Model Molecules Mimicking Asphaltenes

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1 Abstract

Asphalthenes are typically defined as the fraction of petroleum insoluble in n-alkanes (typically heptane, but also hexane or pentane) but soluble in toluene. This fraction causes problems of emulsion formation and deposition/precipitation during crude oil production, processing and transport. From the definition it follows that asphaltenes are not a homogeneous fraction but is composed of molecules polydisperse in molecular weight, structure and functionalities. Their complexity makes the understanding of their properties difficult. Proper model molecules with well-defined structures which can resemble the properties of real asphaltenes can help to improve this understanding. Over the last ten years different research groups have proposed different asphaltene model molecules and studied them to determine how well they can mimic the properties of asphaltenes and determine the mechanisms behind the properties of asphaltenes.

This article reviews the properties of the different classes of model compounds proposed and present their properties by comparison with fractionated asphaltenes'. After presenting the interest of developing model asphaltenes, the composition and properties of asphaltenes are presented, followed by the presentation of approaches and accomplishments of different schools working on asphaltene model compounds. The presentation of bulk and interfacial properties of perylene-based model asphaltene compounds developed by Sjöblom et al. is the subject of the next part. Finally the emulsion-stabilisation properties of fractionated asphaltenes and model asphaltene compounds is presented and discussed.

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3 Background

Asphaltenes are typically defined as the fraction of petroleum insoluble in n-alkanes (typically heptane, but also hexane or pentane) but soluble in toluene[1-3]. They are typically present in concentration varying from 0 to tens of percents[4]. This fraction is responsible for different problems in oil industry that can impart the transportation (flow assurance) and the processing of crude oils. For instance

-asphaltenes can precipitate and give rise to organic deposition phenomena in reservoirs, wells, piping and equipment by change of pressure[5-7] or mixing with incompatible fluids[8, 9]. This can lead to costly production flow restrictions and unplanned production outages.

-they are responsible for formation of stable emulsions[1] created at different stages in the oil production chain. Since these emulsions must be destabilized to get specified values of product quality (generally lower than 0.5 wt % of water), emulsion stabilisation properties of asphaltenes have been thoroughly studied[1, 10-12].

From their definition it follows that asphaltenes are not a homogeneous fraction butconsist of polyfunctional molecules. The complexity and unknown molecular structure of asphaltenes make the understanding of their properties difficult. Two strategies exist to overcome this problem:

-Fractionate the total asphaltene content into sub-fractions of reduced complexity. Different procedures have been used: multiple precipitation of asphaltenes with different n-alkane/crude oil volume ratio[13, 14] or toluene/n-heptane volume ratio[15, 16], ultracentrifugation[17, 18], ultrafiltration[15, 19]… Although this strategy is interesting, the asphaltene fractions obtained are still very complex and polydisperse.

-Develop and study model compounds, i.e. synthesized model molecules with well-defined structures similar to "average" asphaltene molecules and properties similar to real asphaltenes. This strategy represents a fundamental approach since the complexity of asphaltene composition is reduced to the study of solutions containing a single molecular species of known structure.

Over the last ten years different research groups have proposed a variety of asphaltene model molecules and studied them to determine how well they can mimic the properties of asphaltenes and the mechanisms behind the properties of asphaltenes. For instance:

-Akbarzadeh et al.[20] studied the self-association properties of derivatives of pyrene and the properties of hexabenzocoronene as a model for asphaltenes[21].

-The group of Prof. Murray Gray in Canada has studied the self-association properties of pyrene derivatives of 2,2′-Bipyridine[22]. The group has also used other model compounds top study the thermal cracking and coking of asphaltenes. These model compounds were either pyrene-based molecules or derivatives of 5α-cholestane, covalently fused to a range of differentially substituted benzoquinoline groups[23, 24].

-Bhattacharjee and Masliyah in Edmonton studied different model molecules both in bulk and at interfaces by molecular modelling (MD). The molecules studied were chosen to represent different models proposed to represent common structural and compositional aspects of petroleum asphaltenes: continental model, archipelago model and anionic continental model[25-27].

-The Ugelstad Laboratory (Prof. Sjöblom) designed first generation of asphaltene model molecules incorporating a fixed hydrophobic part with a branched alkyl chain attached to a polyaromatic core, while varying the nature of the polar group. This class of model compounds gives polyaromatic surfactants with the number of aromatic rings and molecular weights being in the range of single asphaltene molecules. Moreover a part of the structure can be modulated to determine the influence of the chemical structure. This family of molecules has been shown to account for central interfacial properties of asphaltenes[28-31,32, 33].

In this review article, the different approaches and accomplishments of different schools working on asphaltene model compounds are summarized. The different experimental techniques used to study their properties will not be presented in this review, since most of them have already been presented elsewhere[34, 35].

4 Asphaltenes

4.1 Structure

Crude oils are continuums of tens of thousands of different hydrocarbon molecules. Due to this complexity, characterization of a crude oil sample by determining its composition on a molecular basis is not possible even if attempts in this direction exist (domain of petroleomic[36, 37]). Instead, hydrocarbon group type analysis is commonly employed[38-46]. The traditional SARA-separation is an example of such group type analysis, separating the crude oils in four main chemical classes based on differences in solubility and polarity. These groups are in terms of increasing polarity of molecules: Saturates, Aromatics, Resins, Asphaltenes. At room temperature, saturates, aromatics and resins are liquid while asphaltenes are dark brown or black solids which do not melt.

The determination of molecular weight of asphaltenes has been the object of a long controversy[47]. Indeed the obtained results varied from few thousands to several hundreds of thousands g.mol^{-1}. This was a consequence of the fact that asphaltenes self-associate even in good solvents such as toluene at low concentrations (≈10-100 mg.L^{-1})[42]. Since experimental techniques used to measure the molecular weight generally required the measurements at higher concentration, the obtained results were influenced by the presence of asphaltene aggregates in solution. For instance Small-Angle X-ray and Neutron Scattering (SAXS and SANS) experiments were generally performed at concentrations close to 10 g.L^{-1} for asphaltenes dissolved in model solvents[17, 18, 48-51]. It was not until 1999, using techniques such as fluorescence depolarization technique[52-56], fluorescence correlation spectroscopy[57-59] and mass spectrometry[60, 61] that reliable results, accounting for the molecular aggregation at higher concentrations, became available. These results have shown that typical mean molecular weights of asphaltenes were ~750 g.mol^{-1} with a factor of 2 in the width of the molecular weight distribution.

Two models to describe the structure of asphaltenes have been presented in the literature: the archipelago and the continental models. In the first model asphaltenes were thought to consist of small polyaromatic parts linked together by aliphaltic or naphthenic moieties, while the second model considered asphaltene molecules of a single polyaromatic ring with linked aliphaltic or naphthenic chains[62, 63]. The size of the polyaromatic rings have been assessed by direct molecular imaging with high-resolution transmission electron microscopy[64] and by studying the UV-visible spectra of asphaltenes coupled with molecular orbital calculations[65]. It seems that on average the polyaromatic parts of asphaltenes are composed of 7 fused aromatic rings. Asphaltenes often concentrate the major part of the heteroatoms (Nitrogen, Oxygen and Sulfur) and metallic elements (Nickel, Vanadium) present in a crude oil. It is well established that asphaltenes contain both acid and basic functionalities since they have both total base and acid numbers (TBN and TAN)[66-68]. The basic components are mainly derivatives of pyridines and its benzologs[69, 70] while carboxylic acid and phenolic functions has been indentified in asphaltenes[2].

4.2 Fundamental Properties

4.2.1 Self-Association

Asphaltenes are known to self-associate in solution both in crude oils[71] and in model solvents such as toluene. This association starts at low concentrations in solution. Mullins et al. defined the critical nanoaggregate concentration by observing an anomality in the variations of some solution properties with the concentration at a given asphaltene concentration (~100 mg L^{-1} in toluene[72-75]). The properties they investigated included ultrasonic velocity[72], DC conductivity[74], ultrasedimentation rate[75] and density[72]. They attributed this shift to the appearance of nanoaggregates in solution.

Variations of the surface tension with the asphaltene concentration performed in toluene showed a break point [76, 77]. This abnormality was previously attributed to the formation of micelles as often seen in surfactant aqueous solutions, and hence referred to as "Critical Micellar Concentration" (CMC). Considering special characteristics of asphaltene molecules, new investigation proved CMC concept of asphaltene solutions to be misleading. In fact, the surface tension of pure toluene is quite low. The addition of high interaction energy asphaltene molecules to toluene would increase instead of decrease the surface tension as was measured. As a consequence the association of asphaltenes in organic solvents cannot be compared with surfactants in aqueous solution where the surface tension effects are high (several decades) and the micellization is compared to a phase separation. The small changes in toluene reflects more a stepwise association[78].

The self-association properties of asphaltenes have been extensively studied by measuring the average molecular weight of species in solution. It was noticed that the self-association depends on thermodynamic conditions such as the nature of solvents, temperature and/or pressure as well as the presence of co-solute such as resins[18, 79-81]. Several molecular association models have been proposed in the past to explain the observed self association of asphaltenes molecules. The most relevant are:

-The peptization model proposed by Pfeiffer et al.[82]. They proposed as early as 1940 that asphaltenes form colloids in crude oil that are peptized by resins and the structure is surrounded by lighter constituents of less aromatic nature and so on, until a gradual and nearly continuous transition of the system to the intermicellar phase.

-The fractal model. In this model the asphaltene aggregates are considered as fractal aggregates, indicating a relationship between the molecular weight of aggregates M and their radius R:

$$M = A \cdot R^{Df} \qquad (1)$$

with Df being the fractal dimension of asphaltene aggregates (≈2). The fractal dimension Df represents the compactness of the aggregates (as a comparison Df=1: extended, Df=3: compact). The fractal objects are denser in the centre of the aggregates than at the periphery. This model was proposed based on SAXS and SANS data[17, 48, 79].

-The Yen model. This model was proposed in the 60s from analysis of X-ray diffraction data[83, 84]. This model assumed a first level of aggregation to "particle" by π-π stacking of polyaromatic parts of asphaltene molecules. The particles can self-associate to form the larger asphaltene aggregates per se.

-The modified Yen model[63, 85]. Yen model was further refined by considering 6 asphaltene molecules in self-association to form nanoaggregates. These asphaltene nanoaggregates can then form clusters with aggregation numbers estimated to be ~8.

Finally it must be mentioned that the bulk properties are not homogenous in an asphaltene samples. For instance Barré et al. separated asphaltenes into several fractions by ultracentrifugation[17, 18]. They then dissolved these fractions in toluene and determined that the size of aggregates formed and their viscometric properties vary in large extents and are different from the unfractionated asphaltene. Similar conclusions on the self-aggregation properties were drawn by Fossen et al.[13, 86] for fractions obtained by fractionating asphaltenes using different *n*-alkane/crude oil ratios.

4.2.2 Interfacial properties

Asphaltenes are considered surface active based on the fact that they adsorb at both the solid/liquid[79, 87-90] and liquid/liquid[91] interfaces.

