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ORIGINAL CONTRIBUTION

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Film forming properties of asphaltenes and resins. A comparative Langmuir–Blodgett study of crude oils from North Sea, European continent and Venezuela

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Abstract Asphaltenes and resins were separated from different crude oils, dissolved in different paraffinic and aromatic solvents and studied by means of Langmuir technique. It was found that the resin films are more compressible and more polar than the corresponding asphaltene films. Intermolecular aggregation between asphaltene molecules was more prominent than between resin molecules, and the size of the final aggregates depended on the nature of the solvent and the bulk concentration of the aggregating species. Even when present in smaller amounts than asphaltenes on the surface, the resins dominate the film properties.

Key words Asphaltenes – resins – crude oils – Langmuir films

Introduction

During production of oil, where turbulence in pipe and pressure drops are significant, “water-in-oil” (w/o) emulsions of high stability may form. These emulsions increase the viscosity of the fluid, which entails problems during transport in pipelines and hampers the separation of oil, gas, water and solid materials [1–4]. Emulsion stability is mainly determined by the natural surface active components of crude oils, i.e. asphaltenes and resins [3–7].

Whereas a considerable amount of work has been dedicated to asphaltenes, the resin studies have been less extensive.

Data from spectroscopic studies of asphaltenes [8–17] support the hypothesis that asphaltenes, viewed structurally, contain condensed polynuclear aromatic ring systems bearing alkyl side chains. These systems carry alkyl and alicyclic systems with heteroelements (i.e. N, S and O) distributed throughout the molecule in various locations. It has been stated that asphaltenes from different sources contain similar functionalities but with some variation in the amount of polar groups [18].

Data obtained from studies of molecular weights of asphaltenes indicate that asphaltenes form molecular aggregates even in dilute solutions [19]. This association is influenced by the nature of the solvent, asphaltene concentration and the temperature [20–22]. Possible association mechanisms are hydrogen bonding [23, 24] and formation of charge-transfer complexes [24].

Petroleum resins are the fraction which remain soluble when crude oil is diluted in pentane. Resins can be adsorbed onto solid material from dilute crude oil solutions. However, the character of resins varies with regard to distribution of functional groups, depending on the crude, adsorbent and the choice of eluation solvent [25]. Work done on this fraction indicates that the molecular weights of resins depend upon the molecular weight of the crude oils from which they originate [26]. Crude oils with little or no asphaltenes contain lower proportions of resins than those crudes with a substantial content of asphaltenes [27]. Mack [28] considered resins to represent intermediate products formed in the transformation of oils into asphaltenes. Koots and Speight [27] found a notable decrease in the H/C ratios of the asphaltenes relative to the H/C ratios of the resins, which indicates that aromatization is more advanced in the asphaltenes than in the resins. So if asphaltenes are maturation products of resins, this result shows that one of the maturation processes involves aromatization of the non-aromatic portion of the resin.

According to a dispersion model presented by Pfeiffer et al. [29], the asphaltenes are concentrated in the center of an aggregate and are surrounded by resins. There is a smooth transition between the aromatic center of the aggregate and the continuous medium, which is more aliphatic. If a poor solvent is added to the solution the resins are removed from the aggregate and an accelerated asphaltene aggregation takes place, as in the case of *n*-pentane dilution. Dickie and Yen [30] considered that the petroleum resins prevent the assembly of polar aggregates that would be non-dispersible in the oil. So while asphaltenes associate in a solution [31] this is not necessarily the case in the crude oil. Single asphaltene entities associated with resin molecules could well be the dominant species which allow the asphaltenes to exist in a colloidal state in a crude oil [28]. When introducing a new interface like in an emulsion, there will be a redistribution of the asphaltene and resin molecules.

In order to get a better understanding of asphaltenes and resins effect on emulsion stability, it is of interest to investigate the film properties of these components. Such studies will give information about the rigidity and stability of films consisting of natural stabilizing material. Also the extent of aggregation of asphaltenes and resins in different solvents are possible to determine by means of film studies.

In this work asphaltenes and resins are dissolved in toluene, hexane and mixtures of these solvents. Different solvents have been used in order to characterize the ability of the solvents to prevent aggregation of the heavy fractions. Solvents may be quantified according to three intermolecular forces between solvent molecules: dispersion, polar and hydrogen bonding. They may be grouped into one of four categories according to these forces. Toluene falls into the category of aromatic hydrocarbons. This class of solvents have high dispersion but low polar forces and are weak acceptors for hydrogen bonding. Hexane is an aliphatic hydrocarbon, a class with low dispersion forces, no polar forces and no ability for hydrogen bonding [32].

Experimental

Chemicals

The crude oils were supplied by Elf Aquitaine (crude F), Norsk Hydro (crude N) and Statoil (crude V). Crude F is from a production field in France, crude V from a field in Venezuela and N from the North Sea. *n*-pentane, dichloromethane (DCM), methanol (MeOH), benzene, toluene, hexane and acetone were all of p.a. quality from Merck Darmstadt, Germany. Silanol was obtained from Waters Millipore Corp. Qualitative filter papers used were of type 1 from Whatman, England. The water used in the surface balance experiments was first purified by distillation. The final purification was undertaken by a Seralpur pro 90 water-purification system (Seral), which contains five filter stages: two ion exchangers, one activated charcoal, one adsorbent resin and a 0.2 μm sterile filter.

