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Steady-State Relaxation Times for Surfactant Films at the Water/Air Interface

Dj. Dragčević and V. Pravdić

Laboratory of Electrochemistry and Surface Phenomena, Center for Marine Research, »Ruđer Bošković« Institute, Zagreb, Croatia, Yugoslavia

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Relaxation times were measured for the surface tension relaxation of spread and soluble surface films at the water/air interface. Measurements were done in a modified Langmuir trough with a Wilhelmy Pt sensor attached to an electrobalance using surface sweeping rates between 6.4 and 57.6 Hz^{-1}.

The relaxation times were determined in the stationary state from the phase angle between the perturbation function (surface sweeping) and the response function (dynamic surface tension). The calculated values for the relaxation times of oleic acid films were between 0.25 and 1.25 s, and were inversely proportional to both the rate of sweeping and to the concentration of molecules in the surface film. For the soluble surfactant, sodium dodecylsulfate, the relaxation times were reaching a minimum value of 0.2 s, at a bulk concentration between 9.1 and 18.3 μmol dm^{-3}.

INTRODUCTION

There are two major fields for which the rate of formation of surface films of soluble and insoluble surfactants at the water/air interface is of interest. One, the technology and science of mineral, ionic and bacterial flotation[1]. Two, the science of sea/atmosphere exchange processes[2]. It is the rising bubble which scavenges the aqueous bulk from both film forming surfactant material and of the dissolved/dispersed ionic or particulate material. The efficiency of collection is dependent on the rate of formation of the surface film surrounding the gas(air) bubble[3]. The properties of the film at the bubble surface would determine its penetrability for gases and/or ionic and particulate material. Compressed films have been shown to retard significantly gas exchange and lower the rate of evaporation of water[4]. Thus, bulk surface active material of appropriate composition might produce solid films and influence the overall exchange rate of carbon dioxide and oxygen between the natural water and the atmosphere[5,6]. At least part of the problem whether or not the sea acts as an effective sink for man-made CO_2 would be answered by knowing precisely whether the rate of exchange is influenced by the presence of surface active material[7].

The present paper describes laboratory experiments designed to measure the relaxation times of surface films in the steady-state, non-equilibrium perturbation mode.

EXPERIMENTAL

Techniques

The surface tension relaxation was measured by a conventional, commercially available technique[8,9,10] comprising a Wilhelmy plate surface tension sensor attached to an electrobalance (Dynamic Surface Tension Accessory, Cahn Instruments, Ventron, Palo Alto, California) shown schematically in Figure 1. The surface tension is measured by the platinum plate sensor (1) in a PTFE lined Langmuir trough (5). The surface is swept periodically by two reciprocating PTFE surface sweepers (2) actuated by a motor pulley (4) at controllable rates. The surface tension is measured as the force exerted on the Pt sensor by an electric microbalance (3). The output from the microbalance and of the sweep mechanisms is fed to either an x-y recorder (6) or an x_1, x_2-time recorder (7) the approximate recordings being shown. One analyses either the hysteresis curve in the force — area coordinates, or measures the phase angle between the same, time dependent functions.

