DETECTION OF MICELLAR STRUCTURES IN OIL-WATER-SURFACTANT SYSTEMS WITH A PHOTOACOUSTIC METHOD

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Model studies were performed with a layered system consisting of thin olive oil layers
(25 – 250 μm in thickness) spread over the water surface using a photoacoustic method.
Significant variations in the signal phase and amplitude found out at the interfaces (air/oil
and oil/water) as well as at a depth of 9 – 13 μm beneath the oil surface point to the for-
mation of organized clathrate molecular structures under the film-covered surfaces and
micellar structures of surfactants if present in a bulk oil phase at an appropriate con-
centration (above CMC) and temperature (Krafft point). Such organized structures have
different thermodynamic properties (like specific heat or thermal diffusivity, discussed in
terms of classical thermodynamics of thin surface layers) that is supposed to affect the
photoacoustic effect used for depth profiling.

1. Introduction

Shallow coastal marine waters are enriched in a wide variety of oil and surface-active
substances (surfactants) being a result of pollutant organic slicks from petroleum spills
or municipal effluents containing: detergents, fertilizers, washing agents, chemicals etc.

At an appropriate concentration of surfactants (above CMC — critical micellar con-
centration) and temperature (Krafft point) they form compact monomolecular diffusion-
controlled layers at interfaces and organized molecular aggregates (micelles) in the bulk
water beneath the adsorbed film [8].

Surface film studies performed in coastal regions of the Baltic and Mediterranean
Seas on the film material directly sampled pointed to the vertically segregated film struc-
ture forming nearly separate layers at the interface with the most insoluble surfactant
compound on the top of this layered system [9, 12 – 14].

In model laboratory investigations organic materials of similar physico-chemical prop-
erties as found in nature were spread over the water surface and studied with a photoa-
coustic method to determine their mechano-thermal parameters. Amplitude and phase
dependences of the photoacoustic signal, as a function of sample layer thickness, demon-
strate step changes corresponding to interfacial regions (air/oil and oil/water) and seen

at a certain depth (about $9-13\,\mu m$) in the bulk oil phase. The observed signal features are expected to be useful in detection of the film-induced clathrate organized water molecules in the subsurface water layer (about $190\,\mu m$ in thickness) and in studies of mechano-thermal irregularities in the liquid bulk attributed to the formation of surfactant micellar structures.

The aim of the paper is an attempt to interpret the observed signal variations in terms of the ordering water molecules effect (of negative entropy with a certain loss of the molecules degrees of freedom) taking place under the film covered surface and the occurrence of different quasi-crystal micellar structures of surfactant molecules different in their elasto-thermal parameters than the surrounding liquid phase.

2. Measuring system and theoretical principles

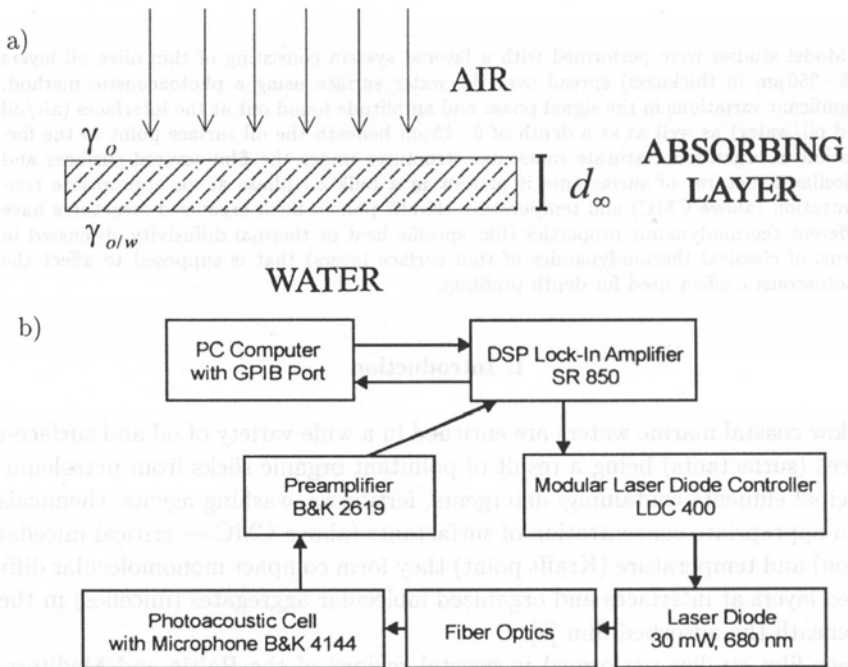A block diagram of the measuring photoacoustic (PA) system is shown in Fig. 1.