4.2.2.1 Adsorption at Solid/liquid interfaces

The adsorption onto solid surfaces has generally been studied by determining the amount of adsorbed asphaltene using the depletion method[90, 92], quartz crystal microbalance[93], photothermal surface deformation spectroscopy[87], and contact angle measurements[94, 95]. Considering a free energy variation of asphaltene adsorption in the order of about 10 kJ mol^{-1} [94], asphaltene adsorption onto solid surfaces is considered of physisorption type. The presence of an adsorbed asphaltene layer causes an increase in the surface contact angle and therefore in the hydrophobicity of adsorbing surfaces such as silica[94, 95]. Determining the organization of adsorbed asphaltenes at a solid/liquid interface has been the subject of several articles, most of them being on adsorption of asphaltenes dissolved in model solvents (mixture of toluene and heptane). Although several authors reported Langmuir-type isotherms, indicating formation of a monolayer of asphaltenes at the interface[79, 90, 94, 96, 97], others found stepwise or linear adsorption isotherms that suggest a multilayer adsorption process[87, 88, 98]. The findings must be related to concentration and state of asphaltenes in the organic solvent.

4.2.2.2 Adsorption at liquid/liquid interfaces

Asphaltenes adsorb at the liquid/liquid (water/oil) interface as showed by interfacial tension measurements. The adsorption kinetics display two distinct regimes, a rapid adsorption followed by a very slow adsorption process which for several hours before the final equilibrium (if any) is reached[91, 99]. Several explanations have been presented to explain this slow adsorption kinetics such as competitive adsorption between different asphaltene molecules, reorganisation of the adsorbed molecules and buildup of 3D interfacial network through interactions/bonds between asphaltene molecules at interface. Several authors have proposed phenomenological equations to fit the asphaltene IFT[13, 91]. Under the assumption that asphaltenes are not adsorbed as single molecules but instead as larger aggregates, Jerebi et al.[91] described the variations of the interfacial tension data of asphaltene solutions in toluene with time using a monoexponential decay equation initially proposed to describe protein adsorption. With this model, they conclude that asphaltenes diffuse very fast and that the changes in IFT are due to reorganization at the interface. Fossen et al. proposed a four-parameter bi-exponential model was proposed to describe the IFT variations with time[13]. The parameters account for rate at which the IFT decays in two parts: fast decrease at short times and slow decay at longer times. This is due to differences in the relaxation processes at the interface which could be a consequence of slow/fast diffusion, adsorption barriers, reorganization of the asphaltene network and partitioning. Similar equation was used by Fan et al.[100] to describe the competitive adsorption between asphaltenes and model demulsifiers.

The adsorption of asphaltenes at oil-water interface depends strongly on a number of physicochemical properties of the system such as pH of the aqueous solution[101], asphaltene solvation state[102, 103] and nature (polarity or aromaticity) of organic phase. Nenningsland et al.[103] studied the influence of solvency on the interfacial properties of asphaltenes by measuring interfacial dilational rheology at varying xylene/heptane ratio. The elastic modulus of the interface displayed a gradual increase when the ratio of heptane increased. This indicates that the asphaltene molecules formed a more elastic film due to stronger interactions between asphaltenes at the interface when their affinity to the solvent decreases. Poteau et al.[101] showed that the interfacial tension of brine/asphaltenes in xylene systems is the highest at neutral pH. This is due to the fact that the functional groups of asphaltenes become increasingly charged at high or low pH, thereby enhancing asphaltene surface activity and lowering the interfacial tension.

It has been discovered that asphaltenes form a rigid film or “skin” at the oil-water interface[91]. When a water drop is formed in an asphaltene-containing oil phase, the surface becomes extremely rigid after aging. This phenomenon is easily observed by contracting the water droplet, shown as visible crimples at the interface. Interfacial rheology is a powerful technique to characterize the “skin” state. In terms of the deformation of the interface, two sub-techniques can be identified: dilational and shear[104]. Dilational experiments involve changing the area of the interface by expansion or contraction of the interface, while keeping the shape intact. Shear experiments, on the other hand, change the shape of the interface without any variations in the area.

Using interfacial shear rheology Fan et al.[105] and Kilpatrick et al.[10, 106] showed that both elastic (G’) and plastic (G’’) moduli increase with time and, similarly to IFT experiments, no equilibrium is reached after a long period of time. Under some conditions, the rheological properties of the asphaltene layer were characteristic of a gel. The authors also noticed that G’ increases when the solubility of asphaltenes in the bulk decreases. Dilatational rheology experiments using an oscillating pendant/sessile drop tensiometer by Bouriat et al.[107] Sjöblom et al.[108, 109] and Yarranton et al.[110, 111] also showed that asphaltenes form an elastic structure at the liquid/oil interface.

Similar to the bulk properties mentioned in section 4.2.1, molecules in asphaltene samples exhibit different surface properties due to the polydispersity. For instance, Fossen et al. fractionated asphaltenes into four different fractions and showed that they decrease interfacial tension when solubilised in toluene to different extends[14, 112].

5 Model Compounds

5.1 Gray, Kilpatrick and Yarranton (2005-2008)

Gray, Kilpatrick and Yarranton designed and characterized a series of model molecules to mimic the solution properties of asphaltenes, in particular the structural factors ruling their self-association tendency[20-22]. Three different families of model compounds were involved:

-first derivatives of pyrenes[20] (list of molecules in figure 1),
-pyrene derivatives of 2,2′-Bipyridine[22] (figure 2 left),
-alkylated hexabenzocoronene[21] (figure 2 right)

The self-association of pyrene derivatives were first studied by determining their aggregation number in aromatic solvent using vapor pressure osmometry and neutron scattering[20]. The non-polar compounds pyrene and alkyl-bridged dipyrene did not present significant association in the solvent tested (compound I and II, figure 1). On the contrary the polar alcohol or ketone-modified pyrene compounds (III, IV and V) all showed evidence for dimer formation in solution, but without further extensive association. Hence the polar functional groups contribute to association behavior. Clearly the limited aggregation properties of pyrene derivatives did not match the observed higher aggregation level of indigeneous asphaltenes in similar solvents. This discrepancy indicates that the pyrene derivatives proposed in Figure 1 lacked central features to mimic the behavior of asphaltenes in solution.

Next the self-association properties of the pyrene derivative: 4,4′-bis-(2-pyren-1-yl-ethyl)-[2,2′]bipyridinyl (PBP) was mapped (Figure 2 left)[22]. The onset of aggregation for PBP in solution was in the same concentration range as asphaltenes. This compound is also shown to form dimers in toluene solution, which does not match the aggregation behavior of asphaltenes. Based on the studies using nuclear magnetic resonance, steady state fluorescence, vapor pressure osmometry, solubility and adsorption behavior, and single crystal X-ray diffraction analysis, the association was attributed to π–π stacking interaction involving both pyrene rings and the bipyridine spacer.

Since pyrene derivatives were found to form, at most, dimers in solution, Rakotondradany et al.[21] studied the solution behaviour of larger polynuclear aromatic hydrocarbons (C_6- and C_9-hexasubstituted hexabenzocoronenes abbreviated HBC) to determine if such molecules would increase their self-association level. It was found that the model compound C_6-HBC starts to self-associate at a lower concentration than asphaltenes. C_6-HBC tends to form only dimers even at concentration of 15 g/L in toluene. Experimental studies at high temperatures showed that unlike simple pyrene derivatives, C_6-HBC could self-associate at temperatures up to 400 °C. Molecular modeling indicates that the self-association of C_6-HBC is due to the favorable interplay of alkyl-alkyl and π-π stacking interactions.

In conclusion, the work above shows that the three categories of asphaltene model compounds do not fully address asphaltene behaviour in solution. In particular these model compounds do not self-associate to the same extent as crude oil asphaltenes. This means that key factor(s) ruling asphaltene self-association has (have) not been identified yet.

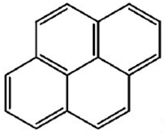
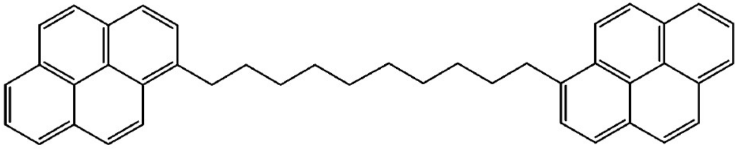
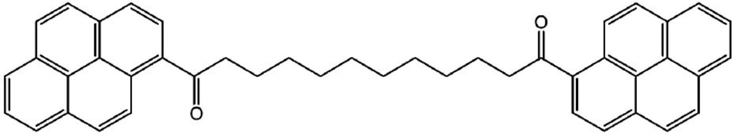
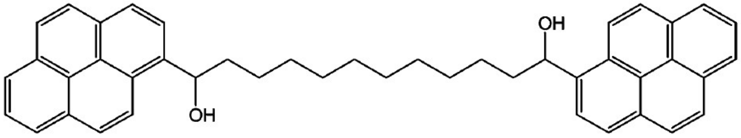
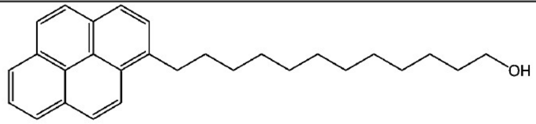
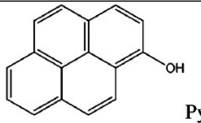
Compound	Structure and Name
I	 Pyrene
II	 1,10-dipyrenyl decane
III	 1,12-di (1-pyrenyl) dodecane-1,12-dione
IV	 1,12-di (1-pyrenyl) dodecane-1,12-diol
V	 1-pyrenyl-dodecane-12-ol
VI	 Pyrenol

Figure 1: Model compounds proposed by Akbarzadeh et al. in 2005 self-association studies of asphaltenes[20]. Reprinted with permission from Akbarzadeh et al.[20]. Copyright 2005 American Chemical Society.

