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ORIGINAL CONTRIBUTION

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An atomic force microscopy study of asphaltenes on mica surfaces. Influence of added resins and demulsifiers

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Abstract Monolayers of asphaltene and resins on the water surface have been transferred at a surface pressure of 10 mN/m onto mica substrates using the Langmuir–Blodgett technique. Atomic force microscopy (AFM) has been used to examine the topography of these layers. Monolayers consisting of pure asphaltene fractions provide a rigid film with a close-packed structure, while the resins build up a continuous open network. Mixed films of these two fractions show that a gradual increase in resin concentration leads to an opening of the rigid asphaltene structure towards a more resin like configuration. Increased aggregation when the two heavy functions are present in one film is seen as larger individual units in the AFM pictures. Addition of high-molecular-weight demulsifiers/inhibitors results in the same kind of influence on the asphaltene film as seen with the resins.

Key words Asphaltenes · Resins · Langmuir–Blodgett · Mica · Atomic force microscopy

Introduction

Asphaltenes and resins are the heavy fractions of petroleum which are responsible for the formation of stable/mesostable emulsions during oil production. Rigid films of mainly asphaltenes accumulate on the water droplets dispersed in the oil phase and stabilise the water-in-oil emulsion towards coalescence.

Asphaltenes are the components of crude oil that are insoluble in light hydrocarbons such as *n*-pentane or *n*-heptane in a volume ratio of 1 (crude oil):40 (*n*-alkane), i.e. asphaltenes are by definition [1] a solubility class. This fraction corresponds to the heaviest and most polar among the constituents of crude oil.

By means of a variety of spectroscopic methods [2–9] the hydrocarbon skeleton can be described to a high degree of detail. From the results of these studies, the asphaltene structure may be characterised as aromatic polycyclic clusters variably substituted with alkyl chains and connected by alkyl and heteroatom bridges. The degree of condensation of each aromatic cluster may be more or less elevated, but generally the number of fused aromatic units does not exceed five to six rings [10]. It has also been shown that the aromatic ring system contains alicyclic substituents [11].

Resins are considered as smaller analogues of asphaltenes with a considerably lower molecular weight. The resin fraction is soluble in the solvents that precipitate the asphaltenes and can be separated from deasphaltened crude oil by chromatographic methods. The adsorbent most commonly used is silica [12–14].

As for the asphaltenes, the resin fraction also contains polyaromatic and naphthenic rings, but the naphthenic character is more pronounced. It has been shown [14, 15] that resins are substituted with longer and a higher number of aliphatic side chains and that they usually contain a highly polar end group with heteroatoms [14].

Since asphaltenes and resins are two contiguous classes of components separated from a continuum of molecules according to their solubilities in a low-molecular-weight alkane, the size and chemical composition of some asphaltene molecules may be quite similar to those of some resin molecules. Considerable overlap