Fig. 1. A block diagram of the measuring set-up, for details see text. a) An open-type photoacoustic cell filled with a layered oil-on-water system of the equilibrium thickness d_∞, irradiated with a laser beam. γ_o, $\gamma_{o/w}$ — surface tension of oil, and oil-water interfacial tension, respectively. b) The associated electronic units for data collection and measurement control with laser beam guiding fiber wires and signal sensors.

In the presented studies, a novel experimental set-up based on a lock-in amplifier SR 850 was used, which not only measured the signal but also controlled operation of the laser diode being a source of modulated light. A laser diode (type SDL-73311) is

a source of modulated light of the wavelength 680 nm. The laser beam is, by a fiber wire, provided to the measuring cell of author's construction. The photoacoustic signal received by a microphone is phase-sensitive detected using a lock-in amplifier (type SR 850). An internal generator of the amplifier is also used for operating the laser diode controller (LPC 400). All data collection and further processing is realized by a PC computer working in the GPIB standard. The introduction of a laser diode and electronic light modulation system allowed receiving a higher signal to noise ratio in reference to its mechanical analogue. The modulation frequency of the light was varied from 1 to 1000 Hz. The adopted modulation frequency range allowed the depth distribution of signal response to be determined for all the studied layers. The PA signals were analysed using the depth profiling in terms of one-dimensionally inhomogeneous materials theory.

Interpretation of our data is based on the results originating from a classical Rosen-cweig–Gersho model [16]. In particular, a one dimensional heat flow in the sample is assumed, and in the framework of the model the thermal diffusion length μ (a certain sample thickness which affects the signal magnitude at a fixed modulation frequency) can be written:

$$\mu = \sqrt{\frac{\alpha}{\pi f}} \tag{1}$$

and

$$\alpha = \frac{k}{\delta c}, \tag{2}$$

where α is the thermal diffusivity, f the frequency of light modulation, k — the thermal conductivity, c — the heat capacity, δ — the medium density.

Such a dependence was adopted in our measurements to derive the thermal diffusivity of the studied samples.

In studied model layered oil-water system, thin layers of olive oil (from 25 to 250 μm in thickness) were formed onto the clean water surface by spreading from a solution of oil dissolved in ethyl ether. After evaporating the solvent, the olive oil layer was formed of equilibrium thickness d_∞ determined by the spreading coefficient and density difference of the liquids in contact [1].

Homogeneity of the formed oil layers were checked by comparing photoacoustic spectra (PAS) (obtained for different modulation frequencies) with those measured with a Fourier Transform Infrared Reflection Spectroscopy (FTIRS) system supplemented with a photoacoustic cell.

3. Results and discussion

In Fig. 2 amplitude and phase dependences of the photoacoustic signal for the studied samples are presented against the square root of the light modulation frequency [17]. They demonstrate significant variations at the interfacial regions certainly correlated with a step character of the thermodynamic properties changes in the liquid layer at a certain depth.

