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Dynamic interfacial properties of marine microlayers

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Abstract

Samples of fulvic acids, extracted from the Tyrrhenian Sea (Leghorn, Italy), are studied by dynamic surface tension and surface shear rheology measurements. The initial adsorption process follows a diffusion-controlled mechanism, while at longer times it is several orders of magnitude slower than expected from diffusion.

The fulvic acids form adsorption layers which exhibit viscoelastic behaviour. Some samples show a continuous increase in shear viscosity and elasticity until the value exceeds the limits of the shear rheometer. For other samples, an increase in these values was only observed during the first hour, after which the values levelled off.

Keywords: Fulvic acids; Marine microlayer; Surface shear rheology; Surface tension

1. Introduction

There are only very few studies on the dynamic surface properties of materials that can take part in the formation of marine microlayers. In the recent literature, some authors analyse the dynamic behaviour of natural slicks (in situ measurements of ripple damping) [1–5]. There are also some recent static measurements of natural slicks sampled using various methods [4]. These authors generally focus their attention on the behaviour of the slicks as a whole.

A portion of the slicks is made up of humic and fulvic acids. The static surface characteristics of humic acids have been studied, for example, in Ref. [6] in a specific environment. The composition and molecular weight of such substances are

variable, and even their precursors can change, depending on the environmental conditions [7]. These substances represent a major component of the refractory fraction of the organic matter dissolved and/or suspended in seawater [8] and, being surface active, contribute to the formation of the sea surface microlayer.

Consistent information is available only if humic substances extracted from the sea environment, instead of commercial fulvics, are used as model substances, because of the great variability of these natural compounds [9]. Structural studies of these samples using various analytical tools, and surface relaxation measurements by means of the elastic ring method described in Refs. [10] and [11], are in progress.

In this work, a different approach to the study of the sea surface microlayer is used. Here, the dynamic surface properties of a fulvic acid sample

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extracted from seawater, which was collected from late spring to summer in a coastal Mediterranean environment, are investigated. The aim of the present paper is to discuss initial results on the dynamic behaviour of solutions of four different samples in terms of surface activity and adsorption layer structure at the water/air interface. Further investigations are under way which aim at obtaining information on the temporal variations in the adsorption layer properties and the related microlayers.

2. Experimental

2.1. Samples

Fulvic acids (FAs) were extracted from seawater sampled in Leghorn, Italy (Tyrrhenian Sea), during a period from May to July 1993. The seawater was sampled 0.5 m below the sea surface with an immersion Teflon pump. Care was taken to avoid contamination from the boat. The samples were taken either at the mouth of the river Calambrone or about 400 m from the shore at Leghorn Aquarium. The extractions were always performed within 24 h after the sampling. The Malcolm–Thurman procedure was used for the extraction of FAs [12]. The origins of the four FA samples are given in Table 1.

2.2. Solutions

Solutions of 0.001 M NaOH were prepared using doubly distilled water and NaOH (ultrapure). FA dissolved better in NaOH solution than in distilled water or artificial seawater. The concentrations

prepared were 1% and 0.5%. After preparation, the solutions were kept at 4°C until use.

2.3. Measurement techniques

To study the dynamic adsorption behaviour of the FAs, two methods of different time windows were used. The drop volume technique (TVT1 from LAUDA) yields surface tensions in a time interval from a few seconds to several minutes. A detailed description of this technique and peculiarities in the data interpretation are reported in Refs. [13]–[15]. The conditions under which the measurements were performed are: temperature, 23°C; time range, 1–400 s; capillary radius, 1.055 mm; syringe volumes, 2.5 ml and 5 ml. For the long time dependence of the surface tension, a ring tensiometer (TD1 from LAUDA) was used. Details of the application of this technique to surfactant solutions are given, for example, in Refs. [16] and [17]. The measurements were carried out under the following conditions: temperature, 23°C; time range from 1 min up to 7 h.

A recently developed shear rheometer was used to study the surface shear rheology of the adsorption layers. A detailed description of this technique is reported in Refs. [18] and [19]. The principle of the measurements is based on the idea of a torsion pendulum. A ring hanging from a torsion wire and touching the liquid surface is deflected by a small angle on turning the head at which the wire is mounted. The deflection of the wire leads to a damped oscillation of the ring which is registered and interpreted. As a result, the surface shear viscosity and elasticity are obtained simultaneously. The parameters used in these experiments

Table 1
Origin of the four fulvic acid samples

Name of sample	Sampling site	Date of sampling	Water temperature
FA3CA	Calambrone river mouth	May 6, 1993	15°C
FA4CA	Calambrone river mouth	June 10, 1993	23°C
FA5CA	Calambrone river mouth	July 13, 1993	22°C
FA5AC	Leghorn Aquarium	June 24, 1993	19°C

were: temperature, 23 °C; time range, 24 h; 30 μm tungsten wire of 30 cm length.