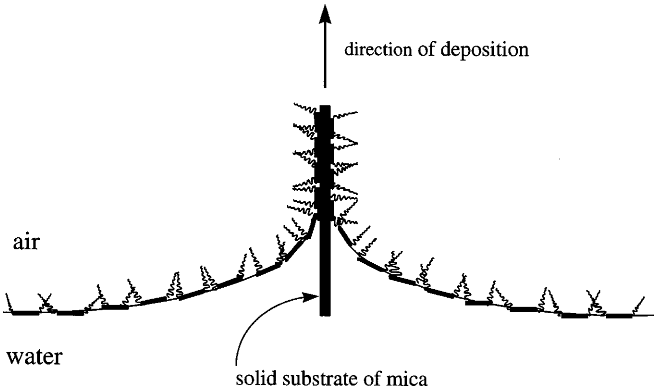


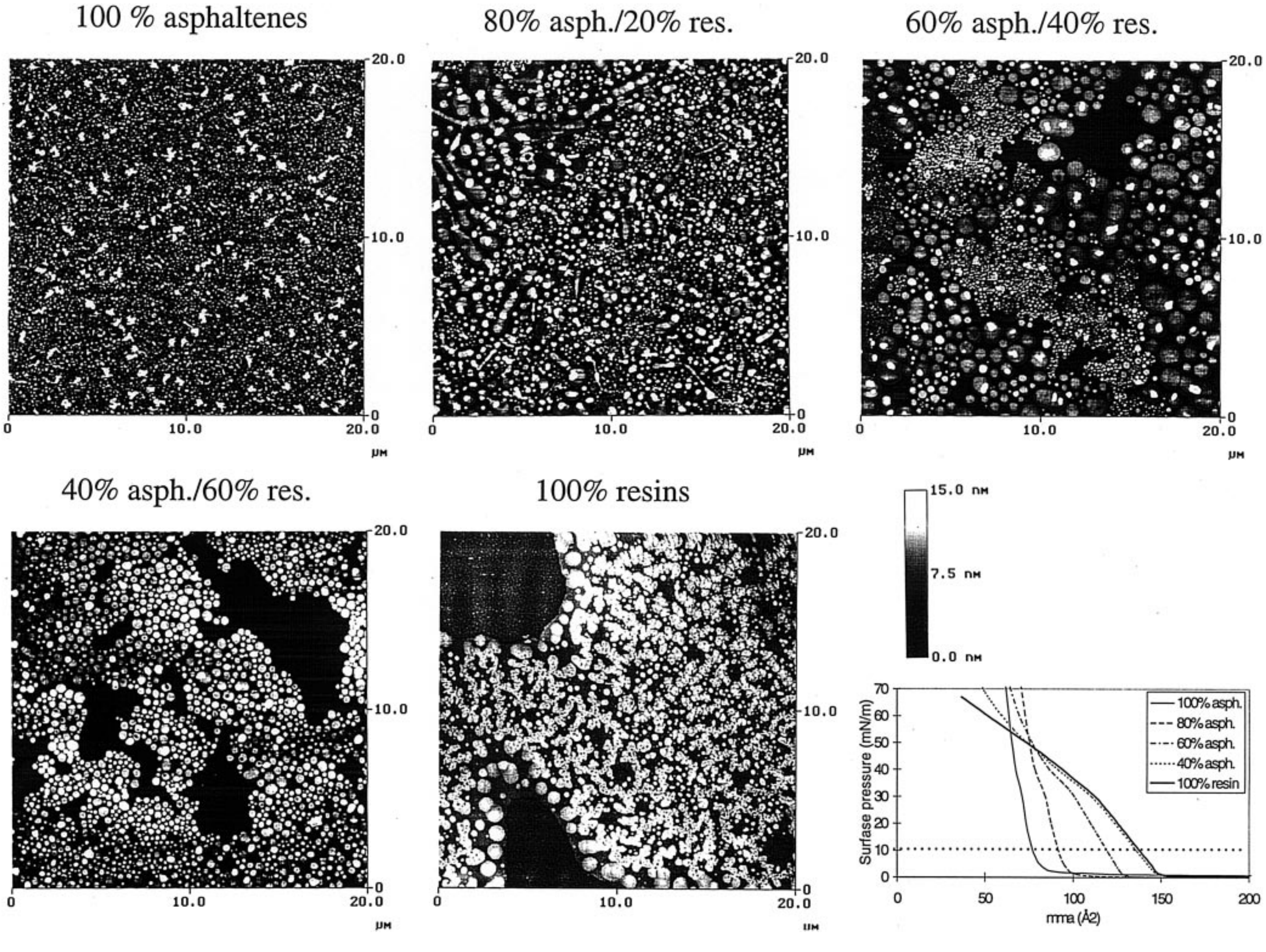
Fig. 1 Schematic drawing of the Langmuir–Blodgett (*LB*) deposition

in size and functionality makes it difficult to come up with universal definitions.

Toulhoat et al. [16] have used atomic force microscopy (AFM) and contact-angle measurements to study adsorption of asphaltenes on freshly cleaved mica plates. Depending on whether the asphaltene solutions where filtered or not, different structures were observed. Adsorption from a filtered solution showed that the contact angle on mica increased significantly in a few seconds, indicating that asphaltenes do have a strong affinity for the mica surface which is in accordance with other work [17]. The adsorption from unfiltered asphaltene solutions studied by Toulhoat et al. [16] resulted in the appearance of largely two-dimensional diffusion-limited aggregates on the mica surface. They concluded that unfiltered solutions contained entities poorly solvated in toluene. Heterogeneous nucleation processes initiate flocculation of these species, giving growth of fractal aggregates at the solid/liquid interface.