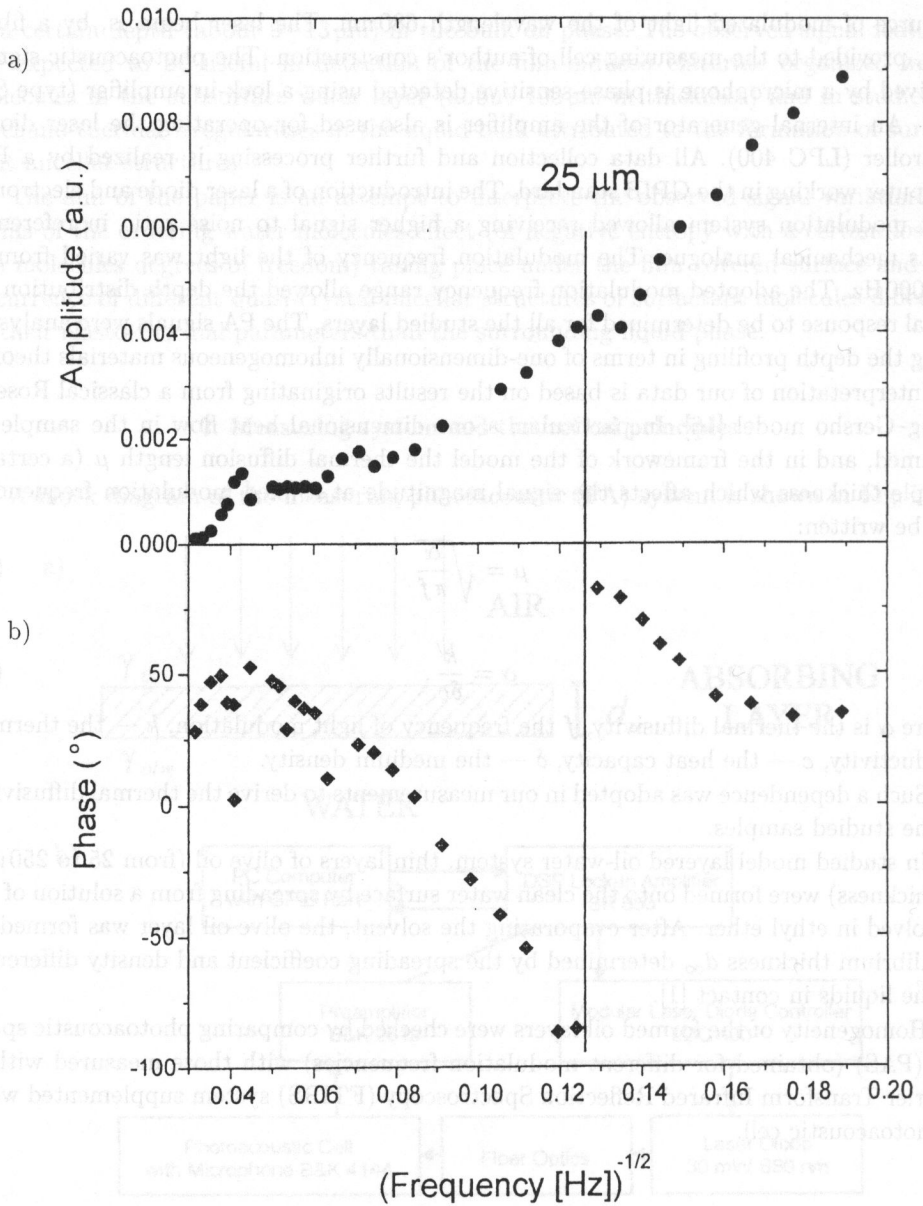In order to describe the results let us perform the following consideration.

Fig. 2. Photoacoustic signal amplitude (a) and phase (b) as a function of sample depth, for a layered olive oil-water system.

3.1. Surfactant monolayers adsorbed at interfaces

Surface-active substances present in both polar (hydrophilic) and nonpolar (hydrophobic) solvents form at interfaces (air/oil or oil/water) a monolayer, as a result

of surface adsorption described by the Gibbs' equation [1]:

$$\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc} \tag{3}$$

with the thickness δ:

$$\delta = \frac{\Gamma_\infty \cdot M}{\rho}, \tag{4}$$

where Γ, Γ_∞ is the Gibbs' excess (adsorption) and its saturation value, respectively, c — the surfactant bulk concentration in the solution, γ — the surface or interfacial tension, T — absolute temperature, R — the gas constant, M — molecular weight, and ρ — density of the dissolved surface-active substance.