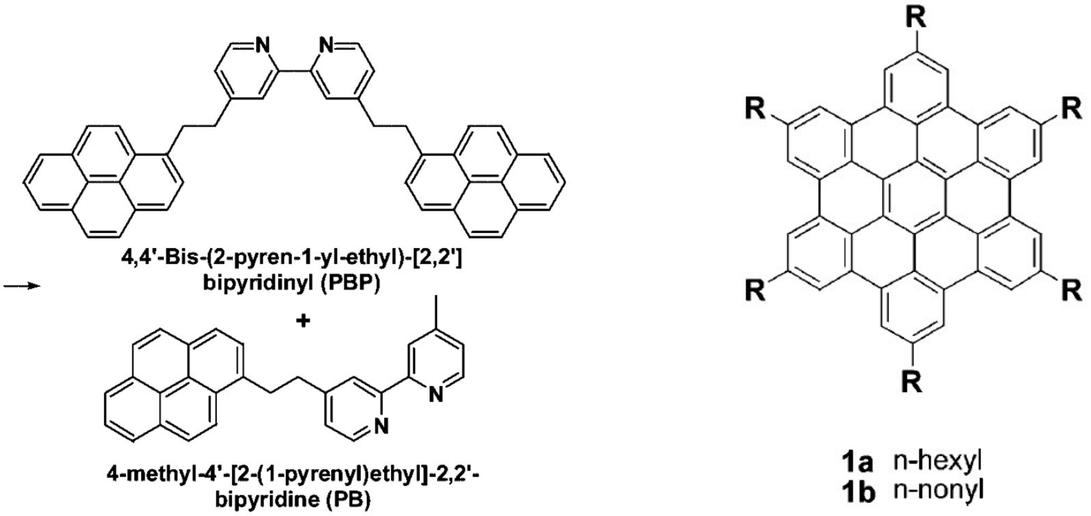


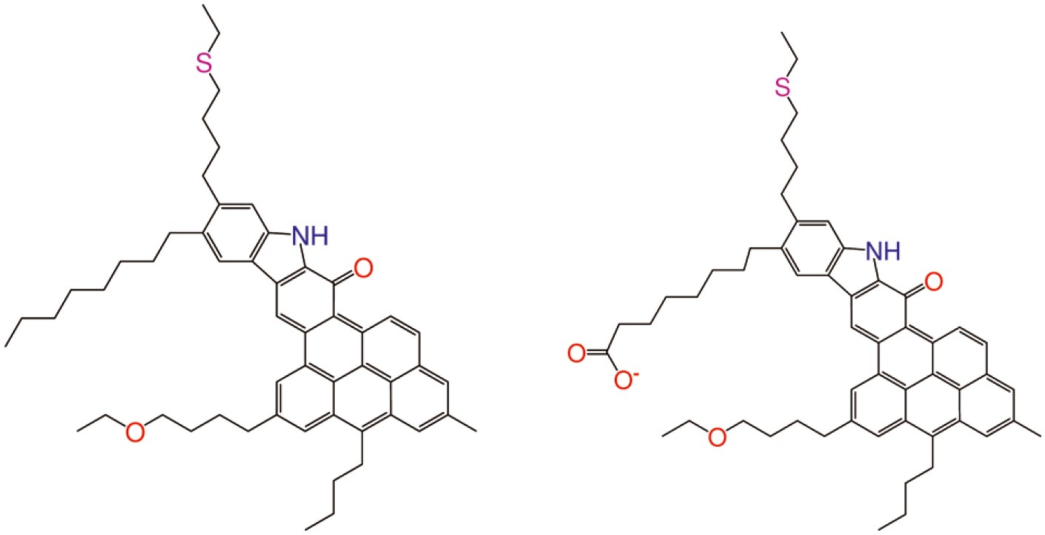
Figure 2: Model compounds proposed by Tan et al.[22] (left) and Rakotondradany et al.[21] (right) for the self-association properties of asphaltenes in bulk. Reprinted with permission from Tan et al.[22] and Rakotondradany et al.[21]. Copyright 2008 and 2006 American Chemical Society.

5.2 Bhattacharjee, Masliyah et al. (2008-)

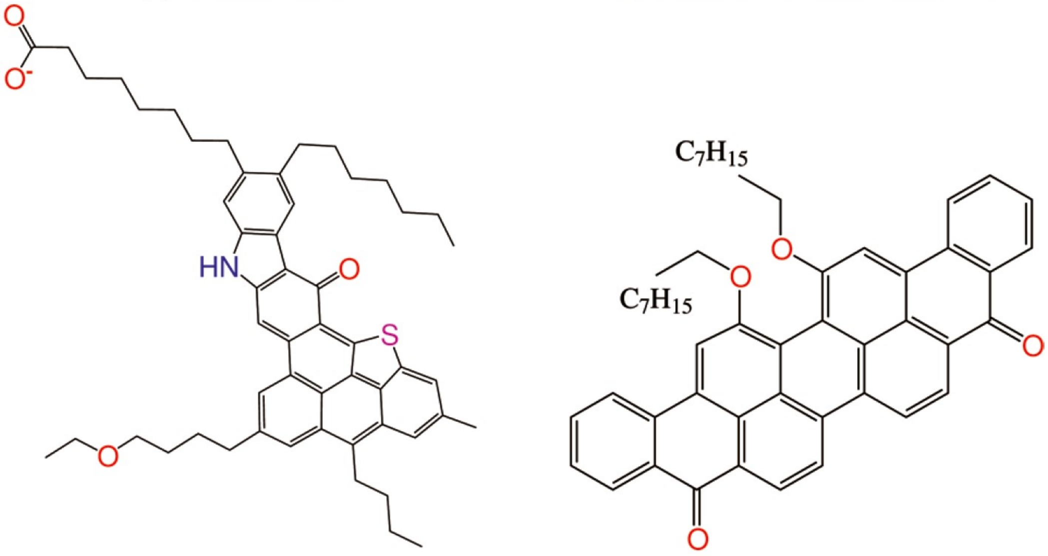
Bhattacharjee and Masliyah in Edmonton, Canada studied different model molecules both in bulk and at interfaces by molecular modelling (MD). The molecules chosen represented different models of petroleum asphaltenes: continental model, archipelago model and anionic continental model (figure 3)[25-27].

MD study started by comparing the aggregation properties in water, toluene, and heptane of three different model molecules after 10 ns[25]. The molecules were found to self-associate in single pure solvents by stacking of their polyaromatic rings. The authors also extended their studies to oil/water system. They determined that the non-charged molecules do not cluster at the toluene-water interface, whereas charged terminal groups had a distinct affinity for the toluene-water interface, as expected.

Next four types of model asphaltenes depicted in figure 3 in binary mixtures of toluene and water were studied[26]. Their first conclusion was that the model molecules always partition completely to the toluene phase of the phase-separated solvent mixture. After this they demonstrated the importance of charged moieties. Molecules carrying a charge (molecules b and c in figure 3) self-associate and the aggregates are adsorbed at the toluene-water interface where the charged terminal groups (COO-) of these molecules seemed to form hydrogen bonds with the water molecules at the toluene-water interface. Nonionic molecules (a and d) seem to self-associate in solution but do not show interfacial activity (figure 4). The influence of non interfacial association was also addressed for the molecule VO-79. It was observed that below a critical concentration, VO-79 does not exhibit any substantial aggregation by sustained stacking.



(a) Continental (b) Anionic Continental, AC



(c) Thiophenic Anionic Continental, TAC (d) Violanthrone-79, VO-79

Figure 3: Model compounds proposed by Kuznicki, Masliyah and Bhattacharjee in 2009[26] for MD studies. Reprinted with permission from Kuznicki et al.[26]. Copyright 2009 American Chemical Society.

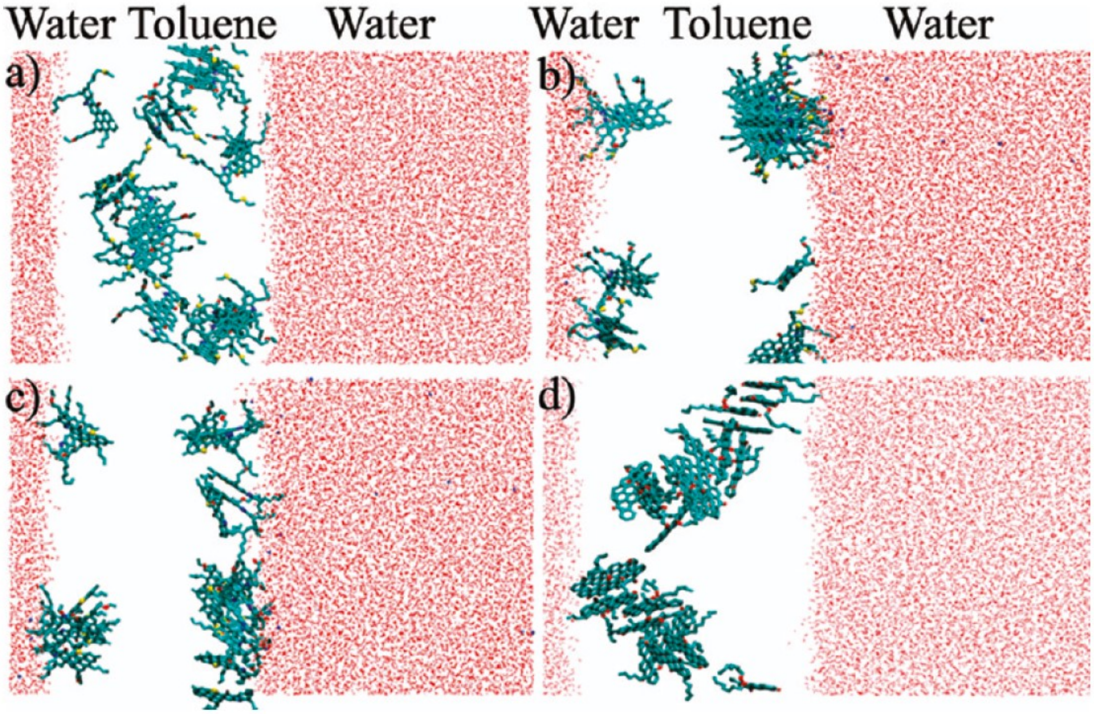


Figure 4: Snapshots taken after 7 ns showing the aggregation and interfacial activity of the model compounds C (picture a), AC (b), TAC (c), and VO-79 (d) in toluene-water mixtures. In all systems, the total numbers of molecules are identical. The toluene molecules are not shown[26]. Reprinted with permission from Kuznicki et al.[26]. Copyright 2009 American Chemical Society.

Their next contribution was to study the effect of side-chain on the self-association properties of molecules similar to Violanthrone VO-79 (figure 3) in water[27]. They found that the extent of aggregation has a nonmonotonic relationship with the side-chain length. Surprisingly the model molecules with very short (C_4) or very long side chains (C_{16}) can form dense aggregates, whereas those with intermediate chain lengths (C_8 and C_{12}) cannot (figure 5). This trend is the result of the balance between interactions involving polyaromatic cores (π-π) on one hand, and between a polyaromatic core and an aliphatic chain (π-θ) or between aliphatic chains (θ-θ) on the other hand. Short side-chains have minimal interference with the stacking of polyaromatic cores, on the contrary to the long aliphatic side-chains (in agreement with the experimental results obtained by HRTEM (Sharma et al.[64]), but the latter promote aggregation through increased θ-θ and π-θ interactions in aromatic solvent.

