New chemical insights into the structure and morphology of sea slicks and their geophysical interpretations

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Abstract. The different morphology of palmitic acid methyl ester (PME) slicks spread from *n*-hexane or ethanol was studied by ‘Brewster Angle Microscopy’ [BAM]. In the latter case, already at large areas per molecule a foam-like structure is being formed on the water surface, i.e., a two-dimensional network which appears to be comparable with the morphological structure of biogenic sea slicks. In line with this assumption, both the magnitudes of the radar backscatter damping ratios and the characteristics of the damping ratio/wave number curves were comparable for the PME slick spread from ethanol and for the biogenic slicks, while in the presence of the PME slick spread from *n*-hexane lower damping ratios were determined. In the first instance, we were able to simulate the water wave damping characteristics of the biogenic sea slicks very well. Furthermore, the relaxation of alkanoic acid esters, which are often being found in biogenic sea slicks, was investigated by ‘Infrared Reflection-Absorption Spectroscopy’ [IRRAS]. It turned out that the ester group is continuously hydrated and dehydrated during compression and dilation on an undulating water wave field. It can be safely assumed that the strong water wave damping induced by these chemical compounds is centrally related to this phenomenon.

1. Introduction

Thus far, different model substances have been used in the open sea to simulate biogenic sea slicks with the aim of studying their influence on various remote sensing signals (Alpers and Hühnerfuss 1989, Hühnerfuss 1986, Hühnerfuss and Garrett 1981, Hühnerfuss et al. 1982, 1984, 1987). The choice of these chemicals was largely based on their physico-chemical characteristics and/or their wave damping potential as inferred from wind wave tunnel investigations. In recent experiments during the SIR C/X-SAR campaign, it turned out that the spreading procedure, be it from frozen chunks or be it with the help of spreading solvents, may give rise to significantly different distribution patterns (the so-called „morphology“) on the sea surface and thus to different influences on remote sensing signals.

Morphology effects reflect the phenomenon that the same film-forming compound may be arranged and distributed at the air/water interface in the following different manners:

- The molecules may be spread homogeneously.
- The molecules may form ‘islands’, so-called domains, of different sizes between microns and several hundred microns in diameter (Benvegnu and McConnel 1992).
- The hydrophobic alkyl chains may be arranged vertically with respect to the water surface (i.e., 90°) or at a specific angle of less than 90°. The hydrophobic alkyl chains may exhibit kinks, i.e., the linear arrangement of the alkyl chain is disturbed by irregularities. The head group structure may vary in dependence on the compression status. For more details on these aspects the reader is referred to (Hühnerfuss 1986, Hühnerfuss et al. 1984, 1994).

The clear correlation between morphology effects and remote sensing signals inspired us to perform systematic laboratory investigations on the influence of the spreading procedure on the surface viscosity, the surface potential and on the morphology. The latter aspect, which will be discussed further in this paper, is being studied with the help of ‘Brewster Angle Microscopy’ [BAM], while the molecular structure of the slick/ adjacent water layer system is being investigated by ‘Infrared Reflection-Absorption Spectroscopy’ [IRRAS]. Both methods allow *in situ* investigations of the monolayer at the air water interface without disturbing the structure and morphology of the film. Comparison with scatterometer results obtained over biogenic and man-made sea slicks during the SIR C/X-SAR campaign will illustrate the morphology aspects and their importance for the simulation of biogenic sea slicks.

2. Methods

In the present study, the water surface is being surveyed by two optical methods, i.e., ‘Brewster Angle Microscopy’ [BAM] and ‘Infrared Reflection-Absorption Spectroscopy’ [IRRAS]. A schematic sketch of the BAM setup is shown in Fig. 1a, while the experimental approach is depicted in Fig. 1b.