3. Results

It should be pointed out that, owing to the differences in the concentration and characteristics of fulvics in the seawater samples, the quantity of material extracted was not constant. Some of the measurements suffered from the limitation in the amount of samples.

Dynamic surface tensions measured with the

drop volume (short time range) and ring tensiometer (long time range) of three solutions are given in Fig. 1 in the form of $\gamma-1/t^{1/2}$ plots. Such plots are useful for the long time approximation of the adsorption mechanism and extrapolation to infinite time in order to obtain the equilibrium surface tension. The same set of data from drop volume measurements is given as $\gamma-t^{1/2}$ plots in Fig. 2. Such plots allow short time approximation of the adsorption mechanism.

The results of the surface shear rheology measurements are summarised in Fig. 3 (shear viscosity) and Fig. 4 (shear elasticity). Every 10–15 min a

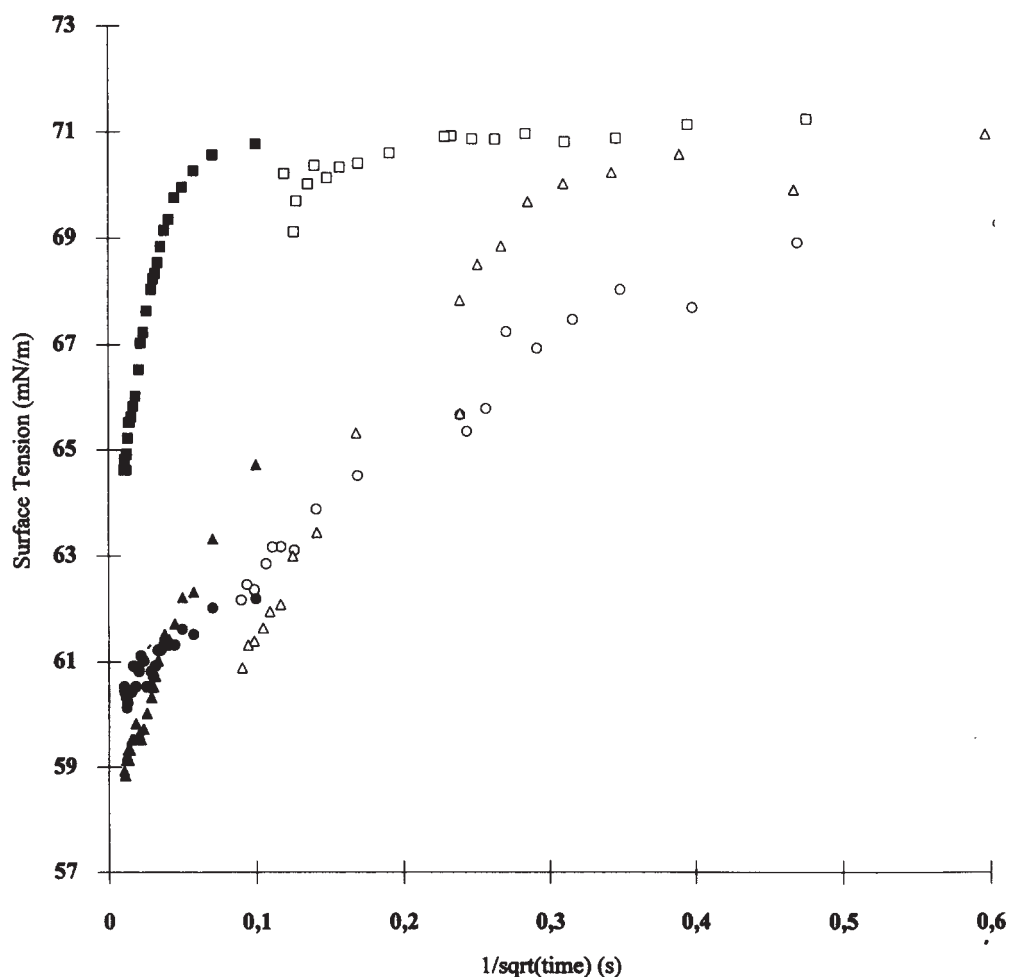


Fig. 1. Dynamic surface tension of FA solutions as a function of $1/t^{1/2}$. FA4CA, 0.5% (□, ■); FA4CA, 1% (○, ●); FA5CA, 1% (△, ▲). Filled symbols — ring tensiometer; open symbols — drop volume tensiometer.