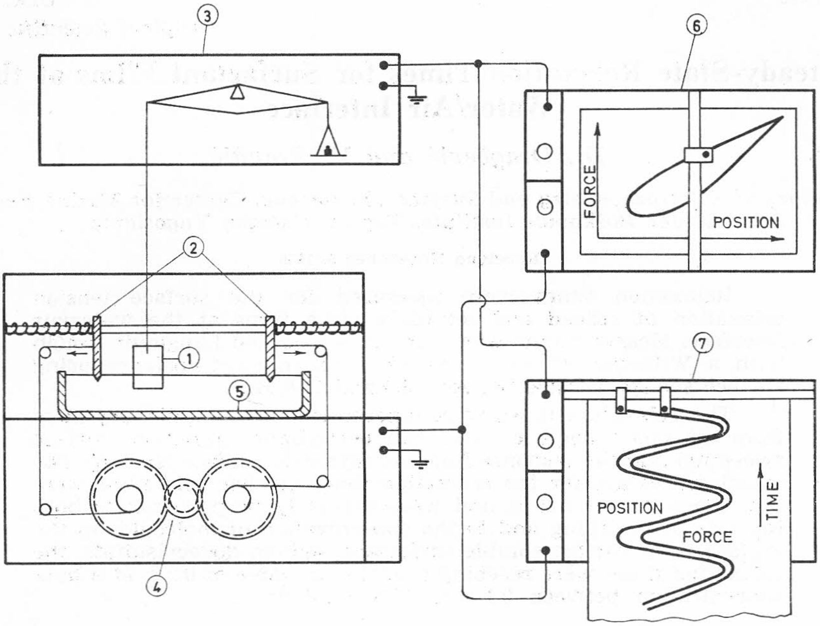

Figure 1. The schematic of the surface tension apparatus with x-y and x_1, x_2-time recorders. For explanation see text.

The rate of sweeping in the present configuration has been varied in 5 steps from 6.4 to 57.6 s per cycle, from an area between the sweepers of 25.4 and 37.0 cm^2 (1 : 1:5 surface area ratio), in a trough of 68 cm^2 of total exposed surface area and of a surface to volume ratio of 0.7 cm^{-1}.

Chemicals and the Techniques of Film Formation

Pure oleic (*cis*-octadecen (9, 10) oic) acid was dissolved in ethanol to a 3×10^{-4} mol dm^{-3} solution. Appropriate aliquots have been taken by micropipettes and spread onto the surface of water in the trough. Sodium, dodecylsulfate (SDS) (Merck, Darmstadt, purum) was dissolved in water to prepare a stock solution of 9.14×10^{-4} mol dm^{-3}. Final concentrations were prepared by dissolution in water in a volumetric flask and this solution was poured into the trough of the surface tension apparatus. The low concentration of SDS in the final experimental solution and the sole aim of this work to measure the overall relaxation times proved satisfactory, without requiring additional purification of the chemicals used.

All experiments were done at 20.0 ± 0.1 °C.

RESULTS

The results of measurement of the relaxation of surface tension for an oleic acid film are shown in Figure 2. In the left part of the figure there are two phase shifted sinusoidal curves. The first one, indicated by the »area« sign is the excitation function: the movement of surface wipers. The second one, marked by γ, is the response of the surface tension sensor. The phase angle between the two, indicated by analogy with electrical phase angle phenomena[11,12], relates to the relaxation time by:

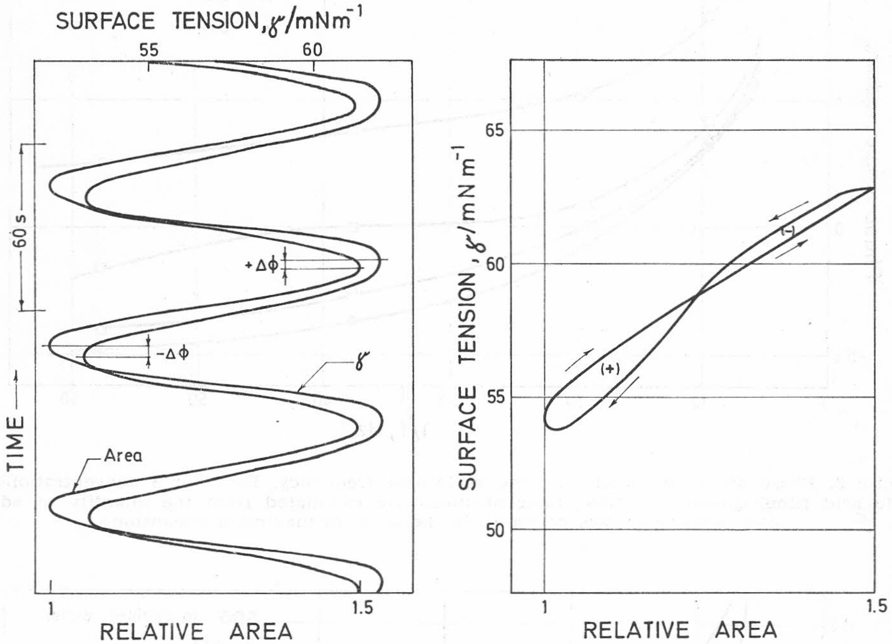

Figure 2. Dynamic surface tension on two recorders for oleic acid. The left hand side shows 2 sinusoidal functions, surface area (2 »area«) and surface tension (γ), with the resulting phase shift $\Delta\varphi$ recorded on a x_1, x_2-time recorder. The right hand side shows the surface tension — area hysteresis curve for the same experiment, recorded on a x-y recorder.

$$\tau = \frac{1}{e}\left(\frac{\tan \Delta \varphi}{2 \pi f}\right)$$

where τ is the relaxation time, φ the phase angle, and $\omega = 2\pi f$ is the angular excitation frequency (sweep rate). The right hand side of the same figure shows the surface tension-area curve. One film was chosen out of many studied, which shows a positive hysteresis at compression (high surface pressure) and negative hysteresis at expansion (low surface pressure).

Calculated phase angles at the point of maximum compression of the surface are plotted against the reciprocal frequency of the sweep rate in Figure 3.

Similar phenomena are observed also for soluble surfactants. Figure 4 shows the results of measurements of the phase angle for 5 concentrations of

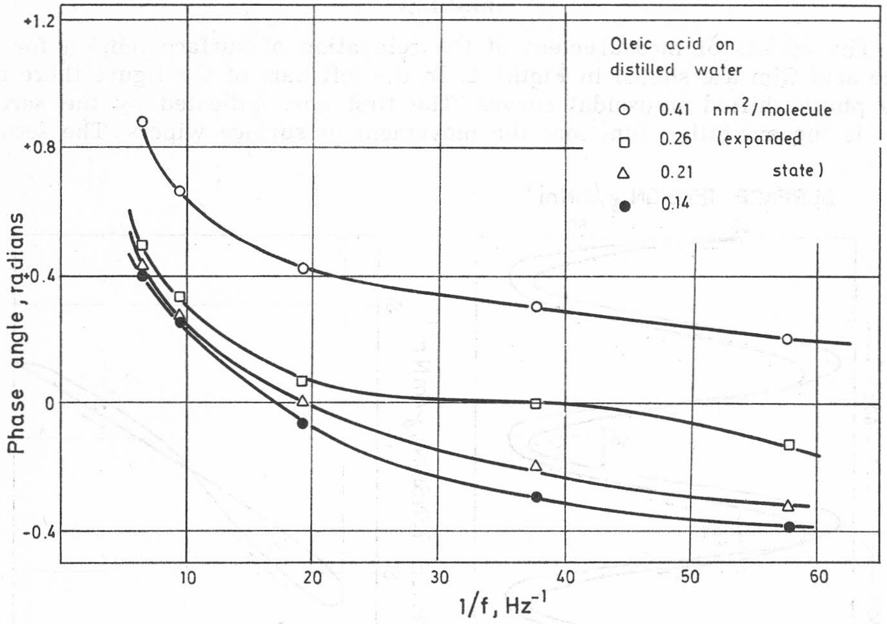

Figure 3. Phase angle in radians vs. the reciprocal frequency, Hz^{-1}, for 4 concentrations of oleic acid films spread on water. Concentrations are calculated from the quantity of added oleic acid to surface of water, in the point of maximum expansion.