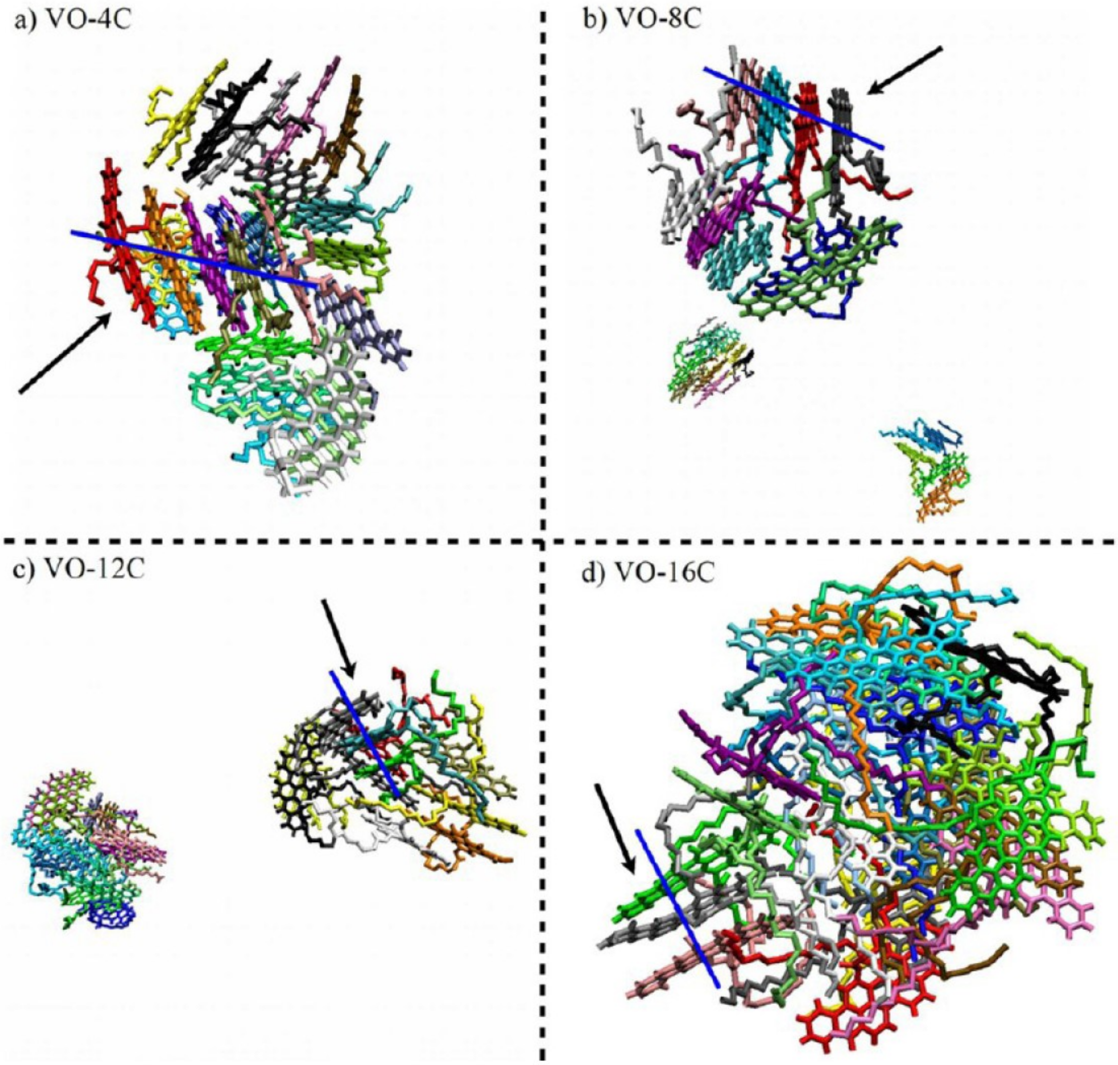
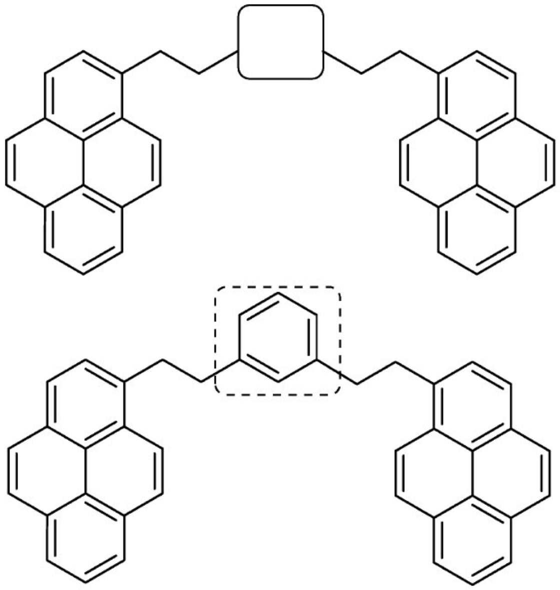


Figure 5: Snapshots of 24 asphaltene model molecules in water after 60 ns: (a) VO-4C, (b) VO-8C, (c) VO-12C, (d) VO-16C (the number indicates the length of the side-chains). The molecules in each system are represented by different colors. Water molecules are removed for clarity[27]. Reprinted with permission from Jian et al. [27]. Copyright 2013 American Chemical Society.

5.3 Gray et al. (2012-)

These authors studied the thermal cracking and coking of two series of model compounds representatives of asphaltenes: pyrene-based compounds (figure 6)[23] and model compounds incorporating the biomarker structure of 5α-cholestane, covalently fused to a range of substituted benzoquinoline groups[24]. The cracking kinetics were followed by ThermoGravimetric Analysis (TGA) and characterization using GC, HPLC and different mass spectrometry techniques of the reaction products.

For the archipelago model compounds (Figure 6), Alshareef et al.[23] determined the initial cracked fragments which were re-combined to form larger structures by a process involving reactions forming alkyl−alkyl and, to a lesser extent, alkyl−aryl C−C bond. These bonds are most likely formed by a sequence of free-radical addition reactions to an unsaturated bond, followed by rearrangement(s), dehydrogenation, and/or further cracking. The presence of heteroatoms incorporated in the central ring was also investigated: Heteroatoms gave higher yields of coke and different selectivity of the cracked products, compared to other hydrocarbon compounds.



1,3-bis(2-pyren-1-yl-ethyl)-benzene
(P-*m*Ph-P)

Figure 6: Archipelago model compounds proposed by Alshareef et al. for mechanistic studies of cracking and coking of Asphaltenes[23]. Reprinted with permission from Alshareef et al. [23]. Copyright 2012 American Chemical Society.

The cracking of substituted cholesterane-bemzoquinoline compounds determined by Alshareef et al.[24] consists mainly of the dehydrogenation of the saturated hydrocarbon rings along with some peripheral demethylation and steroid side-chain fragmentation. However there is no significant ring opening or release of cyclic substructure from the steroid units.

5.4 Sjöblom et al. (2008-)

Johan Sjöblom et al. in Trondheim, Norway launched a series of asphaltene model molecules (figure 7)[28-30] to view the interfacial properties of asphaltenes at the water/oil interface and the corresponding emulsion stability. The asphaltene models they designed incorporate a fixed hydrophobic part with a branched alkyl chain attached to a polyaromatic core (perylene) with the other part of the molecule varied by introducing four groups. This design gives polyaromatic surfactants with the number of aromatic rings and molecular weights in the range of asphaltene monomers as presented in section 4. Moreover a part of the structure can be modulated to determine the influence of the chemical structure. Among the four asphaltene model molecules synthesized, one is apolar with an aliphatic head group (BisA) and the other three consist of a terminal carboxylic group (C5Pe) with phenyl (PAP) or indole (TP) groups.