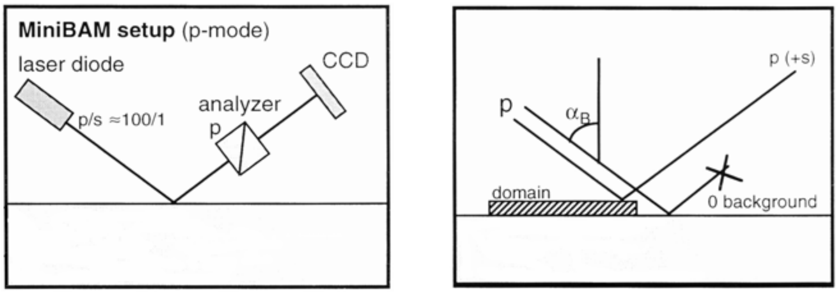

Fig. 1a, left. Schematic sketch of the BAM setup; **1b, right:** Schematic sketch of the experimental approach

If the incidence angle of *p*-polarised radiation is equal to the Brewster angle α_B, the reflectivity from the pure (i.e., slick-free) water surface is close to zero. As a consequence, the water surface appears to be dark. In the presence of a film-forming substance, however, the slick patches represent a different optical medium that gives rise to a measurable reflectivity, which in turn makes the slick domains visible by their lighter appearance. This effect can be recorded by a Charge-Coupled-Device [CCD]-camera.

The infrared reflection-absorption spectroscopy was performed on a Bruker IFS 66 spectrometer (Karlsruhe, Germany) equipped with a MCT detector and a modified external reflection attachment P/N 19650 of SPECAC (Orpington, UK). This included a miniaturized Langmuir-trough, permitting thermostatic measurements. An extensive description of the method can be found in Gericke et al. (1993). The IRRAS set-up as well as the experimental approach can be inferred from the schematic sketch shown in Fig. 2.

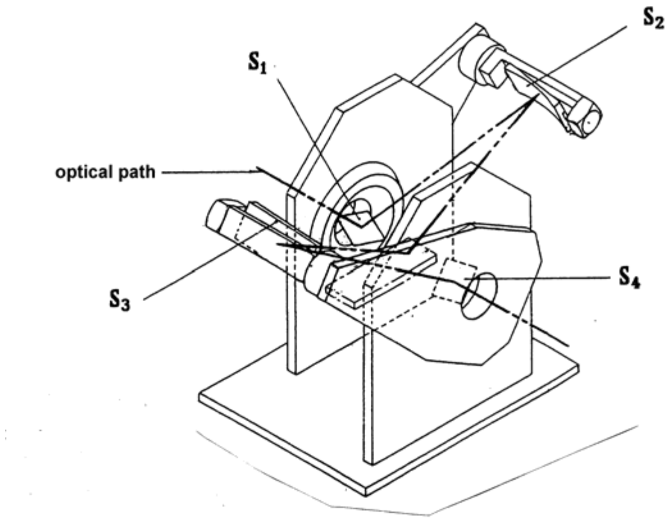

Fig. 2. Schematic sketch of the IRRAS setup: S_1, S_2, S_3, and S_4 are mirrors

3. Results and Discussion

As an illustration of the versatility of BAM, examples of the investigation of two problems will be given:

- the morphology changes during the compression of a slick on an undulating water surface.
- the different morphologies attained by different spreading procedures of slick-forming material.

A sequence of BAM images obtained in the course of compression of a slick consisting of hexadecanoic acid methyl ester (Palmitic acid Methyl Ester = PME) is shown in Figs. 3-5. At large area per molecule, relatively small domains prevail (Fig. 3), which, under compression, combine so that kidney-like shapes are being formed (Figs. 4 and 5). A completely different situation is encountered when the same slick material is being spread from ethanol (Fig. 6). Already at large areas per molecule a foam-like structure is being formed, i.e., a two-dimensional network that is expected to exhibit quite different viscoelastic characteristics compared to those of the morphological structures of the PME film displayed in Figs. 3-5.