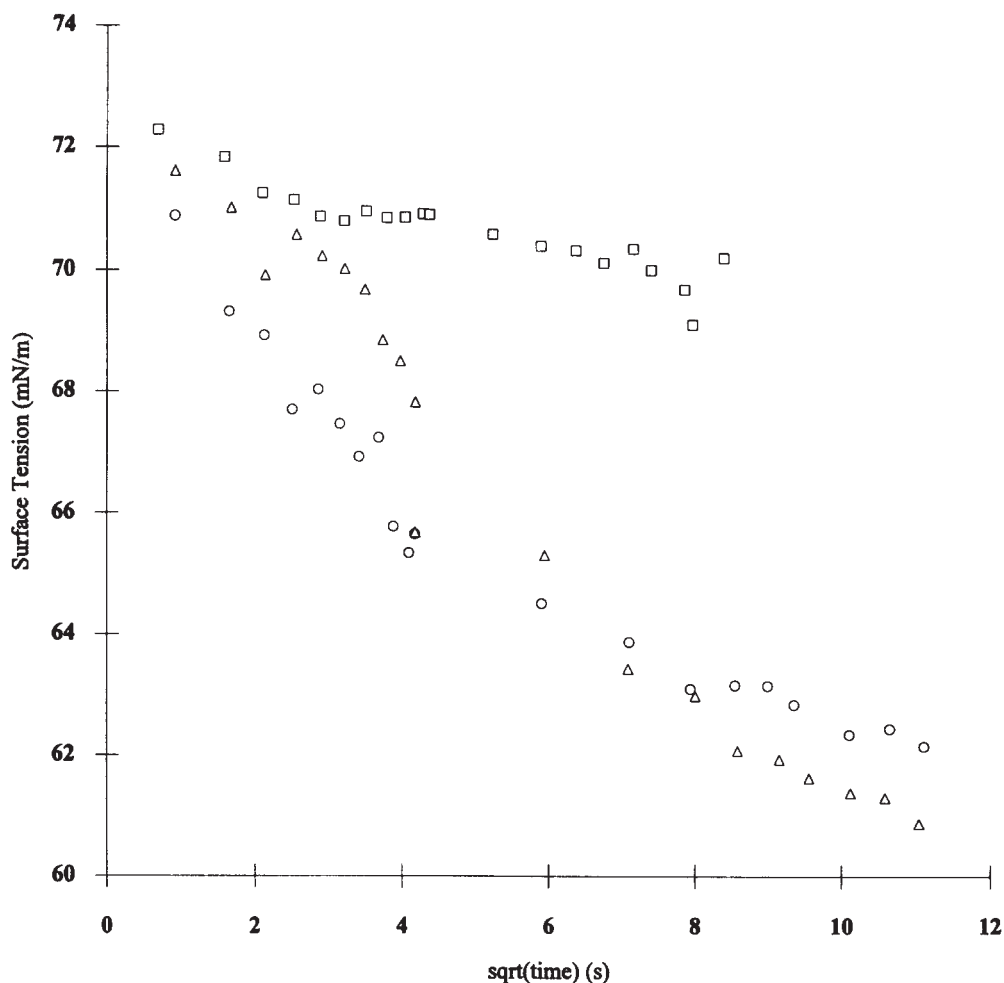


Fig. 2. Dynamic surface tension of FA solutions as a function of $t^{1/2}$. FA4CA, 0.5% (\square); FA4CA, 1% (\circ); FA5CA, 1% (\triangle). Drop volume tensiometer.

pendulum experiment was performed in order to monitor the evolution of surface shear viscosity and elasticity with time.

4. Discussion

The results from TD1 and TVT1, displayed in Fig. 1, show agreement in the overlapping time interval within the error of the two methods. The dynamic surface tension values are shown in the form of γ vs. $1/t^{1/2}$, where t is the effective surface age. The ring tensiometry directly yields the effective surface age when all surface area changes

during the measurement are negligible. For the drop volume tensiometry, the effective age t can be calculated from the drop time t_{drop} using the simple approximation $t = t_{\text{drop}}/3$ [20]. For surfactants following the model of diffusion-controlled adsorption kinetics, the $\gamma(1/t^{1/2})$ plot should give linear dependencies at longer times $t \rightarrow \infty$. The slope of these lines is given by the approximate equation [20,21]

$$\left[\frac{d\gamma}{d(1/t^{1/2})} \right]_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} (\pi/4D)^{1/2} \quad (1)$$

from which the diffusion coefficient can be derived.

