoid tetraacids
# Part II. Interfacial reactions, physicochemical properties and comparison with indigenous tetraacids

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ABSTRACT

Novel model compounds are desired to study properties of a narrow group of tetrameric acids from crude oil mainly responsible for naphthenate deposition. It is important to make a comparison to find to what degree the model compounds can reflect the properties of the indigenous tetraacids and where there are deviations, before using the model compounds in naphthenate research. A comparison between two synthesised model compounds and indigenous tetraacids has been carried out regarding physicochemical properties including thermal solid state properties, critical micelle concentrations, monolayer properties and interfacial reactions. Of the two studied model compounds, one was observed to form the same cross-linked network with $Ca^{2+}$, a typical feature of the indigenous tetraacids. Interfacial reactions using the pendant drop technique also showed that four different divalent cations could all form this network with the model tetraacid. The film formation was however dependent on the ratio $M^{2+}$/TA. The main deviations were in the solid state, where the model compounds showed crystalline transitions, contrary to the indigenous tetraacids. We conclude that the two different model compounds mimic the indigenous tetraacids well with respect to several of their properties and are suitable for use in naphthenate research.

## 1. Introduction

Naphthenate deposition in crude oil recovery and transportation is a severe problem for the oil industry. During transportation from the well, the naphthenic acids dissociate due to pressure drops leading to increased pH. The pressure drop is causing dissolved $CO_2$ to be released as gas which affects the bicarbonate equilibrium in the produced water to consume $H^+$. The formed naphthenates react with metal ions from the produced water to form metal naphthenates [1]. Depending on the type of both the acid and the cation, the metal soaps can either be dispersed in the oil bulk phase or, more seriously, accumulate over oil–water interfaces in topside separators and de-salters. Naphthenates that accumulate at the oil–water interface may contribute to the formation of highly stable emulsions [2].

The naphthenic acids in crude oil are a complex mixture of thousands of different structures. These acids are mainly monoacids which can be either cyclic or linear, in addition to containing aromatic moieties [1]. However, even though the monoacids dominate in the bulk phase, a narrow group of four-protic naphthenic acids with a molecular weight around 1230 g/mol has been shown to dominate in the deposits. These tetraacids are orders of magnitudes more interfacially active than monoacids [3]. The structure of the tetraacids was determined after extensive NMR research by Lutnaes et al. and a $C_{80}$ tetraacid with six cyclic rings was found [4]. Later, HPLC studies showed that the deposits also contain other isomers with 4–8 cyclic rings, including traces of methyl-substituted $C_{81}$ and $C_{82}$ structures [5,6]. The presence of each isomer and relative amount may vary from well to well. Tetraacids are found in crudes all over the world from oilfields offshore Norway to West-Africa and China, among others. An archeal origin has been proposed to be the source of these membrane-like tetraacid structures [4]. The tetraacids from crude oil are sometimes referred to as ARN acids or $C_{80}$ isoprenoid tetraacids. In this paper we refer these as indigenous, native or isolated tetraacids.

While common monoacids have intermediate interfacial activity, the indigenous tetraacids lower the interfacial tension between 10% toluene in hexadecane and a pH 9 aqueous phase to 12 mN/m at only 0.005 mM as determined by the pendant drop technique [3]. In the same study, the molecular area of tetraacids was determined by the Langmuir technique and found to be about 160 Å$^2$. This would indicate that the tetraacids are directing all four acid groups to the interface, and most likely separated by parts of the hydrocarbon chains. Depending on the conditions in the subphase, like pH and presence of divalent cations, the tetraacid molecules

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in the monolayer film might be able to flip from a conformation were all acid groups are pointing towards the interface, to a conformation similar to a trans-membrane structure with two of four acid groups pointing towards air [3,7,8]. Increasing pH and presence of $Ca^{2+}$ appeared to prevent the molecules from flipping. As pointed out by Brandal et al. [8] this is analogous to the conformation of bipolar tetraether lipids in biological membranes. A future commercial use of tetraacids might be preparation of vesicles mimicking a cell membrane. This will however not be an issue in this study.

Calcium is the dominating metal ion species in tetraacid deposits. A cross-linked polymer-like structure is proposed for the calcium naphthenate film [7]. The cross-linking makes the film more elastic than viscous. In fact interfacial dilatational rheology measurements have shown that both the tetraacid and the calcium salt films were elastic in nature, and the elasticity being much larger for the calcium containing system [7]. The high interfacial activity of tetrameric acids in combination with the formation of a cross-linked network is believed to be the most essential factors for the deposition problem. Another feature of the tetrameric naphthenic acids is the presence of glass transitions in DSC measurements, similar to polymer systems, found both for the isolated acid and for the calcium salt [7].