Separation of asphaltenes and resins

The asphaltenes were separated at room temperature by stirring crude and *n*-pentane (ratio 1 : 5). This mixture was then centrifuged at 2400 rpm for 10 min. To extract the resin fraction, 2 g silanol per ml crude was added to the supernatant from the asphaltene precipitation. This mixture was stirred, centrifuged for 3 min at 1000 rpm, and the supernatant removed. The coated particles were then mixed with benzene, stirred and centrifuged for 2 min at 1000 rpm. The next step in the procedure was decantation and filtration of the supernatant. This process was repeated until the supernatant was nearly colorless after centrifugation. The desorption process was repeated using the same procedure with a blend of 7% MeOH in DCM. In the last step the solvent from the solvent/resin mixture was removed at 90 °C in a rotary evaporator and under a N_2 (g) blanket to ensure that all the solvent was removed. This product has been earlier characterised by Midttun et al. [26].

The Langmuir technique

Surface pressure–area (Π–A) isotherms and monolayer stability isotherms were recorded with a KSV 5000 Langmuir through double-barrier system (KSV Chemicals, Helsinki, Finland). The temperature was kept at 294 ± 0.5 K. The trough was made of Teflon and the barriers of Derlin.

The purity of the surface was monitored before each run by moving the barriers across the pure liquid subphase. The experiment was continued if the surface pressure was less than 0.5 mN/m. The isotherms were measured on freshly spread monolayers, if not otherwise mentioned, after allowing the spreading solvent to evaporate for 15 min. Evaporation of solvent may change the structure of the film forming components, but these changes are negligible compared to the interactions taking place when the compression starts, regardless of the solvent used.

Compression of the film was carried out with a barrier speed of 5 mm/min (per barrier), as long as the increase in surface pressure did not exceed 1 mN m^{-1} min^{-1}. For higher rates, the computer automatically adjusted the barrier speed to 1 mN m^{-1} min^{-1}.

When the asphaltenes and resins were dissolved in mixtures of toluene and hexane, the solvent mixtures were prepared before the crude oil compounds were added.

Results and discussion

Phase diagrams of monolayers of amphiphilic molecules at the air/water interface were generally constructed by considering only the major slope changes in the surface pressure–area isotherms. These slopes reflect the compressibility of the film, and analogously to bulk matter were characterised as gas-like, liquid-like and solid-like [33–35]. Also mesophases in Langmuir films have been reported [36–39], but here only the most apparent types of states are considered. For a more detailed discussion of the various monolayer states and the transition, Gaines [40] and Birdi [41] are recommended.

Gas-like films: The area per molecule is large compared to actual molecular areas, and the film may be expanded to infinity without phase change.

Liquid-like films: Such films are coherent in that some degree of cooperative interactions is present; they appear to be fluid and their Π–A plots extrapolate to zero Π at areas larger than corresponding to a molecular cross section so that some disorganisation in the structure is indicated. This type of film has a rather high compressibility.

Solid-like films: These films may show quite linear Π–A plots, of a low compressibility. This state can be related to as an close packing of the molecules at the surface, and such films appear to be quite rigid.

Rigidity is important regarding the stability of emulsions, because a rigid film on the emulsion droplets prevents coalescence. While a highly compressible film are more easily ruptured and the droplets are free to coalesce.

The most important results from the Langmuir study are summarized in Tables 1 and 2. The tables show that analogous results are obtained for fractions of all the three crude oils. As a consequence we will present the findings

Table 1 Surface concentration of asphaltenes and resins (from three different crudes) necessary to obtain surface pressure equal to 10 mN/m

Bulk concentration	Solvent composition					
	100% toluene	80% toluene, 20% hexane	60% toluene, 40% hexane	40% toluene, 60% hexane	20% toluene, 80% hexane	100% hexane
[asph] = 1 mg/ml	F 5.1 mg/m^2 N 5.7 mg/m^2 V 5.3 mg/m^2	F 6.9 mg/m^2 N 6.4 mg/m^2 V 6.0 mg/m^2	F 7.2 mg/m^2 N 6.8 mg/m^2 V 6.4 mg/m^2	F 7.3 mg/m^2 N 7.3 mg/m^2 V 8.1 mg/m^2	F 8.1 mg/m^2 N 9.9 mg/m^2 V 9.4 mg/m^2	F 13.0 mg/m^2 N 11.6 mg/m^2 V 9.8 mg/m^2
[asph] = 2 mg/ml	F 5.8 mg/m^2 N 6.8 mg/m^2 V 6.8 mg/m^2	F 7.1 mg/m^2 N 7.3 mg/m^2 V 7.1 mg/m^2	F 7.8 mg/m^2 N 7.4 mg/m^2 V 7.3 mg/m^2	F 7.9 mg/m^2 N 8.1 mg/m^2 V 9.1 mg/m^2	F 10.3 mg/m^2 N 9.8 mg/m^2 V 9.9 mg/m^2	F 19.0 mg/m^2 N 11.7 mg/m^2 V 9.3 mg/m^2
[asph] = 4 mg/ml	F 7.5 mg/m^2 N 7.7 mg/m^2 V 7.7 mg/m^2	F 7.8 mg/m^2 N 7.7 mg/m^2 V 7.6 mg/m^2	F 7.9 mg/m^2 N 8.1 mg/m^2 V 7.7 mg/m^2	F 7.9 mg/m^2 N 8.4 mg/m^2 V 9.6 mg/m^2	F 11.2 mg/m^2 N 11.3 mg/m^2 V 9.8 mg/m^2	F 20.7 mg/m^2 N 17.8 mg/m^2 V 9.4 mg/m^2
[asph] = 8 mg/ml	F 9.2 mg/m^2 N 9.0 mg/m^2 V 9.0 mg/m^2	F 9.4 mg/m^2 N 9.1 mg/m^2 V 8.7 mg/m^2	F 9.2 mg/m^2 N 8.8 mg/m^2 V 9.0 mg/m^2	F 8.8 mg/m^2 N 8.8 mg/m^2 V 10.1 mg/m^2	F 13.6 mg/m^2 N 12.1 mg/m^2 V 11.2 mg/m^2	F 25.0 mg/m^2 N 22.6 mg/m^2 V 17.3 mg/m^2
[res] = 2 mg/ml	F 2.01 mg/m^2 N 2.59 mg/m^2 V 3.5 mg/m^2	– – –	– – –	– – –	F 2.08 mg/m^2 N 2.26 mg/m^2 V 3.34 mg/m^2	F 2.51 mg/m^2 N 2.71 mg/m^2 V 3.95 mg/m^2
[res] = 8 mg/ml	F 2.10 mg/m^2 N 2.63 mg/m^2 V 3.54 mg/m^2	F 2.27 mg/m^2 N 2.50 mg/m^2 V 3.61 mg/m^2	F 2.45 mg/m^2 N 2.64 mg/m^2 V 3.68 mg/m^2	F 2.41 mg/m^2 N 2.80 mg/m^2 V 3.61 mg/m^2	F 2.36 mg/m^2 N 2.92 mg/m^2 V 3.84 mg/m^2	F 2.65 mg/m^2 N 2.84 mg/m^2 V 4.10 mg/m^2