In earlier work [18] the Langmuir technique was used in order to achieve a better understanding of the film and interface properties of the heavy fractions and the mechanisms of demulsification of water in crude oil emulsions by use of chemical additives (demulsifiers/

Fig. 2 Atomic force microscopy (*AFM*) images (20 × 20 μm) of monolayers with increasing resin-to-asphaltene ratio, LB film deposited onto mica substrates. The fractions were extracted form crude F



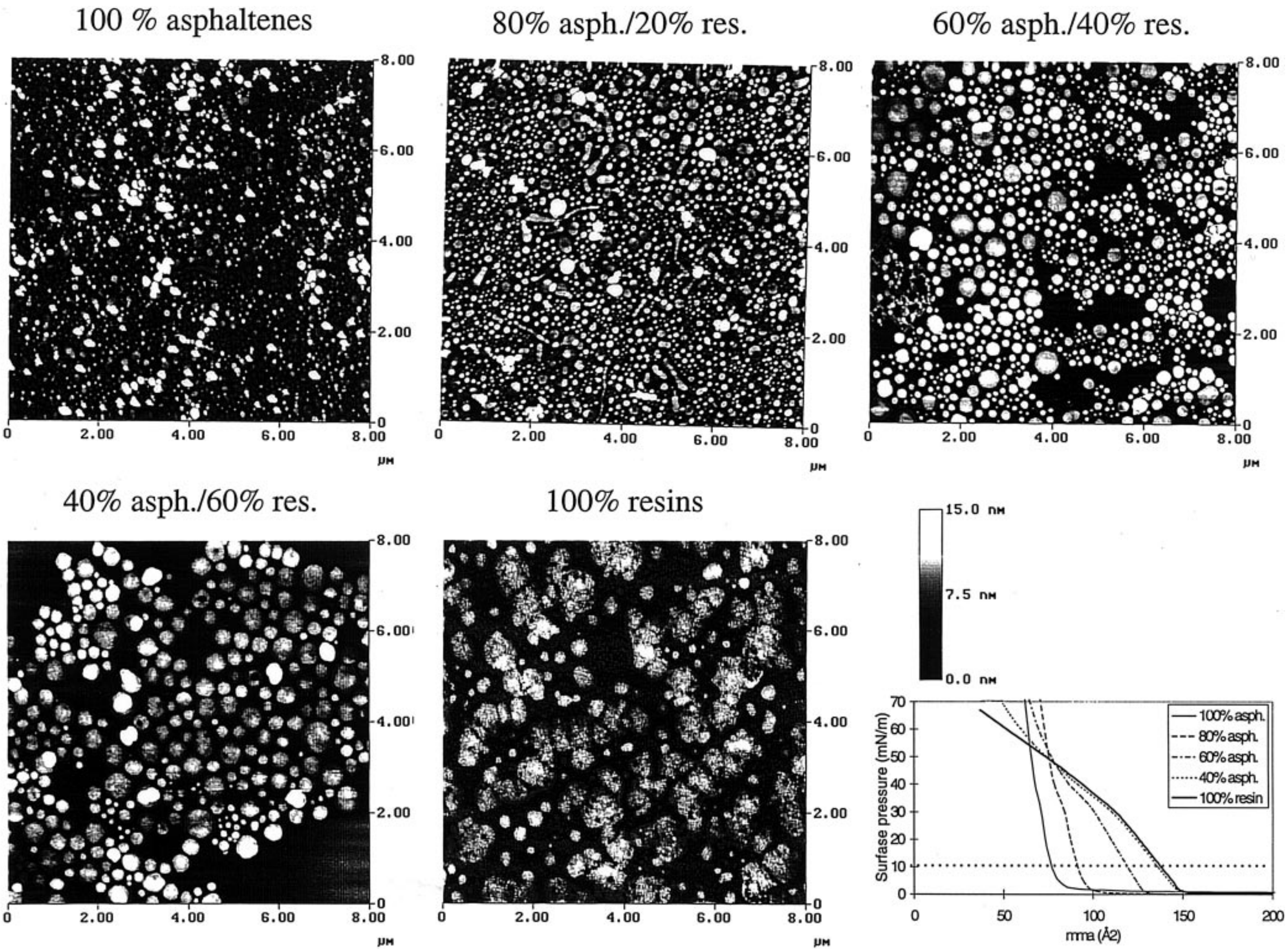


Fig. 3 AFM images (8 × 8 μm) of monolayers with increasing resin-to-asphaltene ratio, LB film deposited onto mica substrates. The fractions were extracted form crude F