Values of δ, for lipid substances, are of the order of $10-25$ Å[1] that is comparable to the intermolecular distance between the water molecules in the surface layer ($= 5.8$ Å, [2]). In the presence of a monomolecular surface film intensive hydrophobic and hydrophilic interactions with the adjacent water layer occur [11, 18]. Various spectroscopic studies [6] have shown that the effect of a surface film is largely to hinder the rotational motion and the mobility of the water molecules and enhance the degree of the 0–H...0 hydrogen bonding between water molecules [10].

The reduction in mobility of the water molecules is associated with a decrease of the diffusion coefficient D_o of pure water. If it is assumed that a surface film induced (potential) activition energy ΔE of the order of 5.53 kJ/mol, and the thermal energy kT govern the energy distribution of the water molecules, Boltzmann statistics can be applied to this system and the diffusion coefficient D_s of a surface film covered water surface can be expressed by [7]:

$$D_s = D_o \exp[-\Delta E/kT]. \tag{5}$$

Often the diffusional properties are expressed in terms of a relaxation time τ which is linearly correlated with the surface viscosity of the monolayer [7]. The viscosity increases with increasing alkyl chain length as shown in the homologous series of alkanols and carboxylic acids. Note that in both cases the hydrophilic group of the surfactant was kept constant and only the alkyl chain length of the hydrophobic group was varied.

The modification of the relaxation time by the adsorbed film is given by:

$$\tau_s = \tau_o \exp[\Delta E/kT] \tag{6}$$

(for pure water $\tau_o = 1.19 \times 10^{-11}$ s).

Microwave radiometer measurements at $f = 1.43$ GHz over a sea surface covered with a monomolecular 9-octadecen-1-ol, Z isomer (oleyl alcohol), surface film lead to the value of τ_s equal to 1.11×10^{-10} s. The thickness of the emitting surface layer d, i.e., the penetration depth at which the surface film induced activation energy ΔE decreased to $1/e$ (37%) is $\leq 1.9 \times 10^{-4}$ m [4]. It is concluded from the obtained values that icelike clathrate structures are induced by the surface film in a water layer of underneath the surface that is schematically illustrated in Fig. 3.

At first glance the obtained value appears to be surprisingly high. However, an extensive evaluation of the literature showed an evidence of long-range effects within interfacial
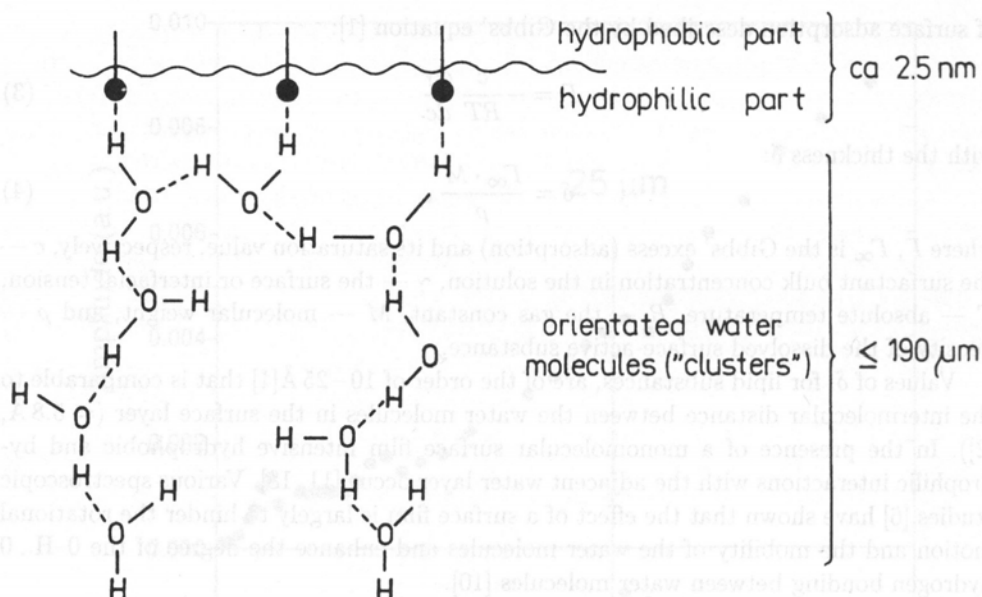
Fig. 3. Interaction of the film-forming molecules of a surfactant with the water molecules in the subsurface region [7].