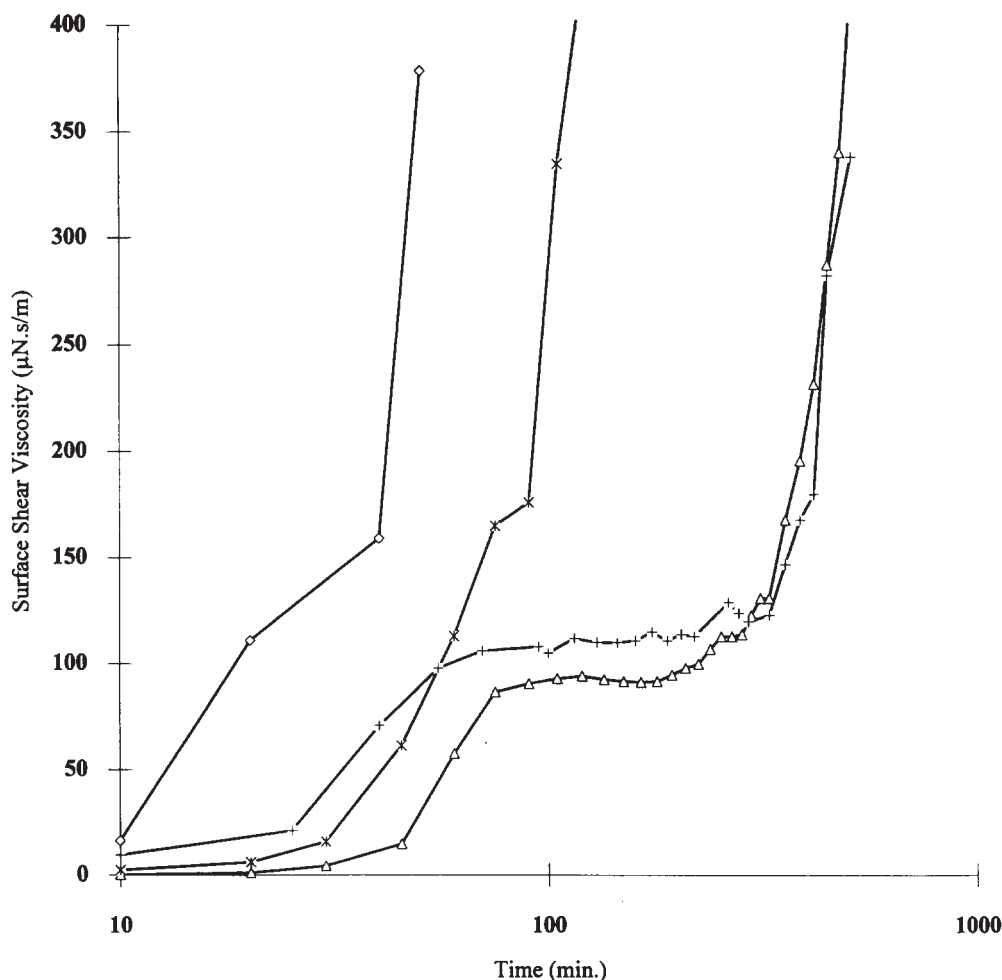


Fig. 3. Time dependence of surface shear viscosity of FA solutions. FA3CA (+); FA4CA (◇); FA5CA (△); FA5AC (*).

Using the data from Fig. 1 and taking reasonable values for Γ and c_0 , we can compute diffusion coefficients between $D=10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and $D=4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. In these calculations, an average molecular weight of $M=50\,000$, corresponding to a concentration of $c_0=10^{-7} \text{ mol cm}^{-3}$ at 0.5 wt.%, and a surface concentration of $\Gamma=10^{-10} \text{ mol cm}^{-2}$ were assumed. As the FA concentrations in this study are relatively high, the majority of the molecules are probably aggregated; therefore, a value of 50 000 for the molecular weight is very reasonable and corresponds to such aggregates [22]. The values of D are much lower than the physically expected ones. Thus, we can conclude that at a long adsorption time the transport

of the biopolymers does not control the adsorption process. A model taking into consideration transport by diffusion and rearrangements of the molecules at the interface has been discussed by Serrien and co-workers [23,24].