inhibitors). It was found that at a water surface, asphaltene films have more pronounced close packing, i.e. give a more rigid film, than the resins. The resin films exhibit a high degree of compressibility, which indicates formation of a multilayer. Introducing these two components together in mixed monolayers gives rise to a gradual increase in compressibility as the amount of resin in the film increases. When present as 40 wt% of the total film material, the resins start to dominate the film properties. Also addition of efficient high-molecular-weight demulsifiers reduces the film rigidity, i.e. increases the compressibility. In addition to changing the film properties of asphaltenes in the same way as the resins, these chemicals form films at the water surface with properties similar to the pure resin film.

The intention of the present study was to visualise the mentioned film properties by means of AFM [19]. AFM is a convenient technique in providing a molecular scale, topographical view of a variety of solid surfaces: organic, inorganic or biomolecular. Under optimum conditions this microscopic technique is capable of producing images showing details of molecular resolution on Langmuir–Blodgett (LB) films. The use of AFM and related probe techniques to image LB films has been reviewed [20, 21].

Experimental

Chemicals

The crude oils were supplied by Elf Aquitaine (crude F) and Norsk Hydro (crude N). Crude F was from a production field in France and crude N was from the North Sea. The information available for the demulsifiers with regard to functionality is summarised in Table 1. *n*-pentane, dichloromethane, methanol, benzene, toluene and acetone were all of p.a. quality form Lab-Scan, Dublin, Ireland. Silanol was obtained from Waters Millipore. The qualitative filter papers used were of type 1 from Whatman, UK. The water used was first purified by reverse osmosis (Millipore RO Plus) and then using a Millipore Milli-Q Plus 185 unit. The mica used as a substrate for the LB films was muscovite mica from various suppliers.