water layers at the boundary water organic substance (as summarized in Tab. 1 of [7]). The obtained values are as follows: $25-200\,\mu m$ (fatty acids), $2.2-190\,\mu m$ (long-chain alcohols), $0.1-19\,\mu m$ (polymeric macromolecules) and originate from a variety of different measurements and methods.

Note, that "classical" theories include penetration depths of only 10^{-9} m due to direct interactions between the hydrophilic group of the surface-active compound and adjacent water molecules by forming "shells" of structured water [6, 18]. The results cited above however, give experimental evidence for the penetration depth, which are 10^2-10^5 times larger.

From a thermodynamic point of view, the surface activation energy ΔE ought to be substituted by the term "free activation enthalpy" ΔG. In the upper water layer, which is influenced by the surface film, the activation enthalpy ΔH is connected with the free activation enthalpy ΔG by the Gibbs–Helmholtz equation [7].

$$\Delta G = \Delta H - T\Delta S, \tag{7}$$

where ΔS is the entropy change in the surface layer due to the surface film, ΔG can be expressed by using relaxation frequencies f_o and f_s corresponding to the mentioned relaxation times τ_o and τ_s measured for clean and film-covered water surfaces, respectively in the following form [7]:

$$\Delta G = kT \ln(f_o/f_s). \tag{8}$$

The enthalpy change per mole is, $\Delta G = 2.32\,RT = 5.53\,\text{kJ/mol}$.

It can be deduced that clathrate-type arrangements of the water molecules are formed, which implies changes of the specific volume. Therefore, in the presence of

surface film the energy term associated with volume changes has to be added and we thus obtain the activation enthalpy ΔH.

Since different arrangements of molecules must be concerned with the entropy, the hysteresis of the compression/dilatation surface film isotherms is presumably correlated with the change of entropy ΔS of the interfacial system. Consequently, the well-known negative entropy effect — ΔS, of a regular monomolecular surface film on the adjacent water layer was observed by several authors [10, 11, 18], which reflects the formation of the organized water molecules and a certain loss of the system degrees of freedom.

Values of ΔS, obtained for natural marine films from surface isotherm hysteresis measurements, are ranging from -36 to $-133 \, \text{J/mol K}$ [13].

As a consequence, the thermodynamic parameters (specific heat, thermal conductivity) exhibit a step change in the air/liquid interfacial region. Thermal properties affect to a great extent the photoacoustic effect used to the layered air/water system sensing.

3.2. Organized surfactant structures in water-oil-surfactant systems

Moreover, amplitude and phase dependences of the photoacoustic signal clearly demonstrate rather rapid changes at a certain depth ($h \sim 9 - 13 \, \mu\text{m}$) underneath the oil phase surface. As mentioned above, that fact could result from the formation of 3-dimensional molecular structures at that oil layer having different thermo-mechanic properties than the surrounding oil.

Surface-active substances (surfactants) occurring in the oil phase at the critical micellar concentration (CMC) and appropriate temperature (so-called Krafft point) form aggregates or micelles [8, 15]. In such a state of the surfactant solution many physico-chemical parameters (surface tension, density, electric and thermal conductivity etc.) demonstrate rapid changes arround CMC [1]. For the same homologous series of surface active substances, CMC decreases with increasing the hydrocarbon chain length as well as with the addition of electrolytes (for ionic surfactants). At first, an increase in the surfactant concentration (above CMC) leads to the creation of spherical then rod-like, and finally lamellar micelles. These molecular structures possess an apparent anisotropy with a tendency for a long-range order similar to found in liquid crystals.