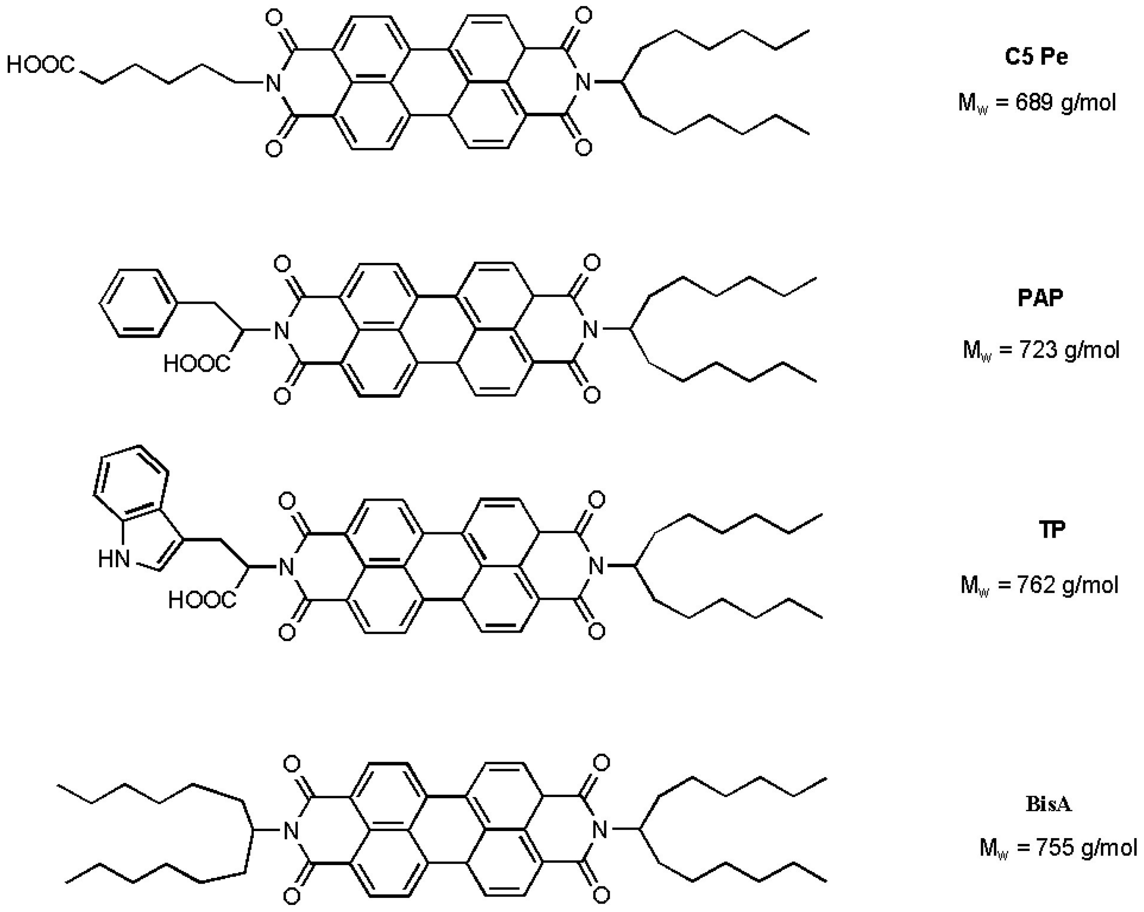


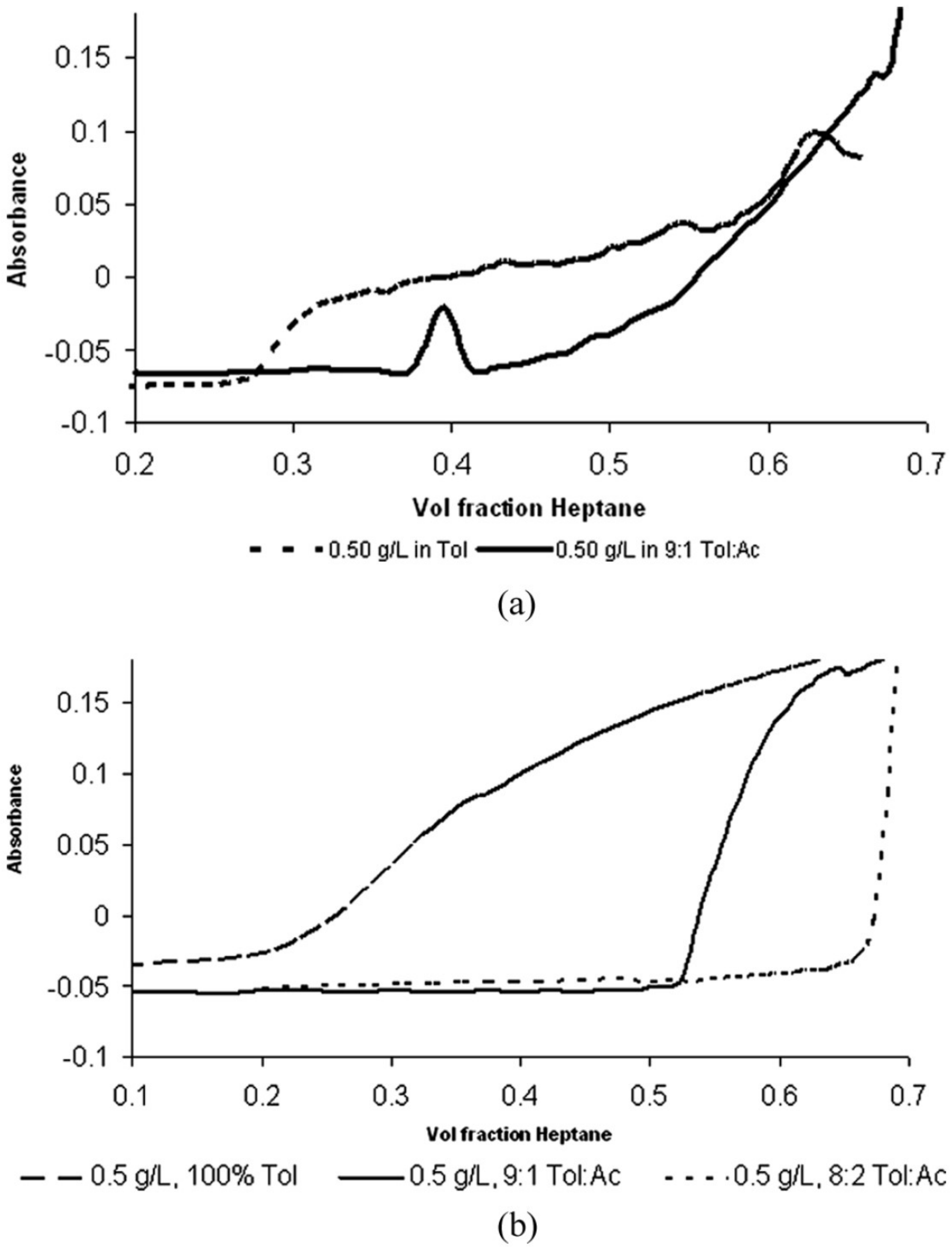
Figure 7: Model compounds proposed by Nordgård and Sjöblom[28-30] to mimic the interfacial properties of asphaltenes. The name abbreviations indicate the name of the head group (from top to bottom: hexanoic acid, PhenylAlanine, Tryptophan) and the aromatic core: perylene. Reprinted with permission from Nordgård et al.[28]. Copyright 2008 American Chemical Society.

The calculated acid numbers (TAN) of C5Pe, PAP and TP varies from to 74 to 81 mg KOH / g. In comparison the TAN of extracted asphaltenes measured by potentiometry varies from 2.01 to 2.75 mg KOH / g while their TBN is comprised between 11.34 and 13.38 mg KOH / g [66, 67]. Therefore the asphaltene model compounds aims to represent only a fraction of asphaltenes which corresponds to acid molecules.

6 Perylene-Based Model Compounds

6.1 Solubility

In order to correctly represent the properties of asphaltenes, the perylene-based asphaltene model compounds must present similar solubility properties. Nordgård and Sjöblom[29] extensively investigated the solubility of PAP and TP (figure 8). Using the same definition of asphaltenes precipitation, the precipitation onset of TP and PAP was determined at ≈ 20 and ≈ 27 v/v % of heptane in mixture of heptane and toluene, respectively. The solubility of these two model compounds increases in the presence of small amount of a polar compound such as acetone.



(a)

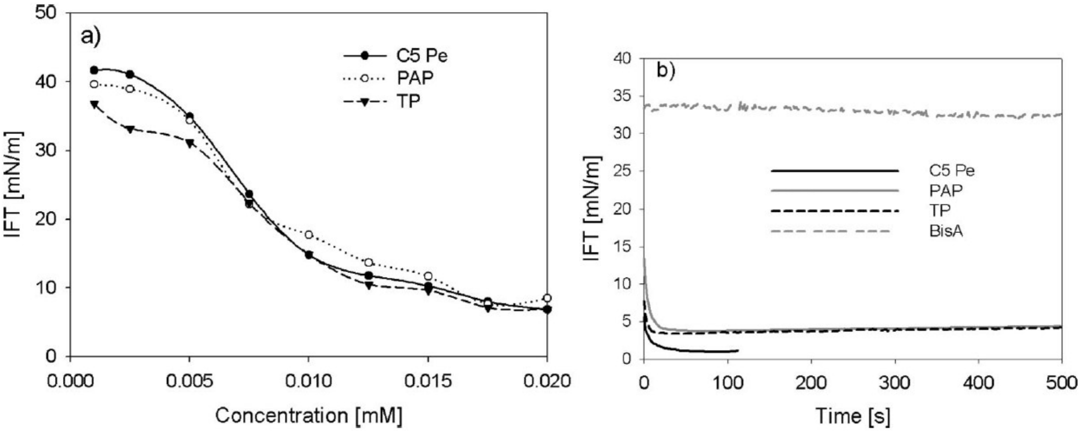
(b)

Figure 8: Precipitation of (a) PAP and (b) TP with n-heptane and different starting solvent conditions and followed by NIR spectroscopy: an increase of absorbance indicates formation of particles in the solution. Absorbance measured at 10000 cm^{-1}.[29]

6.2 Interfacial Properties

The interfacial properties of asphaltene model compounds were assessed by measuring their interfacial tension at the toluene/water (pH=9) interface (figure 9). At this pH the acid molecules (C5Pe, PAP and TP) should be fully ionized (carboxylate form). All the acid molecules present similar high interfacial activity and the shape of the curves are similar. As expected the non-acidic molecule BisA does not show any noticeable surface activity. This shows the importance of a strong polar head group because the multiple polar carbonyl groups in the aromatic core are not enough to induce any measurable adsorption at the liquid/liquid interface.

The IFT of the acidic molecule at the liquid/liquid interface was then measured as a function of pH (example given in figure 10 for TP)[29]. This figure shows that the IFT decreases with increasing pH of aqueous phase due to the ionization of the carboxylic acid groups. Consequently the perylene-based model compounds are surface active when they are charged. This conclusion is in agreement with the results obtained by Bhattacharjee and Masliyah in their MD simulation study (section 5.2).



<u>Figure 9:</u> (a) Interfacial tension of three acidic asphaltene model compounds between toluene and pH=9 buffer. (b) Time-dependent interfacial tension curves at 50 μM for all model compounds[28]. Reprinted with permission from Nordgård et al.[28]. Copyright 2008 American Chemical Society.

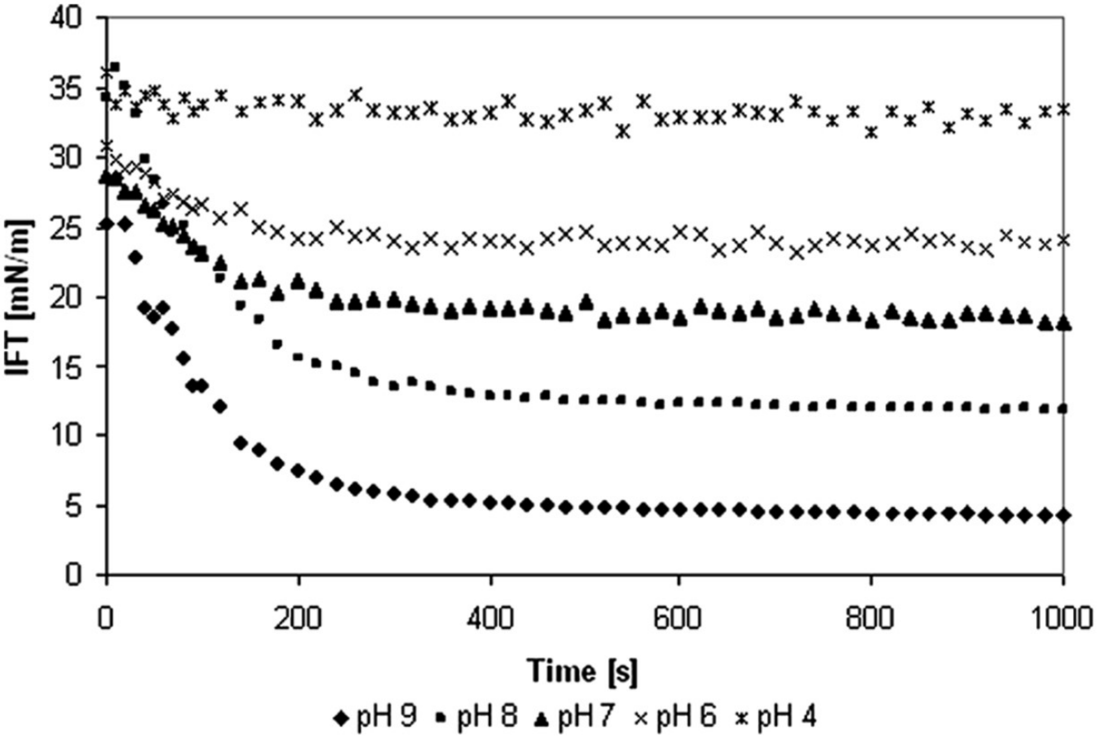


Figure 10: Plots of IFT of TP at varying buffer pH. The concentration of TP in toluene was 0.020mM in all cases[29].