Table 2 Surface concentration of asphaltene/resin combinations necessary to obtain surface pressure = 10 mN/m (Bulk concentration = 4 mg/ml)

Bulk composition	Solvent composition			
	100% toluene	60% toluene, 40% hexane	20% toluene, 80% hexane	100% hexane
100% asph	F 7.5 mg/m^2 N 7.7 mg/m^2 V 7.7 mg/m^2	F 7.9 mg/m^2 N 8.1 mg/m^2 V 7.7 mg/m^2	F 11.2 mg/m^2 N 11.2 mg/m^2 V 9.6 mg/m^2	F 20.7 mg/m^2 N 17.8 mg/m^2 V 25.5 mg/m^2
80% asph, 20% res	F 6.3 mg/m^2 N 6.2 mg/m^2 V 6.6 mg/m^2	F 6.0 mg/m^2 N 6.5 mg/m^2 V 6.8 mg/m^2	F 5.5 mg/m^2 N 6.4 mg/m^2 V 7.1 mg/m^2	F 6.5 mg/m^2 N 8.1 mg/m^2 V 9.0 mg/m^2
60% asph, 40% res	F 4.21 mg/m^2 N 4.81 mg/m^2 V 4.92 mg/m^2	F 4.17 mg/m^2 N 4.51 mg/m^2 V 5.3 mg/m^2	F 3.89 mg/m^2 N 5.8 mg/m^2 V 5.8 mg/m^2	F 3.99 mg/m^2 N 6.0 mg/m^2 V 7.4 mg/m^2
40% asph, 60% res	F 3.15 mg/m^2 N 3.72 mg/m^2 V 3.93 mg/m^2	F 3.43 mg/m^2 N 3.52 mg/m^2 V 4.21 mg/m^2	F 3.07 mg/m^2 N 3.93 mg/m^2 V 4.92 mg/m^2	F 2.92 mg/m^2 N 4.44 mg/m^2 V 5.5 mg/m^2
100% res	F 2.02 mg/m^2 N 2.58 mg/m^2 V 3.52 mg/m^2	F 2.23 mg/m^2 N 2.54 mg/m^2 V 3.43 mg/m^2	F 2.13 mg/m^2 N 2.88 mg/m^2 V 3.59 mg/m^2	F 2.63 mg/m^2 N 2.83 mg/m^2 V 3.34 mg/m^2

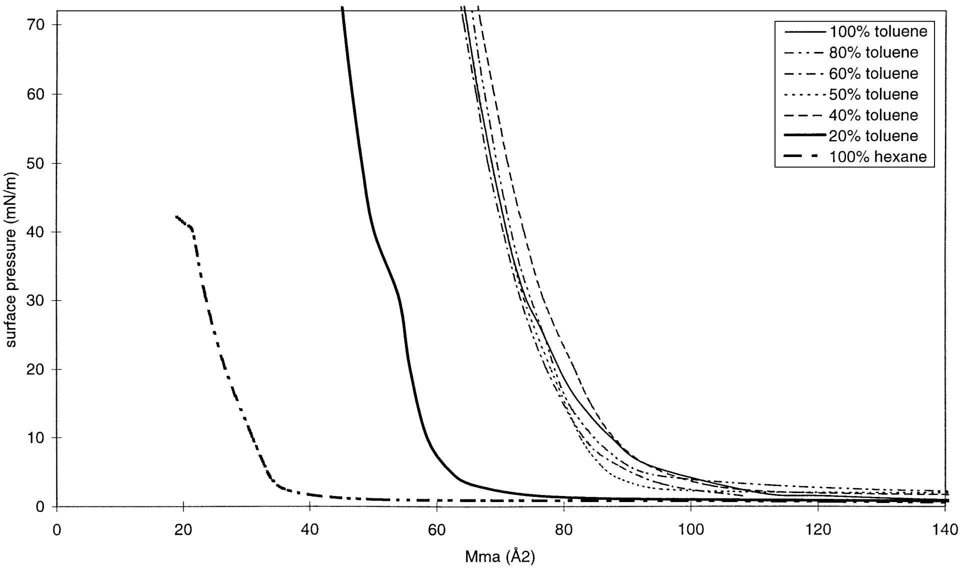


Fig. 1 $\Pi - A$ isotherms of asphaltenes spread from different solvents on pure water (bulk concentration = 4 mg/ml)

and discuss the results in detail for only one crude, i.e. the crude marked F.