In apolar (oil) solvents a degree of aggregation in the micelle (e.q. a number of molecules therein) is much lower than in the polar (aqueous) surfactant solutions [8, 15].

For a particular water-oil-surfactant system, the phase diagrams determining concentration ranges of the compounds corresponding to the presence of the particular kind of micelles are created [8]. It must be pointed out that in the case of our particular oil-water-surfactant system we are concerned with very low concentrations of surfactants and oil fractions in water. Moveover, natural systems are composed of a mixture of different surface-active compounds of differentiated surface activities which likely form various mixed micelles. As a result, micellar structures to be found in the studied system may differ in their structure and thermodynamics if compared to these predicted in an idealised 3-compound surfactant solution. An exemplary phase diagram for a 3-compound surfactant system is reproduced in Fig. 4 [5].
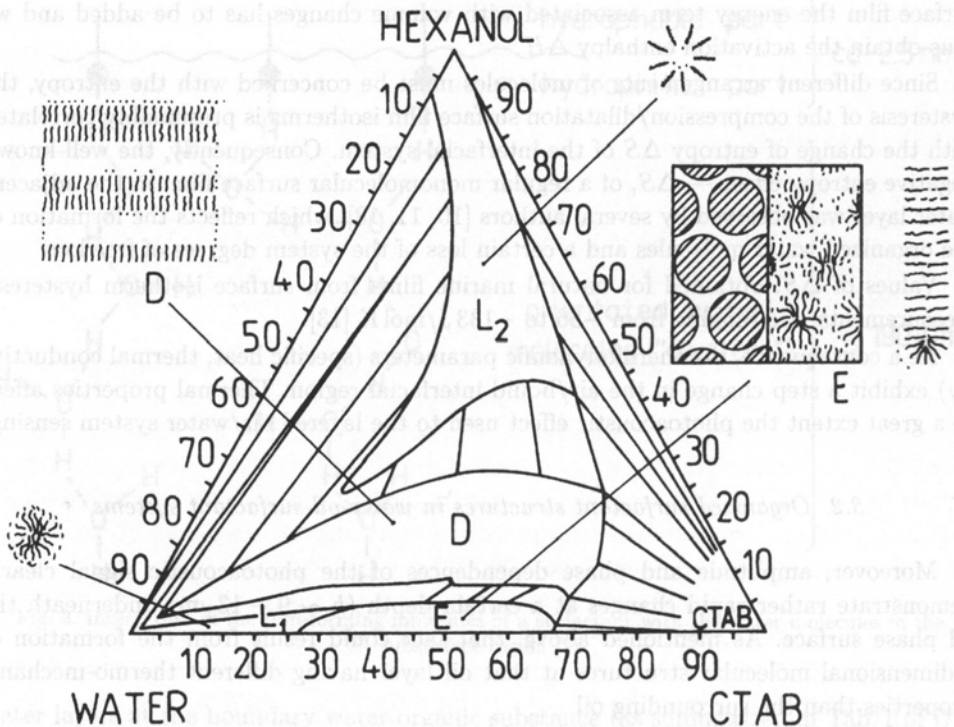
Fig. 4. Phase diagram of the 3-compound system (hexanol-water-CTAB; CTAB — cationic surface-active substance [5]. The specified areas correspond to the presence of: spherical micelles (L_1), inverted micelles sorrounded with oil (L_2), rod-like micelles (E) and lamellar, liquid crystal-like micelles (D).

In such a system we are concerned with a micellar solubilization phenomenon understood as solubilization of insoluble substances in the solution of surface-active substances (above CMC) (for instance, water in oil in our experiment). This effect takes place above CMC, and the mass of the dissolved substance increases proportionally to the concentration of micelles. In oil solvents (apolar media), the inverted micelles are formed with head groups of the surfactant in contact with dissolved water molecules occupying an interior of the micelle whereas the surrounding oil remains in contact with the hydrocarbon chains of the surfactant (as shown schematically in Fig. 5) [5, 8].