Conformational information of asphaltene model compounds at the interface can be obtained by Langmuir trough experiments[113, 114]. This technique consists of a shallow rectangular trough and two moving barriers. On water sub-phase asphaltene model compounds are spread in given concentrations This layer is compressed by the barriers. As the compression proceeds and area per molecule decreases the model compounds will start to interact with each other, causing an increase in the surface pressure (π). This technique along with the results obtained by BAM microscopy and steady-state fluorescence allow us to propose arrangements (orientation) of C5Pe, PAP and BisA at the water-air interface (figure 11)[28]. C5Pe and PAP adopt a head-on conformation with a face-to-face packing of polyaromatic core normal to the surface. This means: the acidic group into the aqueous phase, the branched hydrocarbon chains out from the surface and all the aromatic cores face-to-face. This conformation explains high interfacial activity of acidic model compounds. On the other hand, BisA most likely adopts a flat-on arrangement at the interface since its polar groups are in the core. This flat-on conformation consists of stacked BisA molecules oriented parallel to the interface. In conclusion this study shows the importance of the polar head group to adopt a specific conformation at the interface and the relation between conformation-surface activity.

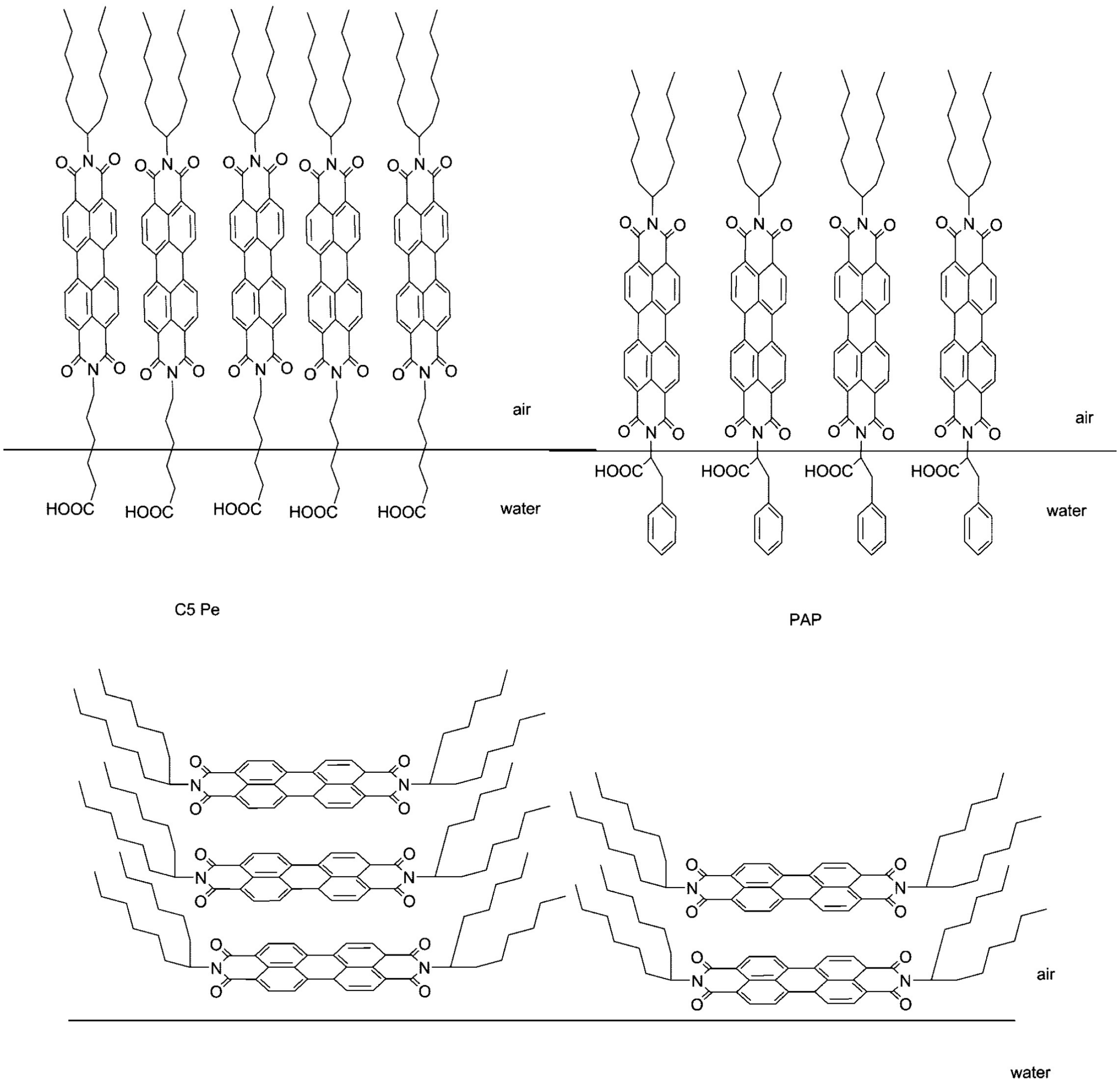


Figure 11: Suggested arrangement of C5Pe, PAP and BisA at the air/water interface in low-compressible ranges[28]. Reprinted with permission from Nordgård et al.[28]. Copyright 2008 American Chemical Society.

6.3 Surface Forces

The Surface Force Apparatus (SFA) is a technique used to measure the force acting between two surfaces. Wang et al. in Edmonton, Canada applied this technique to measure the interactions between mica surfaces covered with the model compound C5Pe both in organic solvent (toluene and heptane)[115] and aqueous phase[116].

In a first set of experiments the authors let asphaltenes or C5Pe adsorb from toluene onto mica surfaces[115] and measured the resulting forces between the covered surfaces (figure 12). The measured force profiles show that the model compounds and the extracted asphaltenes behave qualitatively similar. Indeed a layer of adsorbed compound is observed 10 minutes after the adsorption experiments (seen as a repulsive force profile) and the thickness of the adsorbed layers continued to increase even after several hours. The interactions between C5Pe-adsorbed surfaces was fitted with the Alexander-de Gennes scaling theory with a good fit obtained at short distances under high compression, illustrating the steric nature of repulsion between two interacting brush layers. Despite the measured steric repulsion on approach, the measurement during separation of the surfaces from each other after putting them into contact showed the presence of adhesion for both C5Pe and extracted asphaltenes for the first several hours of adsorption. This adhesion disappeared after 20 hours of adsorption or so. The adhesion is attributed to the interdigitation of adsorbed molecules from two interacting surfaces, which disappeared due to conformational rearrangement of the C5Pe layer with time.

Experiments were also performed on pre-adsorbed C5Pe films in toluene and heptane. Now no significant adhesion between the films was detected in toluene, while strong adhesion was measured in heptane.

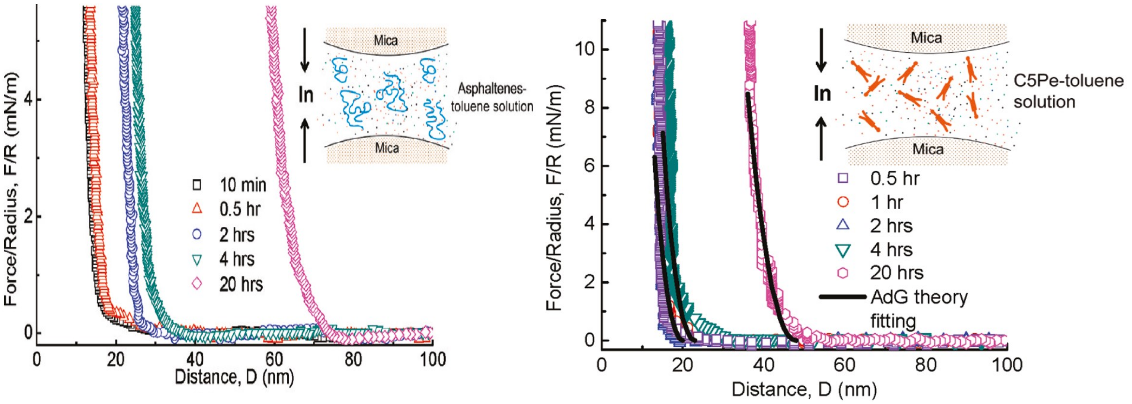


Figure 12: Force-distance profiles of two mica surfaces approaching to each others in (a) 0.01 wt% asphaltene-toluene solution or (b) 0.02 wt % C5Pe-toluene solution. The fitting was based on the Alexander-de Gennes scaling theory at different time intervals[115]. Reprinted with permission from Wang et al. [115]. Copyright 2012 American Chemical Society.

To probe the role of charges on C5Pe model compound for the interfacial activity, Wang et al. continued to measure the interactions between mica surfaces covered with the model compound C5Pe both in aqueous phases[116]. Repulsive forces were detected between two adsorbed C5Pe layers. These forces are of steric and electrostatic origins (due to the presence of carboxylate functions) and can be fitted by the Alexander-de Gennes scaling theory at short distances and by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory[117, 118] at longer distances, if the pH of the aqueous phase is higher than 4, i.e., when the COOH starts to be ionized. In addition, an attractive term attributed to hydrophobic interactions was also observed at pH=2. This term decreased sharply with increasing pH and became rapidly negligible.

Finally the influence of Ca^{2+} ions in the aqueous solution on the forces was investigated. This divalent cation induced the formation of large C5Pe aggregates on the mica surfaces, resulting in longer range steric repulsion.

6.4 Molecular Dynamic Simulations

In order to further elucidate molecular association and interaction, Teklebrhan et al.[32, 119] studied by Molecular Dynamics Simulation (MD) the self-association properties of perylene-based model compounds (figure 7) in the bulk of toluene and heptane [24, 102] as well as their adsorption properties at the water/toluene or heptane interface[102]. It must be noticed that all the perylene-based compounds were not ionized as the compounds studied by Kuznicki et al.[25, 26] (section 5.2).

By MD and dynamic light scattering experiments (DLS), Teklebrhan et al.[32] showed that variations in the structure of side chains and polarity of head groups lead to significant variations in molecular association, dynamics of molecular nanoaggregation and structure of nanoaggregates in bulk (figure 13). BisA and PAP show smaller, less structured aggregates while C5 Pe and TP form larger aggregates in both solvents. BisA does not form polyaromatic $\pi-\pi$ stacking due to the strong steric hindrance by its aliphatic head groups in both solvents. For the formed nanoaggregates, it was found that all of the solvent molecules were excluded from the interstices of the stacked polyaromatic cores, regardless of whether the solvent molecules are aliphatic or aromatic. Overall the self-aggregation properties of asphaltene model compounds is stronger in heptane than in toluene due to hindered molecular association by weakening π–π stacking from the aromatic solvent.