Asphaltenes

Figure 1 shows the isotherms for asphaltenes spread from different solvents. The bulk concentration in this case is 4 mg/ml. The graph provides information about the ability of the heavy fractions to pack into a two-dimensional film on a water surface. At high surface areas there is no variation in surface pressure, until a sharp increase is observed. Here the asphaltene molecules/aggregates start to interact, and after this the film has a low compressibility. The rise in surface pressure is likely due to interactions between the rigid aromatic hydrocarbon parts of the asphaltenes. The relatively few polar groups are probably still so far apart that interaction between these does not play a major role.

The quantity mean molecular area along the *x*-axis does not give the correct size of the molecules, since the asphaltenes form particles or association structures. It is the shape of these isotherms, and the relative variations that are of interest. In order to get comparable results along the x-axis, the readings are converted to barrier positions. From these values we have calculated the surface concentration of asphaltenes needed to create a pressure equal to 10 mN/m. These calculations are presented in Table 1. The uncertainty in these numbers is about ±2% (which also is the case for the results in Table 2). Table 1 shows that an increased surface concentration of asphaltenes is required in order to achieve the same surface pressure when going from pure toluene to pure hexane. Further there is an increase in the surface concentration when the bulk concentration varies from 1 to 8 mg/ml. The results are better illustrated in Fig. 2, where the surface concentration is plotted against vol% toluene in the solvent.

Toluene is a better solvent for asphaltenes than n-hexane, due to the presence of larger dispersion and polar forces in the aromatic solvents. Also the tendency of the aromatics to act as weak acceptors for hydrogen bonds will facilitate the dissolution of asphaltenes in these solvents. As a consequence larger association structures are built up in n-hexane. As demonstrated by Moschopedis et al. [22] the decrease in the size of the asphaltene aggregates can be related to the increase in the dielectric constant of the solvent. Toluene has a dielectric constant of

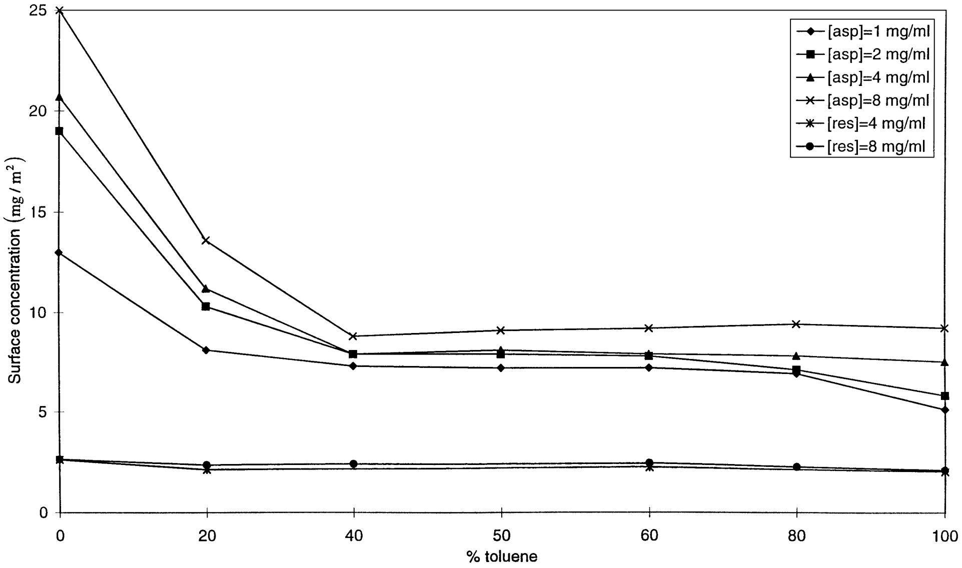


Fig. 2 Surface concentration of asphaltenes and resins needed to obtain Π = 10 mN/m vs. vol% toluene in the spreading solvent with varying bulk concentration

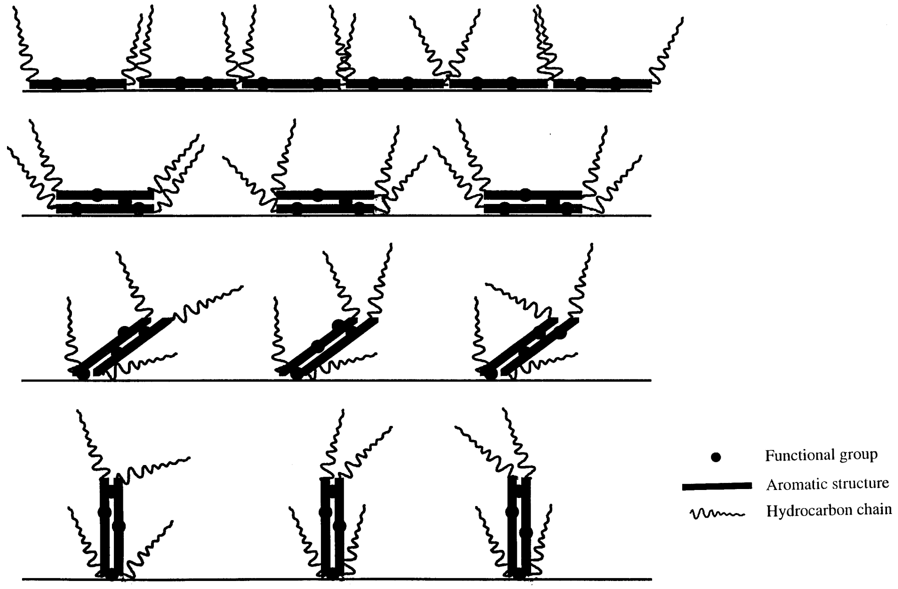


Fig. 3 Illustration of possible orientations of asphaltenes on a liquid surface and possible aggregation structure of these segments at different surface pressure