The versatility of IRRAS for the *in situ* investigation of slick structures on the air/ water interface is demonstrated in Fig. 7, which summarizes the results of a relaxation experiment: a PME monolayer was generated at a water surface and then compressed to 0.272 nm^2/molecule. In the course of the compression procedure, some disorder is induced within the monolayer. After stopping the compression, the molecules tend to arrange themselves such that an optimum order of the alkyl chains and of the head groups is attained. This is largely the relaxation process that is also encountered on a slick-covered undulating water surface. With regard to the PME films, it is well-documented [4] that the ester head group performs a "flip-flop"-like change in its orientation (the so-called *E/Z*-isomerisation). As a consequence, the head group is prevented from hydration by the adjacent water layer during compression of the monolayer, and, *vice*

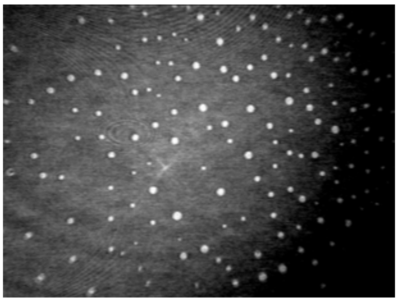

Fig. 3. Morphology of a PME-film spread of *n*-hexane as determined by BAM; compression status 0.34 nm^2/molecule; 1 mm = 100 μm

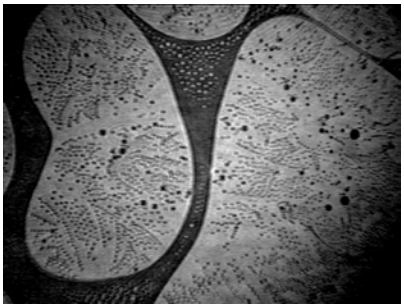

Fig. 4. Same as Fig. 3, but compression status 0.24 nm^2/molecule

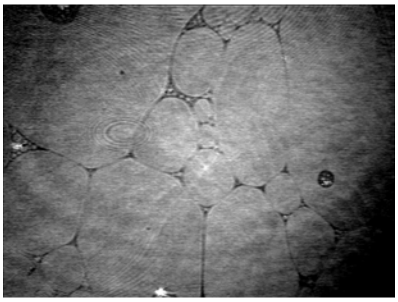

Fig. 5. Same as Fig. 3, but compression status 0.20 nm^2/ molecule

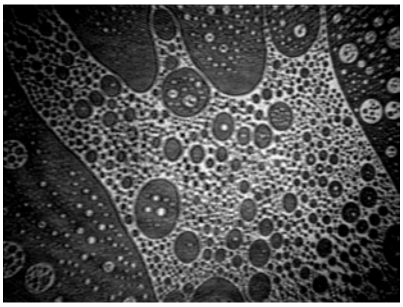

Fig. 6: Morphology of a PME-film spread of ethanol as determined by BAM; compression status 0.415 nm^2/ molecule; 1 mm = 100 μm

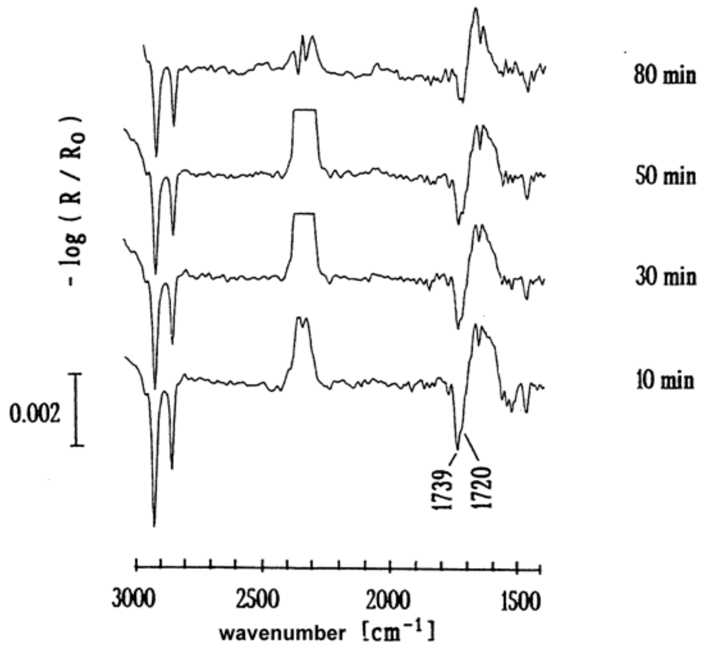

Fig. 7. IR reflection-absorption spectra for a PME slick at the air/water interface after compression to 0.272 nm^2/molecule and subsequent relaxation, from bottom to top after 10, 30, 50, and 80 min, respectively