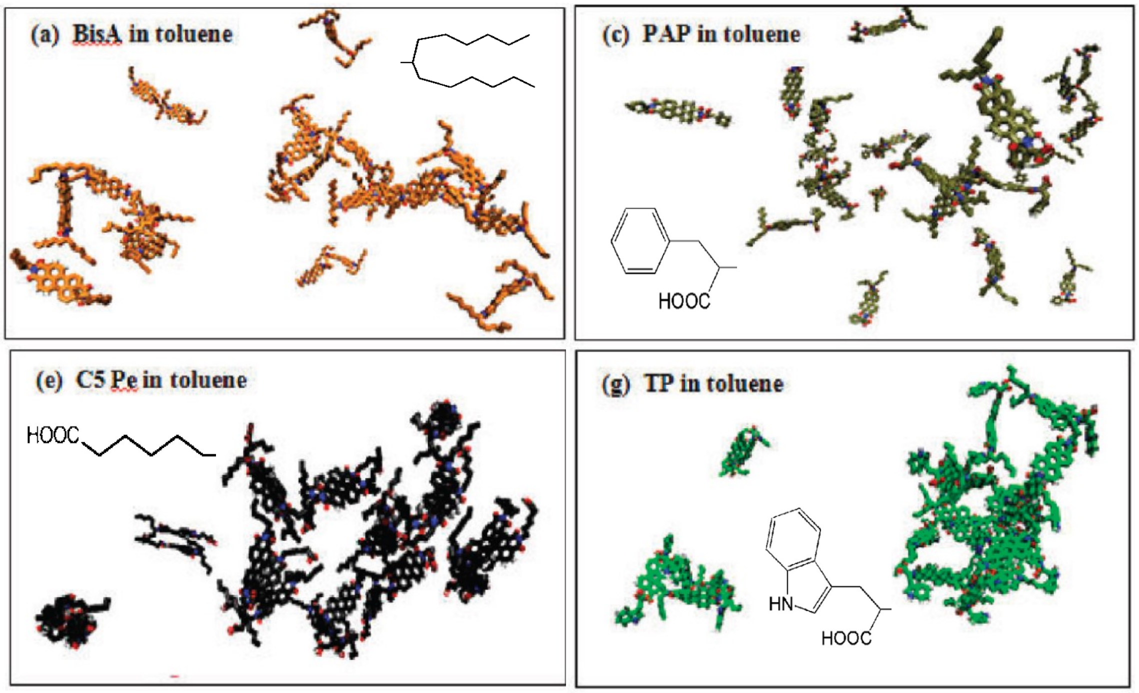


Figure 13: Snapshots of molecular configurations of the five PA surfactant molecules in toluene after 20 ns simulation time[32]. Reprinted with permission from Teklebrhan et al.[32]. Copyright 2012 American Chemical Society.

Teklebrhan et al. also introduced a water phase (and consequently a oil/water interface) in their systems[119]. The asphaltene model compounds were found not to partition in water bulk phase. However the partition between the bulk organic phase and oil–water interface was highly dependent on the polar head group of the asphaltene models and the aromaticity of the organic phase. The presence of aromatic function in the head groups lowered the interfacial activity due to strong intermolecular π–π interactions and molecular aggregation in the bulk oil phase: C5Pe partitions more to interface than PAP and the latter more than TP.

The conformation of C5Pe and PAP at the oil-water interface was determined by the angle between the polyaromatic core of adsorbed model compounds and the oil-water interface (figure 14). Results show that both C5Pe and PAP, irrespective of the side-chain substituents and solvent property of the oil phase, tend to orient more head-on at the oil−water interface, in agreement with the experimental results by Nordgård et al.[28] (in section 6.2).

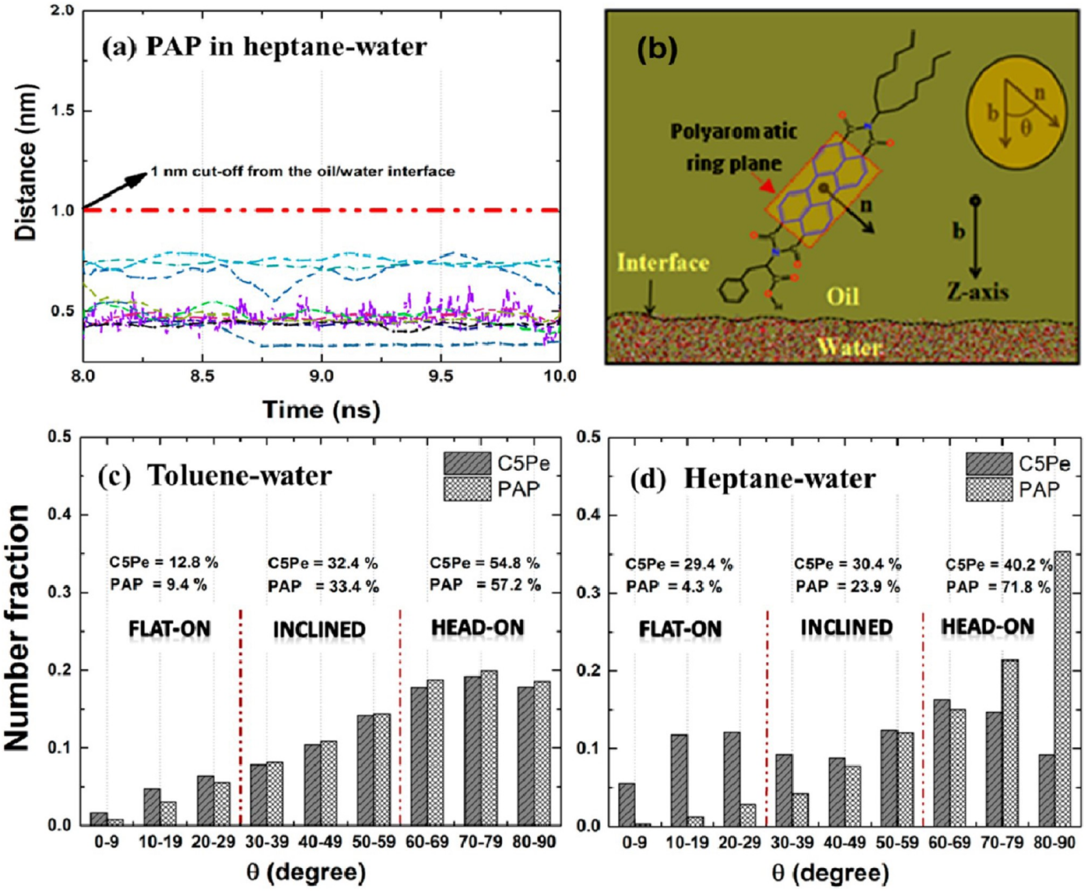


Figure 14: (a) Distance of the interface-bound PAP molecules from the heptane−water interface as a function of time. A 1 nm cutoff from the heptane−water interface was used to count the number of interface-bound PAP molecules in the system. (b) The schematic representation of the angular distribution (θ) of the polyaromatic ring plane of the PA molecules at the oil−water interface. The number fraction (Nf = Ni/NTotal) of polyaromatic molecules averaged over the last 2 ns of the simulation time (8−10 ns) in toluene−water (c) and heptane−water (d) at 298 K[119]. Reprinted with permission from Teklebrhan et al. [119]. Copyright 2014 American Chemical Society.

7 Emulsions

Asphaltenes are one of the fractions in crude oil responsible for the stability of crude oil emulsions[1]. In this section we review the emulsion stabilisation properties of fractionated asphaltenes and we show the usefulness of perylene-based model compounds for an understanding of the petroleum emulsion stabilisation mechanism. This understanding is of course linked to the interfacial properties exhibited by these model compounds presented in section 6.

7.1 Dynamic Surfactant Concentration

General stabilization mechanisms for emulsions regardless if they are o/w or w/o are electrostatic, steric, particle and multi-layer stabilization. Entities important in this context are surfactants, nanoparticles, polymers and surfactant blends. In 2011 a new surfactant related mechanism was introduced, i.e. the dynamic surfactant concentration. This effect will relate to partial destabilization through coalescence and its consequences for the remaining droplets[120].

The dynamic surfactant effect has been best documented for water-in-oil emulsions although it should have general validity. We study a w/o emulsion where a restricted binary or homophase coalescence has taken place. As a consequence a free water phase emerges and stabilizer is released through the coalescence process. Water droplets settle to form a concentrated emulsion layer or dense-packed layer. Due to the decrease of the total interfacial area (coalescence), the surfactants present around water droplets will increase or be released into the oil phase. As a result in the vicinity of the interface the bulk surfactant concentration will increase, which could lead to a locally, dynamically stabilized emulsion at this interface. The released surfactants will then diffuse away from the interface in the oil phase to establish equality in the surfactant concentration all over the bulk oil phase (figure 15).

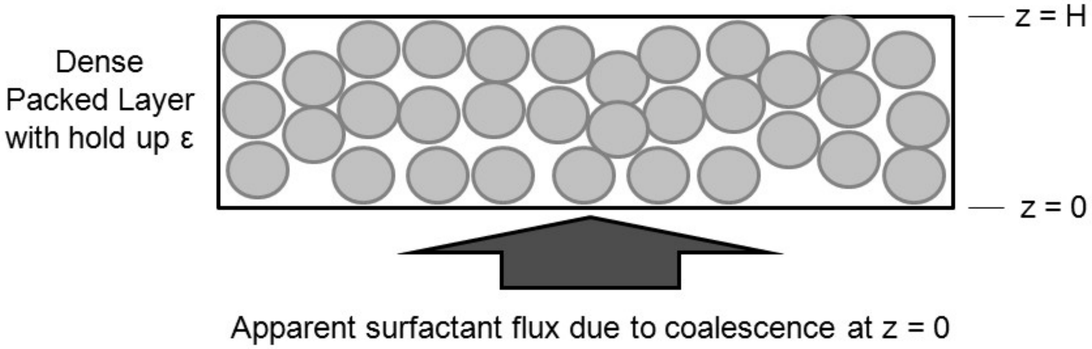


Figure 15: Schematic diagram of the model domain for the surfactant mass balance. An apparent flux of the surfactant is introduced at the bottom of the dense packed layer to account for the surfactant phase partitioning that occurs after a coalescence event[120]. Reprinted from Journal of Colloid and Interface Science, Vol 348, Grimes, B. A.; Dorao, C. A.; Simon, S.; Nordgard, E. L.; Sjoblom, J., Analysis of dynamic surfactant mass transfer and its relationship to the transient stabilization of coalescing liquid-liquid dispersions, Pages Number 479-490, with permission from Elsevier.

The veracity of the dynamic surfactant concentration effect was checked by a combination of experimental (bottle testing of C5Pe stabilized emulsions) and modelling work. For the latter a simple model was constructed and solved to account for the apparent flux of surfactant into the continuous phase of the dense packed layer and to evaluate the effect of the dynamics of the surfactant concentration on the dynamic stabilization of the dense packed layer. From this simple model, it was shown that the rate at which the surfactant is released to the oil phase relative to the rate at which it diffuses away from the interface plays a key role in the stabilization of the dense packed layer.

7.2 Asphaltenes as Stabilizers

As previously mentioned, during petroleum crude oil production, water is generally present as water-in-oil (w/o) emulsions[1]. The stability of these emulsions varies strongly as a function of the origin and composition of the crude oil[4, 121, 122]. As a general rule the emulsion stability increases with the crude oil density. As a result a heavy crude oil emulsion is much more stable than a light oil emulsion. The different components responsible for the stabilisation of petroleum emulsions are:

-asphaltenes [1, 11, 12, 123]

-naphthenic acids[124-126]. It must be noticed that their properties strongly depends on their ionization degree, i.e. the pH of the produced water[127].