2.438 at 0 °C, while the corresponding value for *n*-hexane is 1.89 at 20 °C [42]. From Fig. 2 we observe increased surface concentrations of asphaltene when the hexane content exceeds 60 vol%. This is caused by the size of the aggregates. When the asphaltenes are associated, all the present polar groups do not reach the surface. For larger asphaltene structures, more material is needed to give rise to the same pressure. If the asphaltene molecules in a monomolecular film at the surface would be non-interacting species, the surface area/molecule would be completely governed by the interaction between the molecules and water. This is more or less the situation when spreading from solvents with a high content of toluene. The aggregation of the asphaltene molecules will completely change this pattern. An interaction between the condensed and flat parts of the asphaltene molecules, would most likely result in sandwich-type of structure where these structures could have different angels with the surface (Fig. 3).

The observed increase in surface concentration at $\Pi = 10$ mN/m when the bulk concentration is changed 1 to 8 mg/ml, is probably a consequence of transition from oligomer to polymer order of the asphaltenes. If the hexane content in the spreading solvent exceeds 60 vol%,

Fig. 4 Monolayer stability of asphaltenes at $\Pi = 10$ mN/m spread from different solvents on pure water

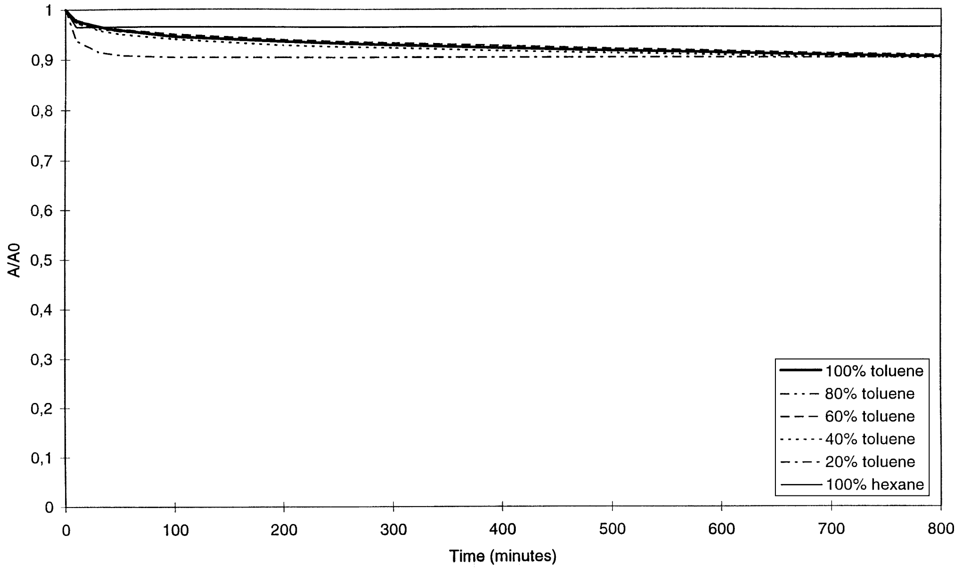
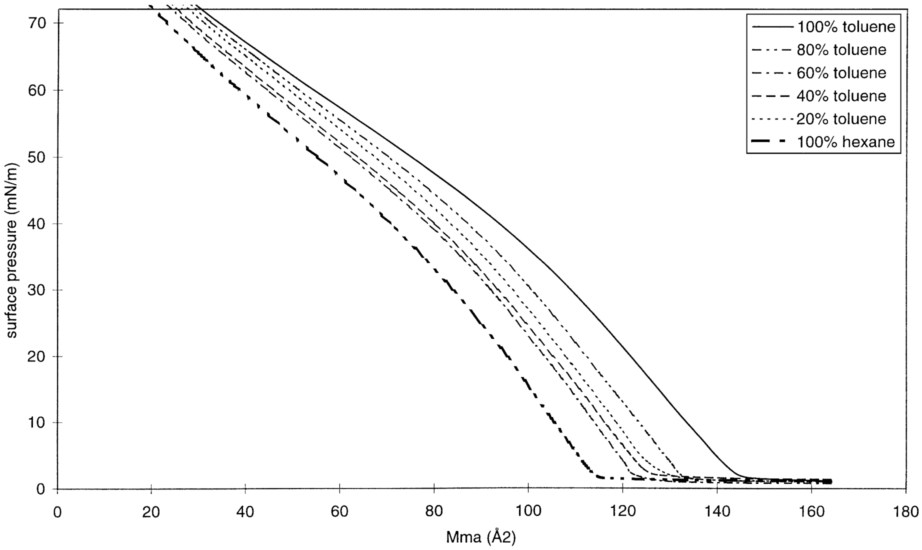


Fig. 5 Π–A isotherms of resins spread from different solvents on pure water (bulk concentration = 4 mg/ml)



the perceptible increase in surface concentration seen in the transition from 4 to 8 mg/ml solutions is not necessarily a result of increased particle size, because 8 mg/ml asphaltenes spread from aliphatic solvents gives films that no longer are a monolayer. On the contrary, when studying these films at constant surface pressure the pressure was observed to continue to increase above 10 mN/m when the barriers were not moving. This indicates a multilayer structure on the surface, since the available area no longer is sufficiently large to maintain the film at a stable pressure.