versa, accessible to water molecules during dilation of the film. The same hydration effect can also be observed during the increasing ordering of the film molecules, i.e., a higher order means more space per molecule and thus an increased possibility for a hydration of the head group. This phenomenon can be followed by IRRAS: In the spectra shown in Fig. 7, a strong band is observed at 1739 cm^{-1} directly after spreading and also 10 min thereafter. This band represents the C=O vibration of an unhydrated carbonyl group. In the course of the relaxation procedure (Fig. 7, $t > 10$ min), a second band appears at 1720 cm^{-1} which indicates the C=O vibration of a hydrated carbonyl group. This results shows that alkanoic acid esters, which are often being found in biogenic sea slicks, are continuously hydrated and dehydrated during compression and dilation on an undulating water wave field. It can be safely assumed that the strong wave damping effect of these compounds is centrally related to this phenomenon.

With the aim of simulating biogenic sea slicks, we generated PME slicks at the sea surface by distributing the film-forming material with the help of different spreading solvents, i.e., by the application of ethanol or *n*-hexane. These man-made sea slicks were overflown by a helicopter carrying a five-frequency multi-polarization radar scatterometer, the so-called HELISCAT of the University of Hamburg. During the same flight, we also overflew biogenic sea slicks, which had been forming sufficiently close to this sea area, under the same meteorological and oceanographic conditions. It turned out that both the magnitudes of the damping ratios as well as the characteristics of the damping ratio/wave number curves determined for the PME slick spread from ethanol (Fig. 8) and for the biogenic slicks (Fig. 9) were very comparable, while in the presence of the PME slick spread from *n*-hexane lower damping ratios were determined.

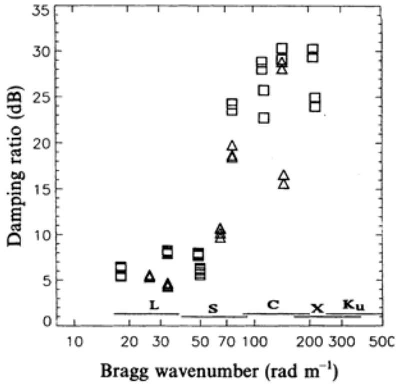

Fig. 8. Damping ratio, i.e., reduction of the backscattered radar power (in dB) induced by a PME slick, which was spread from ethanol, as a function of the Bragg wave-number. The measurements were performed at *L*-, *S*-, *C*-, *X*-, and K_u-band using both *VV*- and *HH*-polarisations (up- [tri-angles] and downwind [squares] look directions)

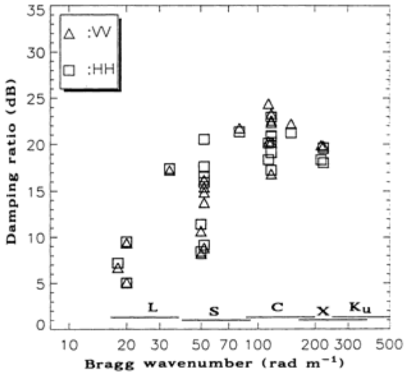

Fig. 9. Damping ratio, i.e., reduction of the backscattered radar power (in dB) induced by natural sea slicks, as a function of the Bragg wave number. The measurements were performed at *L*-, *S*-, *C*-, *X*-, and K_u-band using both *VV*- [triangles] and *HH*-polarisations [squares]

Obviously, we were able to simulate the water wave damping characteristics of the biogenic sea slicks, in this case largely secreted from *phaeocystis globosa*, as well as their influence on backscattered radar signals very exactly by spreading PME from ethanol. This result is conceivable, because biogenic slicks are being formed from microdroplets that are secreted by plankton, i.e., many tiny point sources will appear at the sea surface, if the wind speed and thus the turbulence of the upper water layer will be sufficiently reduced, say below about 7 m/s wind velocity. Furthermore, many alkanoic acid esters have been found in biogenic sea slicks, i.e., chemical compounds exhibiting structures very similar to PME. Therefore, it can be safely assumed that very comparable morphological structures are prevailing in biogenic sea slicks and in PME slicks spread from ethanol.

4. References

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