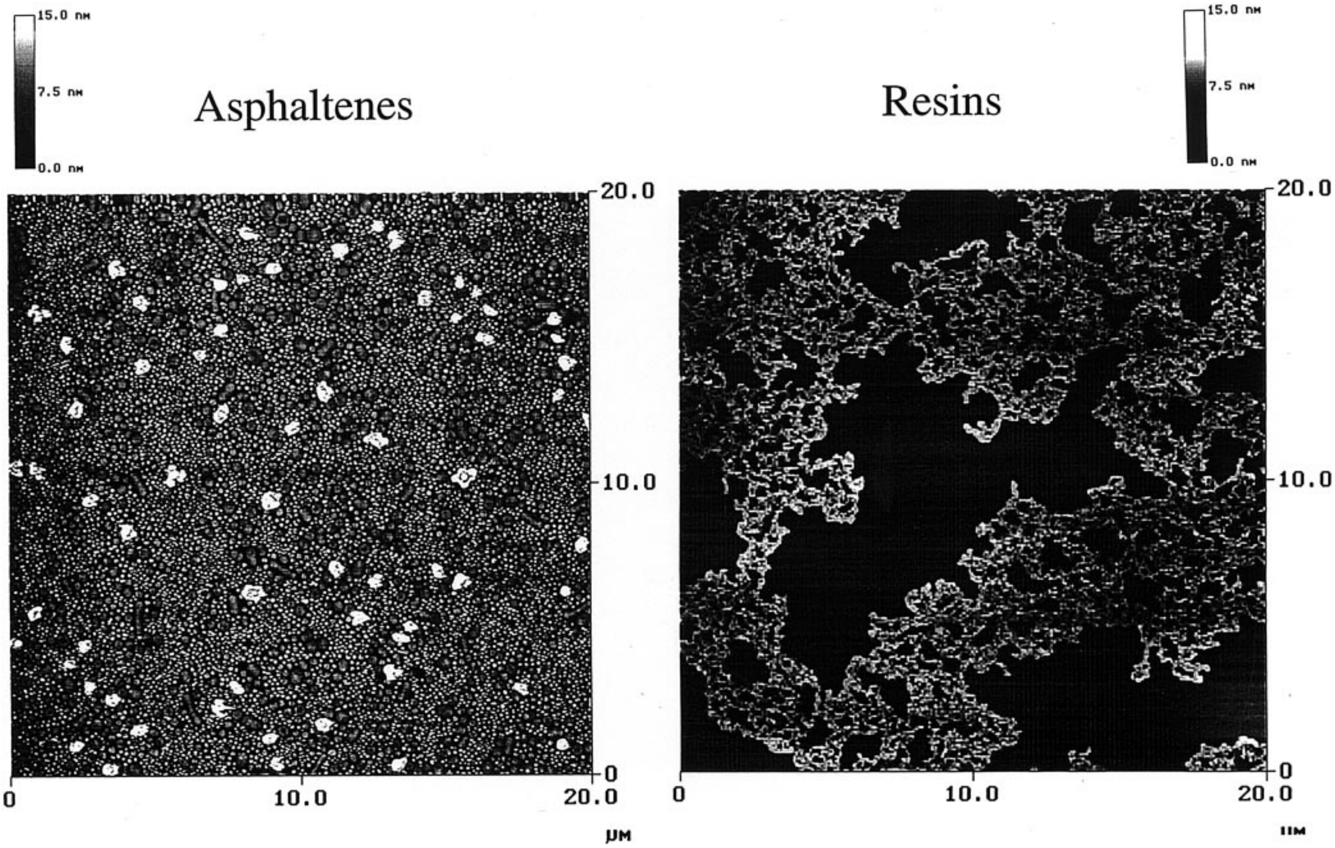


Fig. 4 AFM images (20 × 20 μm) of monolayers of pure components from crude N, LB film deposited onto mica substrates

Separation of asphaltenes and resins

This procedure has been described elsewhere [18].

LB deposition

The surfaces used for microscopic analysis were prepared using a single-barrier KSV trough. The trough was made of Teflon and the barrier of Delrin. The film solutions were spread dropwise at the air–water surface, while the substrate (freshly cleaved mica) was kept submerged in the water phase. After allowing the spreading solvent (toluene) to evaporate for 15 min, the LB film was compressed to a predetermined surface pressure. All depositions were carried out by withdrawing the substrate from the solution at a speed of 5 mm/min, while the surface pressure was held constant at 10 mN/m (Fig. 1). When the substrate had completely emerged from the subphase, it was dried in contact with air and then stored in a vacuum until the AFM analysis had been carried out. The substrates were fixed by a piece of double-sided adhesive tape on a steel sample holder magnetically attached to the AFM stage.

AFM imaging

AFM imaging was performed using a Nanoscope III from Digital Instruments with a J-scanner. Cantilevers (125-μm long) with silicon tips were used. The imaging took place in air at room temperature using the tapping mode [22].

Results and discussion

Langmuir isotherms of all the films analysed by AFM have already been published [18] and the characteristic behaviour of asphaltene and resin films were discussed, together with the effect of chemical additives.

AFM images of 20 μm × 20 μm regions of mica surfaces containing LB-deposited films with increasing resin-to-asphaltene ratio are shown in Fig. 2. These pictures visualise the structural change in the monolayer at a surface pressure of 10 mN/m, when the composition of the film gradually changes from pure asphaltenes to pure resins extracted from crude F. Corresponding Langmuir isotherms are also given in Fig. 2. This is a plot of surface pressure versus mean molecular area, which is a measure of the surface occupied by each molecule. These isotherms show an increase in compressibility with increased resin content. The AFM pictures give an explanation of why the film behaviour changes in this way. The first picture shows a close-packed structures of asphaltenes. Addition of small amounts of resins disturbs the film to some extent, giving a small opening of the structure, but the properties of the monolayer are still dominated by the rigid structure of the asphaltene fraction. A further increase in the resin content affects the film dramatically. The network of the