Figure 4 shows the monolayer stability isotherms (loss of monolayer area) at constant surface pressure (10 mN/m) for the series of different solvents when the bulk concentration is 4 mg/ml. This figure indicates a small area loss in the beginning of the measurement before it stabilises at constant pressure, which verify the stability of the investigated monolayers. Since these films are stable we have reason to believe that the same is the case if the bulk concentration is less than 4 mg/ml.

Resins

In Fig. 5 the isotherms of resins spread from different solvents are presented. The bulk concentration is 8 mg/ml. In contrast to the results seen for the asphaltenes, these films show high degree of compressibility at high surface pressures. This phenomenon indicates that other processes than straightforward compression of the hydrocarbon chains is taking place. This process, involving higher compressibility and enabling the units to pack into very small areas, is probably a collapse of the segments, which pass out of the surface plane and gradually building up an overfilm. So the increase in surface pressure, which describes the energy needed to compress the film is partly used to overcome repulsions between the molecules, and partly to force some of the residues away from the surface. As the pressure rises, more and more energy is dissipated in forcing groups into the overfilm.

These properties resemble those for films of polymers as reported in Group I [43], which consists of amorphous, usually soft polymers giving stable fluid films gelating at high surface pressure (20–30 dyne/cm.), e.g. polyvinyl acetate, polyacrylates, cellulose ethers, aliphatic aldehyde compounds of polyvinyl alcohol. Some polymers from this group shows no heterogeneity at rather small areas, where it must be more than a monolayer in thickness. These films are well spread, and remain uniform even when thickened by compression into a multi-molecular layer, which eventually collapses into folds.

Films having long hydrocarbon chains show greater resistance to collapse than polymer films. Since forces between interlocking $-CH_2-$ groups provide a high-energy barrier to be overcome before the molecules can enter a crystalline state. These forces are revealed by the rigidity of solid films and the high viscosity (relative to bulk viscosities) of liquid condensed films [44].

The necessary amount of resins on the surface to achieve $\Pi = 10$ mN/m is given in Table 1, and these results are illustrated in Fig. 2 along with the corresponding results for the asphaltenes. These figures indicate that the solvent has less influence on the resins than on the heavier fraction. For 4 mg/ml solutions of resins there is a reduction in surface concentration at $\Pi = 10$ mN/m of 23% from pure hexane to pure toluene, while for

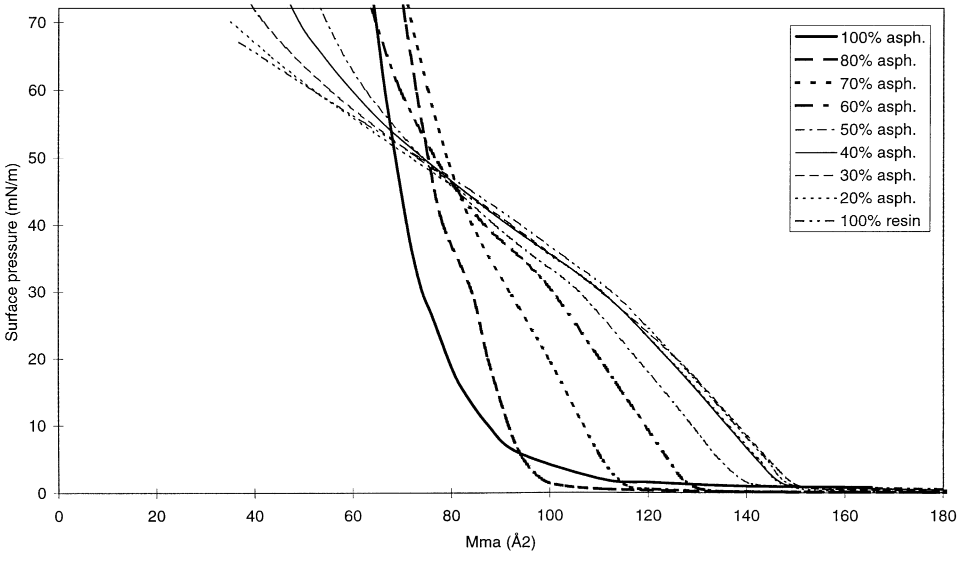


Fig. 6 Π–A isotherms of asphaltene/resin mixtures spread from pure toluene on pure water (bulk concentration = 4 mg/ml)

asphaltenes the reduction is 64%. The bulk concentration is of no major importance with regard to the resins film properties.

Compared with asphaltenes, smaller amounts of resins are needed on the surface to achieve increased surface pressure. This is probably a consequence of more polar groups, which will demand more space at the surface, in the resin fraction than in the asphaltene fraction.

Introduction of the aromatic solvent increases the dispersion forces between the solvent molecules. It seems like an inversion from big aggregates to monomer-like structures in the asphaltene fraction demands a higher degree of aromaticity, than needed with only resins present. After the aromaticity is high enough to dissolve the resins, only small variations are observed. Small variations in surface concentration at $\Pi = 10$ mN/m with increased bulk concentration, indicates no major increase in the resins association structures. These results shows that the resins do not associate to the same extent as asphaltenes (also reported by Koots and Speight [27]), so there are weaker intermolecular interactions in the lighter than in the heavier fraction.