-organic and inorganic particles such as clay, sand, minerals etc. It must be noticed that the emulsion stabilization properties of particles depend on their wettability and therefore the extent of asphaltene-like compounds adsorbed on their surface[95, 128-130].

-Finally it seems that formation of liquid crystals, i.e. multilayers, could play a role in the stabilisation of petroleum emulsions under some conditions[131-134]. However this aspect needs more work to document a universal mechanism.

Using model systems (asphaltenes dissolved in mixtures of hepane and toluene), it has been shown that asphaltenes only form water-in-oil emulsions in batch condition even at high pH[101]. The presence of naphthenic acids at high pH (naphthenates) seems to be required to create oil-in-water emulsions[124]. This is consistent with the Bancroft's rule that "the phase in which an emulsifier is more soluble constitutes the continuous phase". The efficiency of asphaltenes to stabilize emulsions is attributed to the ability of the asphaltenes to form a rigid protecting layer or "skin" at the liquid/liquid interface. This aspect has already been discussed in part 4.2.2.2. Using xylene as organic solvent, it was shown by Small-Angle Neutron Scattering (SANS) that the thickness of the asphaltene layer stabilizing water droplets is close to the diameter of asphaltene aggregates between 110 to 150 nm or so[135] as formed in the bulk.

The influence of different parameters on the emulsion stabilisation properties of asphaltenes has been studied using systems composed of:

-fractionated asphaltenes dissolved in a mixture of heptane and toluene. Generally the flocculation onset, i.e., the volume fraction of heptane at which the asphaltenes start to precipitate and form micrometer-sized flocs[136, 137], is measured. Sometimes fractionated resins are added in the organic solution.

-water phase generally containing NaCl at different pH to mimic offshore salinity conditions.

The emulsions were then prepared using a homogeniser such as ultra-turrax. The stability of resulting emulsions is assessed by measuring the free water appearance kinetics (bottle test). Low Field Nuclear Magnetic Resonance (LF-NMR) can also be studied[138-140].

Using these systems and methodology it was shown that the stability of asphaltene-stabilized emulsions is governed by the solvation state of asphaltenes and the pH of the aqueous phase. About the solvation state, it was shown that asphaltenes are the most effective in stabilising emulsions when they are near the point of incipient flocculation/precipitation. [10, 11, 81, 141]. Under good solvent conditions (such as in toluene or in the presence of a large amount of resins), asphaltenes are well dissolved. Under precipitating conditions (in heptane for instance), asphaltenes form large flocs that will not diffuse to the interface. These results are in good agreement with interfacial rheology results presented in section 4.2.2.2. For instance Nenningsland et al.[103] showed that the interfacial dilational elasticity modulus of asphaltenes at liquid/liquid interface increases gradually when the fraction of heptane in xylene/heptane solvents increases until the flocculation onset xylene/heptane ratio. This finding is also in agreement with shear interfacial rheology measurements[105]: the asphaltenic interface displays the rheology properties of a viscoelastic material at low heptane content and gradually reaches the features of a gel at high heptane content mixed solvents.

The stability of asphaltene emulsions also depends on the pH of the aqueous phase[31, 101]. These emulsions exhibit a minimum stability at intermediate pH, while the stability is higher at low and high pH. This variation is attributed to the ionization state of the asphaltenes with the pH: protonation of the bases at low pH and formation of carboxylate functions at high pH. As for the solvation state, the variations in stability of asphaltene emulsions with the pH are well-correlated with the variations in the elastic interfacial dilational modulus of the interface with the pH, especially at high pH[103].

Asphaltene-stabilized emulsions show time dependence properties: the stability of asphaltene emulsions increases with time. This behaviour is attributed to the very long reorganization time of asphaltene molecules at the interface and to increased thickness of the complex interfacial layers[101].

7.3 Model Compounds as Stabilizers

The emulsion stabilisation properties of perylene-based compounds were studied first by Nordgård et al.[30] and then by Nenningsland et al.[31].

Nordgård et al.[30] compared the stability of emulsions stabilized by C5Pe, PAP and BisA. BisA did not form emulsions contrary to the acidic model components, which shows the importance of the head groups. This result is consistent with the interfacial properties of the three compounds presented in section 6.2. The authors further investigated the conformations of C5Pe and PAP to explain the stability of corresponding emulsions. It was determined that these compounds most likely form a monolayer at the w/o interface. The measured mean molecular area suggested a tilted geometry of the aromatic core with respect to the interface. Finally PAP was shown to stabilize emulsions to a less extent than C5Pe. A possible explanation is that PAP may not pack in the same way at the interface due to the more bulky head groups, causing the angle between aromatic cores to align in a less favourable way to effectively stabilize emulsions.

Grimes et al. have determined the adsorption isotherm of C5Pe at the xylene/water interface[120]. It was found that the interfacial tension data are well-fitted by a Langmuir type isotherm which confirms the fact that C5Pe forms a monolayer at the w/o interface. By measuring the concentration of C5Pe in the bulk, these authors have determined the C5Pe-stabilized emulsions are stabilized when the value of the excess surfactant concentration, Γ, is approximately 89 % of the maximum excess surfactant concentration Γmax.

Finally the ability to stabilize water-in-oil (w/o) emulsions for asphaltenes and C5Pe was compared[31]. The results indicated that C5Pe describes the behaviour of asphaltenes relatively well at high pH. The emulsion stability increases with the pH for the two systems. However 30 times less C5Pe is required to obtain the same emulsion stability as for asphaltene-containing systems at pH=8. This could indicate that only a small part of asphaltenes is required to stabilize emulsions i.e. only the interfacially active fraction. The main difference between asphaltenes and C5Pe is their behaviours at low pH. The stability of C5Pe emulsions is not improved at low pH contrary to asphaltenes' . This difference is of course attributed to the presence of bases in indigenous asphaltenes.

7.4 Particles as Stabilizers

The fact that particles can act as stabilizers of emulsions was discovered early in the 20th century [142, 143]. These emulsions are called Pickering emulsions from the name of one of its discoverers. The stability of these emulsions and their types (w/o vs o/w) are strongly correlated to the wettability of particles quantified by the contact angle θ[144-147]. Particles with $\theta < 90°$ measured through the aqueous phase are water-wet particles and stabilize oil-in-water (o/w) emulsions, while oil-wet particles ($\theta > 90°$) stabilize water-in-oil (w/o) emulsions. If particles are either too hydrophilic (low θ) or too hydrophobic (high θ) they tend to remain dispersed in the aqueous or oil phase, respectively, giving rise to very unstable emulsions [148, 149]. This dependence of the type of emulsions with the particle wettability is called transitional phase inversion[148, 150]. The type of formed emulsions also depends on the oil over water ratio. This dependence is known as catastrophic phase inversion [145].

It was indicated in section 7.2 that asphaltenes form nanoaggregates in aromatic solvents like toluene or xylene and bigger flocs at the asphaltene precipitation onset. This could indicate that asphaltenes behave more like particles than molecular surfactants to stabilize emulsions and could be the reason behind the elasticity of the interface. In order to test this hypothesis, Nenningsland et al.[31, 102] compared the free water release kinetics of emulsions stabilized by extracted asphaltenes, the model compound C5Pe (part 5.4) and hydrophobized silica particles at different stabilizer concentrations (figure 16).

The percentage of separated water from emulsions stabilized by the model asphaltene C5Pe (figure 16 middle) decreased steadily as a function of initial concentration. The separation of water as a function of time (not presented here) showed that at low concentrations (0.01 – 0.03 g/l) the separation is very rapid, while at intermediate concentrations (0.04 – 0.05 g/l) there was only an initial period of instability. Afterwards the remaining emulsified water (30 – 40 %) did not separate within 2 weeks.

The particles showed very distinct and different features (figure 16 right). The transition from unstable to completely stable emulsions occurred very abruptly at a critical concentration, which in this case was located around 1.24 g/l. Additionally the evolution of separated water with time (not shown) also presented a very distinct behaviour. The destabilization of the particle-stabilized emulsions was time-independent, so there was no gradual coalescence with time. This could be explained by high adhesion and desorption energies due to the larger size of particles compared with surfactants.

Finally Figure 16 (left) shows that the separation of water from the extracted asphaltene-stabilized emulsions proceeded in a similar fashion as for C5Pe contrary to hydrophobic particles. Indeed the % of free water released displays a close to linear transition from unstable to stable as a function of initial asphaltene concentration. The time-dependent destabilization had the same features as with C5Pe, where the emulsions with intermediate asphaltene concentrations only separate partially. The main difference between the two cases is the amount of stabilizer required to stabilize emulsions, a result already discussed in section 7.3.

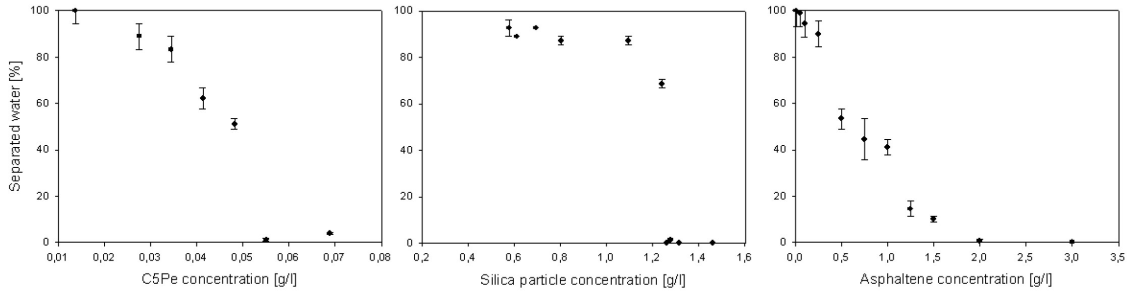


Figure 16: Separated water 24 hours after preparation as a function of the stabilizer concentration for left: extracted asphaltene as stabilizer with xylene as the oil and water phase at pH 8; middle: C5Pe as stabilizer with xylene as the oil and water phase at pH 8; right: hydrophobic silica particles as stabilizer with decane as the oil phase and a 3.5 wt % NaCl solution as the water phase[31]. Reprinted with permission from Nenningsland et al. [31]. Copyright 2011 American Chemical Society.

8 Concluding Remarks:

Asphaltenes are currently one of the most problematic fraction of crude oils due to all the problems they cause to the transportation (flow assurance) and the processing of crude oils. To understand the mechanism behind these problems, different research groups have, over the last 10 years, synthesized several families of asphaltene model molecules that can mimic the properties of asphaltenes. As shown in this review, the asphaltene model molecules have increased our knowledge of chemical functionalities of bulk and interfacial asphaltene properties. Moreover, due to their well-defined structure, these model compounds constitute the basis of MD modelling work. The calculated properties can then be compared with experimental data. Due to these advantages, the asphaltene model compounds have become a viable strategy to study asphaltenes.

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