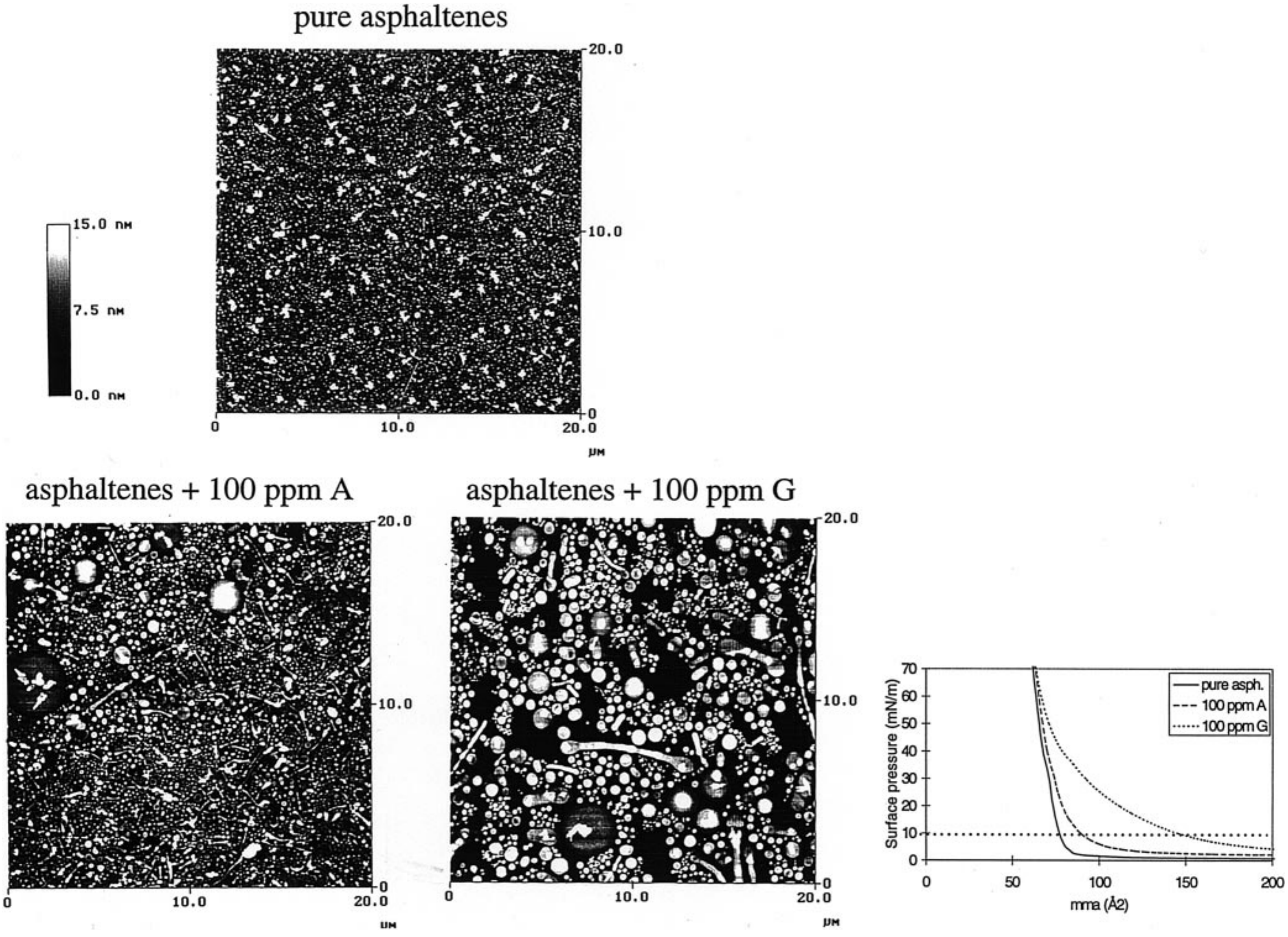


Fig. 5 AFM images (20 × 20 μm) of monolayers consisting of asphaltenes from crude F and 100-ppm high-molecular-weight demulsifiers/inhibitors, LB film deposited onto mica substrates

film material changes towards a more open structure with regions completely uncovered by film material. Pure resins build up a monolayer with an open network. A comparison of the isotherm of the film containing 40 wt% asphaltenes/60 wt% resins with the isotherm obtained for a pure resin film indicates that these two films have the same compressibility, i.e. similar opening of the structure. The AFM images show that the main difference between these two films is the structure of the individual film components.