Monolayer stability isotherms at constant surface pressure (10 mN/m) for resin-films, resulted in a similar trend as for 8 mg/ml asphaltene in pure hexane. But for the resins there was an increase in pressure only during the first couple of hours, before the pressure stabilized at a constant value (still with stationary barriers). This is in

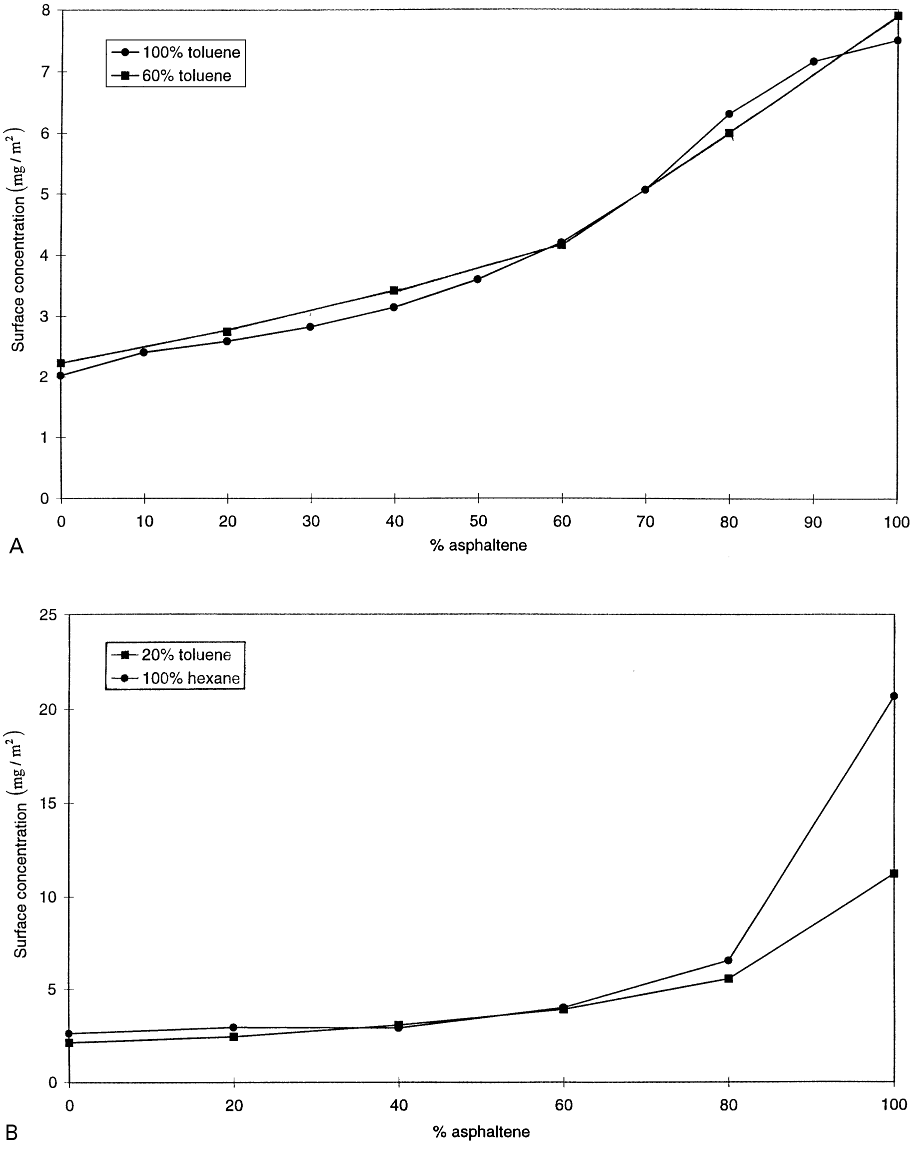


Fig. 7 (a) Surface concentration of mixed film material needed to obtain $\Pi = 10$ mN/m vs. wt% asphaltene in the asphaltene/resin mixture when spread from aromatic solvent (b) Surface concentration of mixed film material needed to obtain $\Pi = 10$ mN/m vs. wt% asphaltene in the asphaltene/resin mixture when spread from aliphatic solvent

accordance with a multilayer formation at the surface. In addition the effect may be due to oxidation of the surface layer, which would result in higher polarity of the film. This process entails increased affinity of the film material towards the surface, giving increased pressure. In order to understand this effect, a film of 8 mg/ml resin in pure toluene was spread at the surface and left there, free to interact with the air, for three hours (instead of 15 min) before the compression was started. The surface concentration to achieve $\Pi = 10$ mN/m was now reduced from 2.10 to 1.88 mg/m^2. The reduction indicates that the increase in surface pressure over time likely is an effect of oxidation in addition to formation of a multilayer.

Mixtures of asphaltenes and resins

Combinations of asphaltenes and resins gave the isotherms in Fig. 6, when spread from pure toluene. Surface concentrations to obtain $\Pi = 10$ mN/m for combinations of the two fractions spread from different solvents are given in Table 2, with an uncertainty of ±2%. These results are illustrated in Fig. 7. There is a gradual increase in repulsion at moderate surface pressures as the amount of resin in the film increases. This is a consequence of increased polarity in the film. This trend is seen regardless of which solvent the films are spread from (Fig. 7), but the variation is more gradual if pure toluene is used (Fig. 7). An effect which may be explained by the state of the asphaltenes in the aromatic solvent. The smaller the asphaltene species are, the more space at the surface are occupied by the asphaltenes. Hence, the dominating affinity of the resins will be restricted.

When the resin content exceeds 40% a distinct increase in compressibility at high surface pressures is observed. So for these amounts, the more polar fraction starts to predominate the film properties due to the higher affinity of the resins towards the surface (water/air). This tendency has been verified by independent surface tension measurements showing that the resins have a much higher affinity towards the water/air surface than the asphaltenes [45].

Stability isotherms for the combinations of asphaltenes/resins gave the same result as for the pure resin fractions. The increase in surface pressure with stationary barriers became more prominent as the resin content increased.

