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COLLOIDS AND SURFACES A

Nonequilibrium properties of fluid interfaces: aperiodic diffusion-controlled regime 2. Experiments

G. Loglio [a,*], R. Miller [b], A. Stortini [a], U. Tesei [a], N. Degli Innocenti [a], R. Cini [a]

[a] *Department of Organic Chemistry, University of Florence, Via G. Capponi 9, 50121 Florence, Italy*
[b] *Max Planck Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5, D-12489 Berlin-Adlershof, Germany*

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Abstract

We have investigated the surface dilational properties of a submicellar aqueous solution of *n*-dodecyldimethyl-phosphine oxide. We compared (a) the steady-state responses of dynamic surface tension, induced by small-amplitude harmonic disturbances of surface equilibrium (at different frequencies), and (b) the transient response induced on the same sample by a single trapezoidal-pulse disturbance. Using the equations for a diffusive model, we determined the fit parameters from the observed response values both in the frequency and in the time domains. The results enabled us to predict satisfactorily the harmonic dynamic behaviour of the surface, from the relaxation data. The prediction–observation agreement supports the theoretical treatment and, in particular, the assertion that the viscoelastic link, between surface excitation and response, is a constitutive property of a liquid solution. The experiments also show the existence of a linearity range and the repeatability of measurements.

Keywords: Diffusive surface relaxation; Dynamic surface tension; Nonequilibrium surface thermodynamics; Surface dilational modulus; Trapezoidal-pulse perturbation

1. Introduction

In a previous article [1], we dealt with the principles which govern the surface relaxation processes occurring in liquid solutions, under not-far-from-equilibrium conditions.

Within a theoretical context, adopting a linear model, we have emphasized the conclusion that the viscoelastic link, between surface excitation and surface response, is a constitutive property of a solution. In other words, such a link (referred to as the surface dilational modulus) is an intrinsic thermodynamic quantity, independent of the type of excitation, which manifests itself under harmonic as well as under aperiodic disturbances of surface equilibrium and characterizes the dynamic behaviour of adsorption layers [1,2].

Moreover, we have discussed how the square pulse or, in practice, the trapezoidal pulse may result in a suitable and useful form of aperiodic surface excitation (i.e. of relative surface area variation $\Delta A/A$) to induce observable responses of dynamic surface tension $\Delta\gamma(t)$ [1,3].

The objective of this work is to show that certain sentences and assumptions in the theory have a correspondence with experimental observations. Namely, we give experimental support to the following statements: (a) harmonic and trapezoidal-

* Corresponding author.

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pulse responses have in common the same physical quantity, i.e. the above-mentioned modulus; (b) a linearity range actually exists for small disturbances of surface equilibrium, i.e. the response is proportional to the disturbance amplitude, and (c) the repeatability of trapezoidal-pulse responses is definitely good.

2. Experimental

2.1. Materials

We used submicellar aqueous solutions of a standard surfactant, i.e. of *n*-dodecyldimethylphosphine oxide ($DC_{12}PO$), at concentration $c = 4 \times 10^{-3}$ mol m^{-3}. Water was doubly distilled from alkaline permanganate and checked with respect to surface purity.

2.2. Apparatus and procedure

Details of the apparatus for the measurement of the dynamic surface tension resulting from small-amplitude area perturbations, are described elsewhere [3,4]. In short, the apparatus was a computer-driven Wilhelmy-plate Langmuir trough. The area-confining barrier consisted of an elastic cylindrical ring (diameter $d = 5.15$ cm, height $h =$ 1 cm), with the lower edge immersed at 1 mm depth under the liquid surface. A mechanical device allowed the ring to be deformed by diametrically-opposing forces and, hence, the inner surface area to be contracted, according to a selected time function.

To attain the surface equilibrium state, the sample of $DC_{12}PO$ solution was left standing in the measurement vessel for 15 h, prior to measurements.