The components in the film increased in size of the individual units upon addition of resins. This indicates interactions between asphaltenes and resins, providing aggregates of larger dimensions than observed for the pure fractions. Small and moderate amounts of resins give rise to a more polydisperse distribution of the film material, while a further increase in the resin content (i.e. 60 wt% resins) reduces the polydispersity, i.e. the monolayer becomes more uniform in component size when one of the pure fractions dominates the film properties.

AFM pictures obtained with a scan width of 8 μm are shown in Fig. 3. These images provide a better resolution of the same sequence as given in Fig. 2. Some information about the total film structure is lost, but these images give more detailed information about the individual structure of each component in the film. With asphaltenes present, the film material consists of round disks or rod-formed units, while the pure resin film consists of bulky nonuniform structures.

Regarding emulsion stability, Figs. 2 and 3 may indicate why asphaltenes stabilise emulsions while the pure resin fraction does not [23]. On adding small amounts of resins, the rigidity of the film is not lost, but the film components grow in size. McLean and Kilpatric [24, 25] have proposed that the heavy fractions are most efficient as emulsifiers when the stabilising units are at or near the point of precipitation. In accordance with this, a weak increase in component size, as long as the rigid film structure is not dramatically affected, may result

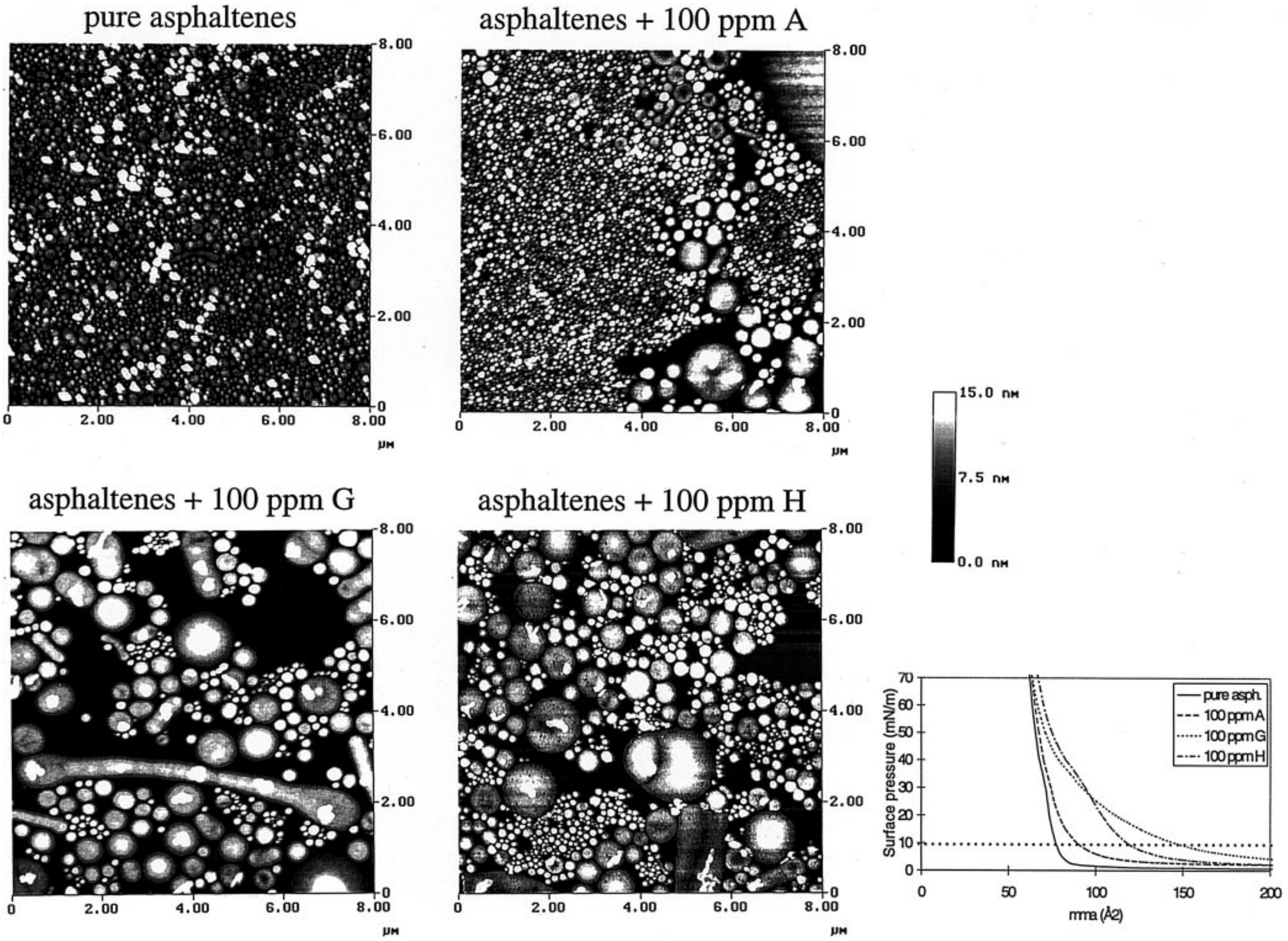


Fig. 6 AFM images (8 × 8 μm) of monolayers consisting of asphaltenes from crude F and 100-ppm high-molecular-weight demulsifiers/inhibitors, LB film deposited onto mica substrate

in more stable emulsions. When the amount of resins present in the film is so large that the structure in the film changes towards a more open network, the efficiency of the film components as emulsifiers is reduced.

AFM pictures of the pure asphaltene and resin fractions from crude N are shown in Fig. 4. A marked difference in film structure is also observed for this crude. Asphaltenes provide a film consisting of a close-packed structure of round disks or rod-shaped components, while the resins build up a continuous and open network.

The regions which emerged, “white spots’, with asphaltenes present in the film, resemble the fractal aggregates observed by Toulhoat et al. [16]. So this may be explained by the same phenomenon, i.e. a heterogeneous nucleation process giving growth of fractal aggregates at the mica surface.