To obtain information about the mechanism at the beginning of the adsorption process, the slopes of the curves given in Fig. 2 and a short time approximation, derived in Ref. [21], can be used:

$$\left[\frac{dy}{d(t^{1/2})} \right]_{t \rightarrow 0} = -RTc_0(D/\pi)^{1/2} \quad (2)$$

From these data we obtained an average diffusion coefficient of $D=5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, which is of

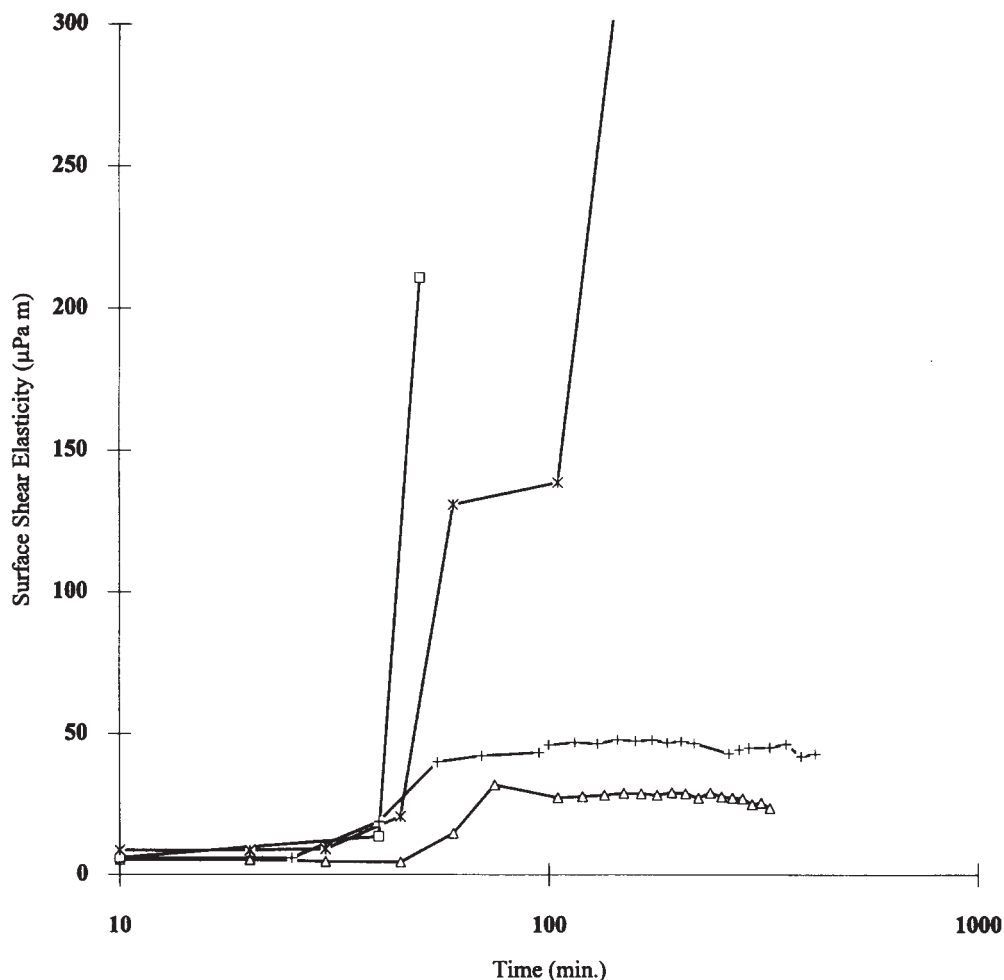


Fig. 4. Time dependence of surface shear elasticity of FA solutions. FA3CA (+); FA4CA (□); FA5CA (Δ); FA5AC (*).

the right order of magnitude and shows that the adsorption of the FA molecules at the freshly formed surface follows a diffusion mechanism.

The results of the shear rheological studies are summarised in Figs. 3 and 4. Some of the systems under study show definite viscoelastic behaviour, for example FA4CA and FA5AC. For FA4CA, this behaviour is also detectable at lower concentrations. Other systems show adsorption layers with lower viscoelasticity, such as FA3CA and FA5CA. At low concentrations, rheological properties are not detectable.

The above-cited samples were obtained from both selected places, and the data do not show a

significant dependence on the sampling site. All samples were taken after the spring algae bloom, so differences due to this cannot be discussed here. At first glance, it could be surprising that there is no influence of freshwater on the samples taken at the river mouth; however, it should be noted that the distance between the two sites is only about 5 km.

Work is presently under way to try and find out the effect of the time of sampling on the surface activity and adsorption layer structure of FAs. The present report can only show the ability of FAs to form viscoelastic–elastic adsorption layers at the water/air interface.

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