The surface of the solution was displaced out of equilibrium by imposing a change of relative surface area, $\Delta A/A$. The subsequent variation of dynamic surface tension, $\Delta\gamma(t)$, was measured by a 2.46 cm × 0.01 cm Wilhelmy plate, made of sand-blasted platinum foil, hanging from an arm of a Cahn RTL electrobalance. The electrobalance $\Delta\gamma$ response signal and the (analogue) $\Delta A/A$ signal, produced by the computer, were continuously recorded in synchronism, using a strip-chart recorder, as a function of time (for aperiodic surface perturbations) or in x–y mode (for harmonic surface perturbations).

All measurements were conducted at room temperature (22–23 °C).

2.3. Experimental errors

Barrier position reproducibility

A digitally-controlled mechanism governed the barrier position. Such a device made it possible to reproduce the ring-diameter shortening, Δd, with an experimental error as small as $\epsilon_d = \pm 5$ μm.

Surface area

The surface area, inside the ring, was determined by the computer with an approximate relationship (i.e. with a truncated expansion in Taylor's series) as a function of diameter shortening, $A = f(\Delta d)$ [4]. The estimated systematic uncertainty on A-values was $\epsilon_A = \pm 0.1\%$. This systematic error propagated on the relative surface area variations $\Delta A/A$ ($\epsilon_{\Delta A/A} = \pm 1\%$ for $\Delta A/A = 0.1$). Furthermore, considering a surface deformation (compression or expansion) accomplished in successive steps $\Delta(\Delta A/A)$, the error for each step increased with decreasing the selected step amplitude (up to $\epsilon_{\Delta(\Delta A/A)} = \pm 10\%$ for an imposed $\Delta(\Delta A/A) = 0.01$).

The cyclic experiments were definitely repeatable (as well as the transient ones) but, because of the above-noted systematic error together with other possible instrumental failures, the $\Delta A/A$ perturbations were not purely harmonic.

Surface tension

$\Delta\gamma$-values were visually read from the recorded curves. Bearing in mind the purposes of this work, this procedure was considered as the major source of error (estimated $\epsilon_{\Delta\gamma} = \pm 3\%$).

Perturbation–response phase angle

An instrumental time-delay (estimated $\Delta t \approx 1$ s) affected the value of the phase angle in the harmonic experiments. The error, however, becomes negligible at the lowest frequencies. Also, the travel-time of the longitudinal waves on the liquid surface,

inside the ring, is completely negligible under the present experimental conditions [5].

3. Results and discussion

3.1. Comparison between transient and harmonic responses

The sample of $DC_{12}PO$ solution was subjected (1) to ($\Delta A/A = 0.05$) trapezoidal-pulse perturbations and (2) to ($\Delta A/A = 0.05$ peak-to-peak) sinusoidal perturbations, at different frequencies in the range $\omega = 0.57$–0.015 rad s^{-1}. Transient and steady-state harmonic responses were registered and manually digitized.

The experimental $\Delta\gamma$–t and $\Delta\gamma$–$\Delta A/A$ values were fit to Eq. (1) and to Eq. (2) (see Eqs. (23) and (27) in Ref. [1]), respectively, by using a nonlinear least-squares procedure [6]

$$\Delta\gamma(t) = \Delta\gamma_1(t) = \frac{\epsilon_0\Theta}{2\omega_0}\cdot\left[\exp(2\omega_0 t)\cdot\mathrm{erfc}(2\omega_0 t)^{1/2} + \frac{2\sqrt{2\omega_0 t}}{\sqrt{\pi}} - 1\right], \quad 0 < t \leqslant t_1$$

$$= \Delta\gamma_2(t) = \Delta\gamma_1(t) - \Delta\gamma_1(t - t_1), \quad t_1 < t \leqslant t_1 + t_2$$