It is important to consider the difference in the surface activity of the two fractions, i.e. the different amount of material needed to obtain the same pressure (10 mN/m). From earlier work [17] it has been found that less resin fraction than asphaltene fraction is needed on the surface in order to increase the surface pressure. The open structure of the resin film is partly a consequence of less film material, but is mainly due to the characteristic packing behaviour of resins on a water surface.

Introduction of chemical additives to asphaltene films might change the film properties in the same way as the addition of resins. AFM pictures of asphaltene films containing 100 ppm of different high-molecular-weight demulsifiers/inhibitors are given in Figs. 5 and 6. In Fig. 5 the effect of two different chemicals is visualised. The scan width of these images was 20 μm. Langmuir isotherms indicate that chemical A has limited influence on the film rigidity, while component G gives rise to a marked increase in the compressibility of the film. The pictures of the corresponding monolayers show that the film containing additive A remains close-packed with a minor disturbance in structure and the appearance of some larger units. Chemical G introduces dramatical changes in the film. It gives rise to both increased size of the individual units and a more open film structure.

Figure 6 shows AFM pictures obtained with a scan width of 8 μm. In this case of third chemical (H) is analysed in addition to A and G. The Langmuir isotherms show that H has an intermediate influence on the film compressibility compared to A and G. Again the pictures illustrate a clear difference between additives A and G, while chemical H seems to give rise to film properties in the region between the two extremes, i.e. A and G.

The effect on the film structure when adding demulsifiers/inhibitors compared to the changes caused by the resins is quite similar. These results indicate that the structural changes observed in the film, i.e. opening of the structure and increased size of the film components, are qualitatively essential in order to reduce the stability of emulsions.

Conclusions

A study of film structures of deposited asphaltene and resins by means of AFM reveals that the resin fractions open up the rigid film formed by asphaltene particles. A second effect is the observed increase in aggregation when both heavy fractions are present, which is seen as larger individual units in the AFM pictures. Chemical additives of high molecular weight were shown to introduce similar changes in the asphaltene film as for the resins.

A comparison of the AFM pictures with earlier Langmuir film studies illustrates that the observed increase in compressibility found is a consequence of changes towards a more open film structure.

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