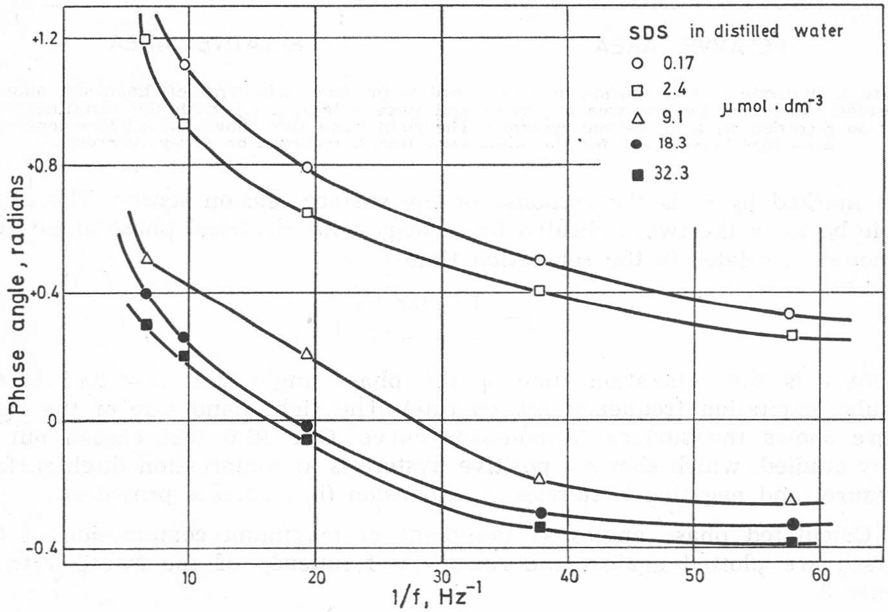

Figure 4. Phase angle in radians vs. the reciprocal frequency, Hz^{-1}, for 5 concentrations of sodium dodecylsulfate. Average bulk concentrations are indicated.

SDS in water. The general phenomenology is the same as for insoluble films. The phase angle is reverted from positive to negative with increasing concentration and with decreasing rate of perturbation.

However, the calculation of the relaxation times, obtained from the phase angle at maximum expansion, show different patterns. Table I summarizes the calculations done for the insoluble surface films of oleic acid spread on distilled water. The relaxation times, in seconds, are seen to decrease with the increase in the perturbation rate (Hz^{-1} = seconds per sweep cycle). Also, the increase in the surface coverage (decrease in the area per molecule) tends to produce shorter relaxation times.

Table II summarizes the corresponding data for the soluble SDS. Here the tendency is shown towards constant values of the relaxation times; if there is a change observed, then the values tend to increase with the increasing sweep rate. The concentration dependence shows little general influence, indicating possibly a minimum value of 0.20 s for concentrations of 9.1 and 18.3 $\mu mol\ dm^{-3}$.

TABLE I

Relaxation Times, s, for Oleic Acid Spread on Distilled Water

Sweep rate Hz^{-1}	Area per molecule*/nm^2				
	0.41	0.26	0.21	0.14	0.10
57.6	1.00	0.90	0.90	0.81	0.67
37.8	0.68	0.68	0.68	0.68	0.45
19.2	0.65	0.65	0.47	0.39	0.38
9.5	0.65	0.56	0.33	0.28	0.28
6.4	1.24	0.31	0.25	0.25	0.25

* calculated from spreading data at max. expansion

TABLE II

Relaxation Times, s, for Surface Films Formed by Dissolving Sodium Dodecylsulphate (SDS) in Distilled Water

Sweep rate Hz^{-1}	Bulk concentration/$\mu mol\ dm^{-3}$				
	0.17	2.4	9.1	18.3	32.3
57.6	0.67	0.22	0.22	0.22	0.22
37.8	1.04	0.45	0.22	0.22	0.22
19.2	1.00	0.55	0.22	0.22	0.30
9.5	1.16	0.56	0.23	0.20	0.33
6.4	2.09	1.31	0.20	0.20	0.34

DISCUSSION

This paper introduces the measurements and calculations of the relaxation times for relaxation phenomena in surface films, both soluble and insoluble. The simplicity of the technique of the dynamic surface tension measurements in a Langmuir trough with two reciprocating surface sweepers is subject also to some scrutiny. The Wilhelmy plate surface tension measurements are precise only if the wetting angle of the sensor (platinum in the present case) in the film covered surface is constant. This has been difficult to prove, however, two experiments were done in this sense. The film was repeatedly swept until steady state conditions were achieved. In the first experiment the position of the surface tension sensor was changed by rotating it in the plane for 90^0. Thus only the molecular phenomena related to wetting are brought to bear: the direct compression of the surface film by wipers was eliminated, considering the thickness of the sensor (0.01 cm) vs. its perimeter (2×1 cm). No differences were observed. In the second experiment one of the wiper blades was removed: thus the compression ratio was halved and the surface film was compressed assymetrically with respect to the sensor. Once again, the effects were the same within the experimental accuracy.