In our experiment the small dimensions of the photoacoustic cell lead through the spreading effect on the walls, to the particular shape of the layered oil-water interfaces in the form of a concave meniscus. The additional surface pressure resulted from the surface curvature apparently promotes a horizontal orientation of micellar structures situated close to the air/oil interface. Such an orientation is followed by rod-like and lamellar (plate-like) micelles under the condition of no intensive convection and mixing motions. The place of the micelles residence (depth) beneath the air/oil interface results from the balance between the surface tension and gravity (related to the actual density of the micellar solution) forces.
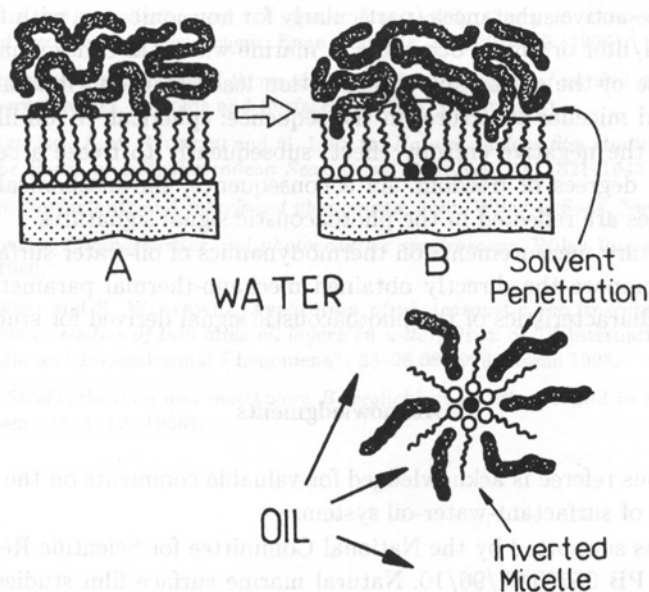
Fig. 5. Organized structures of a surfactant at an oil/water interface (A), and in a bulk oil phase (B). A general picture of micellar solubilization of water in inverted micelles formed in oil.

More compact liquid crystal-like micellar phases have mechano-thermal properties significantly different than the surrounding oil which can be reflected in the photoacoustic signal signatures noticed at the particular layer depth.

Moreover, it has been shown that the acoustic absorption measurements clearly reveal the several structural transitions occurring in the system (see Fig. 2 in [3]).

4. Conclusions

1. Ealier studies on the structure of marine organic films performed in the Baltic and Mediterranean Seas pointed to the complex vertically layered structure of a surfactant mixture consisting of several compounds differentiated in surface activity, solubility and physico-chemical structure [12 – 14]. Photoacoustic investigations were carried out on the physico-chemical model material similar to found in nature and demonstrated that photoacoustic spectroscopy is useful in detection of their formation.

2. Amplitude and phase changes of the photoacoustic signal attributed to a long-range $(d \leq 190\,\mu m)$ organization phenomenon of water molecules in the subsurface region for film-covered surfaces orginate from the thermo-mechanical parameter (mainly in compressibility and specific heat) variations of the formed micellar structures.

Such a local properties variability can be explained in the framework of classical thermodynamics of thin layers.

3. Formation of micellar structures in surfactant solutions at concentrations C > CMC and appropriate temperature (Krafft point) is a common phenomenon observed

for several surface-active substances (particularly for non-ionic ones with CMC very low $10^{-8} \div 10^{-12}$ mol/liter or lower) occurring in marine waters as contaminants [9].

4. An increase of the surfactant concentration leads to the formation of more and more complicated micellar structures in the sequence: spherical $\rightarrow$ rod-like $\rightarrow$ lamellar micelles, and to the negative entropy effect, subsequently to freeze a certain number of the molecules degrees of freedom. As a consequence, the mechanical and thermal parameter changes are reflected in the photoacoustic signal signatures.

5. Supplementary measurements on thermodynamics of oil-water-surfactant systems make possible compare the directly obtained mechano-thermal parameters of layered structures with characteristics of the photoacoustic signal derived for studied layers.

Acknowledgments

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