Even though the knowledge about this interesting class of surfactants has increased during the latest years, the isolation and characterization of tetraacids remain challenging. The isolation procedure is time – and solvent consuming [9], the purity of the isolated product may vary [7] and the chemical structures of tetraacids reveal no UV active moieties, making bulk concentration characterization dependent upon chemical derivatisation [10]. In order to circumvent some of the difficulties associated with the isolation and characterization of native tetraacids, we have recently synthesised tetraacid model compounds [11]. In the model acids an aromatic core is attached to four hydrocarbon chains with terminal carboxylic groups. This allows us to study the compounds by spectroscopic methods. Two model compounds with different aromatic cores were synthesised and investigated. Synthetic model compounds also give a better control over the purity and composition. The model compounds were extensively characterized with respect to interfacial properties. They were found to have similar high interfacial activity as the native tetraacids rendering them suitable model compounds.

In this paper, we present physicochemical properties of tetraacid model compounds, both in bulk and at interfaces, and compare them to those of the indigenous tetraacids. In addition, we have studied reactions between tetraacid model compounds and different divalent cations at the oil–water interface.

## 2. Experimental

All chemicals and solvents used were purchased from Sigma–Aldrich and used without further purification. Tetraacid model compounds were synthesised according to previously reported literature procedure [11]. Their structures, molecular weights and abbreviations are shown in Fig. 1, together with the most common tetraacid found in deposits. Indigenous tetraacids were isolated from a deposit collected at a Norwegian offshore field according to an ion-exhange resin method described elsewhere [9].

Determination of critical micelle concentrations (CMCs) for indigenous and model tetraacids was carried out using two different techniques. First by measuring the dynamic surface tension at equilibrium of an aqueous phase as a function of concentration using a CAM 200 pendant drop equipment (KSV Instruments, Finland). The instrument is equipped with a CCD video camera with telecentric optics, a frame grabber and a LED based background light source. The diameter of the syringe was 0.7 mm for BP10 and indigenous tetraacids, and 1.6 mm for Pe10. Three tetraacids were dissolved in aqueous solutions. The pH was set to >11 in order to gain sufficient aqueous solubility and diluted to the desired concentrations and the equilibrium surface tension was recorded at each concentration. Secondly, surface tension measurements were performed using a Sigma70 Tensiometer (KSV Instruments, Finland) using a De Nuoy ring probe. The solutions were the same as used in the pendant drop experiments. A CMC could not be obtained for the indigenous tetraacids with the latter technique, however.

The pendant drop equipment was also utilized to investigate the dynamic interfacial tension during addition of different divalent cations to an aqueous solution with an oil droplet immersed. A tetraacid, BP10, was dissolved in the oil phase, 1-octanol, (99%, spectrophotometric grade) to a concentration of 1 mM and an oil droplet

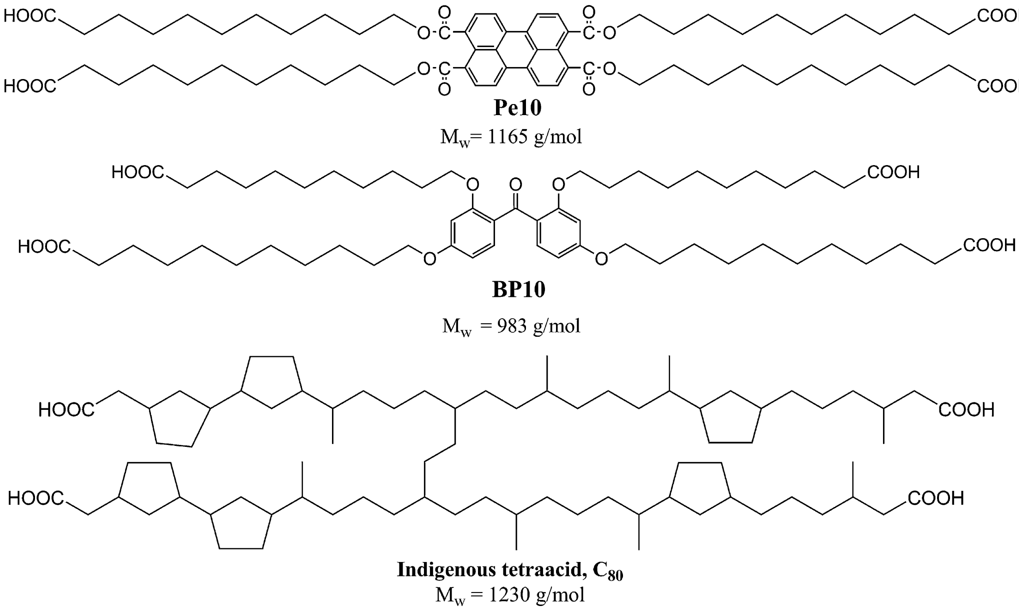

**Fig. 1.** Structures, molecular weights, and abbreviations of tetraacids used in the study. Pe10 and BP10 are synthesized model compounds, while the indigenous tetraacids are isolated from crude oil deposits. Only the most common $C_{80}$ analogue is shown [4].