Film studies of naturally occurring surfactants from curd oil by means of the Langmuir–Blodgett technique provides a model system for investigation of film properties. The main limitation with this technique is that the measurements have to be carried out on a liquid/gas surface and not at an interface between two liquids. However, the interpretations of the film properties done here relates to the interactions within the film, that is internal properties in the film. Comparison of these film behaviours with studies of emulsion stability [46] shows that the rigid asphaltene film stabilises emulsions, while the compressible resin film not alone are able to give a mesostable emulsion. In this way it is possible to relate the results from the L–B studies on the water/air surface to emulsion stability.

Conclusions

The asphaltenes seem to pack closer at the water surface, giving rise to a more rigid film than the resins. The size of the asphaltene aggregates seem to increase when the spreading solvent becomes more aliphatic, and with increased bulk concentration. The concentration effect is more prominent in the aliphatic than in the aromatic solvent. The resin films show high compressibility, which indicates a collapse of the monomolecular film. A comparison between asphaltenes and resins shows that the resins are more polar and that they do not aggregate to the same extent as the asphaltenes. In addition to this, resins show a high degree of sensitivity towards oxidation. Analysing the combination of the two fractions in a mixed film indicates that the resins starts to predominate the film properties when the resin content exceeds 40 wt%.

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References

1. Graham DE (1988) Chemicals in the oil industry. In: Ogden PH (ed) Royal Society of Chemistry, London, pp 155–175
2. Paczynska-Lahme B (1990) Colloid Polym Sci 83:196
3. Sjöblom J, Urdahl O, Høiland H, Christy AA, Johansen E (1990) Colloid Polym Sci 82:131
4. Stockwell A, Taylor AS, Thompson DG (1986) Surfactants in solution, Vol 6. In: Mittal KL, Bothorel P (eds) Plenum Press, New York, pp 1617–1632
5. Sjöblom J, Söderlund H, Lindblad S, Johansen EJ, Skjarvö IM (1990) Colloid Polym Sci 268:389
6. Mingyuan L, Christy AA, Sjöblom J (1992) Emulsions. A fundamental and practical approach. In: Sjöblom J (ed) Kluwer, Dordrecht, The Netherlands, pp 157–172
7. Sjöblom J, Urdahl O, Nordli KG, Mingyuan L, Saeten JO, Christy AA, Gu T (1992) Adv Colloid Interface Sci 41:241

8. Yen TF, Erdman JG (1962) Prepr Am Chem Soc Div Pet Chem 7:99
9. Yen TF (1962) Prepr Am Chem Soc Div Pet Chem 17:F102
10. Haley GA (1972) Anal Chem 44:580
11. Speight JG (1972) Appl Spectrosc Rev 5:211
12. Speight JG (1994) Appl Spectrosc Rev 29:117
13. Dickinson EM (1980) Fuel 59:290
14. Bandurski E (1982) Energy Sources 6:47
15. Sadeghi KM, Sadeghi MA, Wu WH, Yen TF (1989) Fuel 68:782
16. Ali LH, Al-Ghannam KA, Al-Rawi JM (1990) Fuel 69:519
17. Speight JG (1996) Suspensions: Fundamentals and applications in the petroleum industry. In: Schramm LL (ed) American Chemical Society, Washington DC, pp 377– 401
18. Speight JG (1991) The chemistry and technology of petroleum. Marcel Dekker, New York
19. Winniford RS (1963) J Inst Pet 9:215
20. Moschopedis SE, Speight JG (1977) Fuel 56:344
21. Moschopedis SE, Fryer JF, Speight JG (1976) Fuel 55:227
22. Speight JG, Wernick DL, Gould KA, Overfield RE, Rao BML, Savage DW (1985) Rev Inst Fr Pet 40:51
23. Yen TF (1974) Energy Sources 1:447
24. Moschopedis SE, Speight JG (1976) Proc Assoc Paving Technol 45:78
25. Midttun Ø, Sjöblom J, Kvalheim OM (1997) Progr Colloid Interface Chem, submitted
26. Sanchanen AN, Wassiliev L (1927) Petrol Zeit 23:1618
27. Koots JA, Speight JG (1975) Fuel 54:179
28. Mack C (1932) J Phys Chem 36:2901
29. Pfeiffer JP, Saal RN (1940) J Phys Chem 44:139
30. Dickie JP, Yen TF (1967) Anal Chem 39:1847
31. Speight JG (1971) Fuel 50:102
32. Whim BP, Johnson PG (eds) (1996) Directory of Solvents. Blackie, London
33. Dervichian DG (1939) J Chem Phys 7:931
34. Harkins WD, Boyd D (1941) J Phys Chem 45:20
35. Adam NK (1941) Physics and chemistry of surfaces, 3rd ed. Oxford University Press, London
36. Overbeck GA, Möbius D (1993) J Phys Chem 97:7999
37. Lawrie GA, Barnes GT (1994) J Colloid Interface Sci 162:36
38. Kaganer VM, Osipov MA, Peterson IR (1993) J Chem Phys 98:3512
39. Cai Z, Rice SA (1990) Faraday Discuss Chem Soc 89:211
40. Gaines Jr GL (1966) Insoluble monolayers at liquid–gas interfaces, Wiley-Interscience, New York
41. Birdi KS (1989) Lipid and biopolymer monolayers at liquid interfaces. Plenum Press, New York
42. Weast RC, Astle MJ (eds) (1984) CRC handbook of chemistry and physics, 63rd ed. CRC Press, Cleveland, OH
43. Crisp DJ (1946) J Colloid Sci 1:49
44. Joly M (1937) J Phys Radium 11:471
45. Schildberg Y, Sjöblom J, Christy AA (1995) J Disp Sci Technol 16(7):575
46. Ese M-H, Sjöblom J, Førdedal H, Urdahl O, Rønningsen HP (1997) Colloids Surfaces 123–124:225