It is thus quite probable that the data relate to true molecular level phenomena in the surface films. From the dependence of the relaxation times on the perturbation rate it is clear that what one observes is the compound process of surface spreading and of diffusion from the bulk to the surface. Essentially the same conclusion has been reached by Veer and Van den Tempel[10], who have also proposed an equation to resolve for the two contributions, surface spreading and bulk diffusion. However, this proved virtually imposible unless one enters with additional assumptions into the calculations. Lucassen and Van den Tempel[13] have worked out a technique of excitation of the film covered surface by longitudinal waves of a frequency in the range of 1 Hz. Their results indicate the possibility of resolving the dilatational modulus (a component of the surface spreading process) from true relaxation. The latter has been shown to be absent if films were produced of decanoic acid at concentrations of 4.5×10^{-5} mol dm^{-3} or lower. Thus, relaxation phenomena were found in the time scale of about 1 s. At that point the cited papers[10,13] ceased to supply further information on the experimentally observed dynamic behavior of surface films at aqueous interfaces.

It would be impossible by the present techniques to resolve accurately the contributions of each of these processes to the final relaxation times, since the observed phenomena are related to a particular steady state, and not equilibrium conditions. For oleic acid films the surface spreading must be the faster process, since the relaxation times decrease with increasing perturbation rate. The molecules in the collapsed monolayer are progressively prevented to appear and rearrange at the surface by the fast rate of sweeping. For soluble films, it seems, that both of the mentioned transport processes are of the same order of magnitude, and consequently, no much influence is seen whether the control is by surface spreading at fast perturbation, or by diffusion from the bulk, a process of importance at low perturbation rates.

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SAŽETAK

Relaksacijska vremena za stacionarne površinske filmove na granici fazâ voda/zrak

Dj. Dragčević i V. Pravdić

Vremena relaksacije topljivih i netopljivih površinskih filmova na granici fazâ voda/zrak određivana su tehnikom dinamičke površinske napetosti. Mjerenja su izvršena u modificiranoj Langmuirovoj kadi s Wilhelmyjevom pločicom kao senzorom površinske napetosti priključenom na električku vagu. Stacionarno stanje postignuto je kontinuiranom kompresijom i ekspanzijom površinskog filma s pomoću dva reciprocirajuća teflonska brisača brzinom od 6,4 do 57,6 Hz^{-1} (sekundi po ciklusu), u kadi površine 68 cm^2 i odnosa površine prema volumenu od 0,7 cm^{-1}. Izračunavanje relaksacijskih vremena izvršeno je očitavanjem faznog kuta između funkcije pobude površine kompresijom i ekspanzijom, i odgovora sistema dinamičkom napetosti površine.

Istraživani su netopljivi filmovi oleinske kiseline u koncentracijama od 0,41 do 0,10 nm^2/molekuli, kao i topljivi filmovi natrijeva dodecilsulfata u granicama volumnih koncentracija od 0,17 do 32,3 μmol dm^{-3}.

Izračunane vrijednosti vremena relaksacije za oleinsku su kiselinu između 0,25 s i 1,25 s; relaksacijska vremena opadaju kako s koncentracijom molekula u filmu, tako i s brzinom perturbacije. Za natrijev dodecilsulfat karakteristična vremena relaksacije teže prema minimalnoj vrijednosti od 0,2 s koja se postiže za volumne koncentracije između 9,1 i 18,3 μmol dm^{-3}.

LABORATORIJ ZA ELEKTROKEMIJU I POVRŠINSKU KEMIJU
CENTAR ZA ISTRAŽIVANJE MORA
INSTITUT »RUĐER BOŠKOVIĆ«, ZAGREB

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