$$= \Delta\gamma_3(t) = \Delta\gamma_2(t) - \Delta\gamma_1[t - (t_1 + t_2)], \quad t_1 + t_2 < t \leqslant 2t_1 + t_2$$

$$= \Delta\gamma_4(t) = \Delta\gamma_3(t) + \Delta\gamma_1[t - (2t_2 + t_2)], \quad t > 2t_1 + t_2 \qquad (1)$$

where $\epsilon_0 = -(\mathrm{d}\gamma/\mathrm{d}\ln\Gamma)$, $\omega_0 = (\mathrm{d}c/\mathrm{d}\Gamma)^2 \cdot D/2$ and $t = 0$, t_1, $t_1 + t_2$, and $2t_1 + t_2$ are the time instants at the trapezium vertices.

$$\Delta\gamma\left(\frac{\Delta A}{A}\right) = \epsilon'\frac{\Delta A}{A} \pm \epsilon''\sqrt{\left(\frac{\Delta A_{\max}}{A_0}\right)^2 - \left(\frac{\Delta A}{A}\right)^2} \qquad (2)$$

where ϵ' and ϵ'' are the real and the imaginary parts of the (complex) surface dilational modulus

Table 1
Results of the nonlinear least-squares fit of Eq. (1) (for transient responses) and of Eq. (2) (for harmonic responses), for a sample of $DC_{12}PO$ solution subjected to ($\Delta A/A = 0.05$) perturbations

Figure	ϵ_0 (mN m^{-1})	$\sqrt{\omega_0}$ (rad$^{1/2}$ $s^{-1/2}$)
Trapezoidal-pulse perturbation		
Fig. 1	27.5	0.056

Figure	$\sqrt{\omega}$ (rad$^{1/2}$ $s^{-1/2}$)	ϵ_0 (mN m^{-1})	$\sqrt{\omega_0}$ (rad$^{1/2}$ $s^{-1/2}$)
Harmonic perturbation			
Fig. 2(a)	0.755	31.5	0.063
Fig. 2(b)	0.547	35.4	0.105
Fig. 2(c)	0.406	33.1	0.100
Fig. 2(d)	0.290	31.8	0.096
Fig. 2(e)	0.239	32.1	0.078
Fig. 2(f)	0.170	32.0	0.073
Fig. 2(g)	0.122	29.5	0.066

ω is the experimental angular frequency; ϵ_0 (limiting elastic modulus) and ω_0 (characteristic frequency) are the fit parameters.

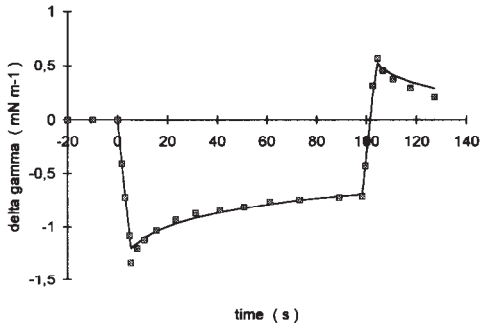

Fig. 1. Time evolution of the $\Delta\gamma$-response to a $\Delta A/A$-trapezoidal-pulse perturbation, for an aqueous solution of *n*-dodecyldimethylphosphine oxide at concentration $c = 4 \times 10^{-3}$ mol m^{-3}. Experimental parameters: initial area $A_0 = 20.56$ cm^2; final area $A_f = 19.54$ cm^2; $\Delta A/A_0 = 0.05$; time instants at the trapezium vertices $t = 0$ s, $t_1 = 5.4$ s, $t_1 + t_2 = 98.4$ s, $2t_1 + t_2 = 103.8$ s. Shaded squares, experimental points; solid line, least-squares fit curve.

for the simple diffusion model [7]

$$\epsilon' = \epsilon_0\frac{1 + \sqrt{\frac{\omega_0}{\omega}}}{1 + 2\sqrt{\frac{\omega_0}{\omega}} + 2\frac{\omega_0}{\omega}}$$

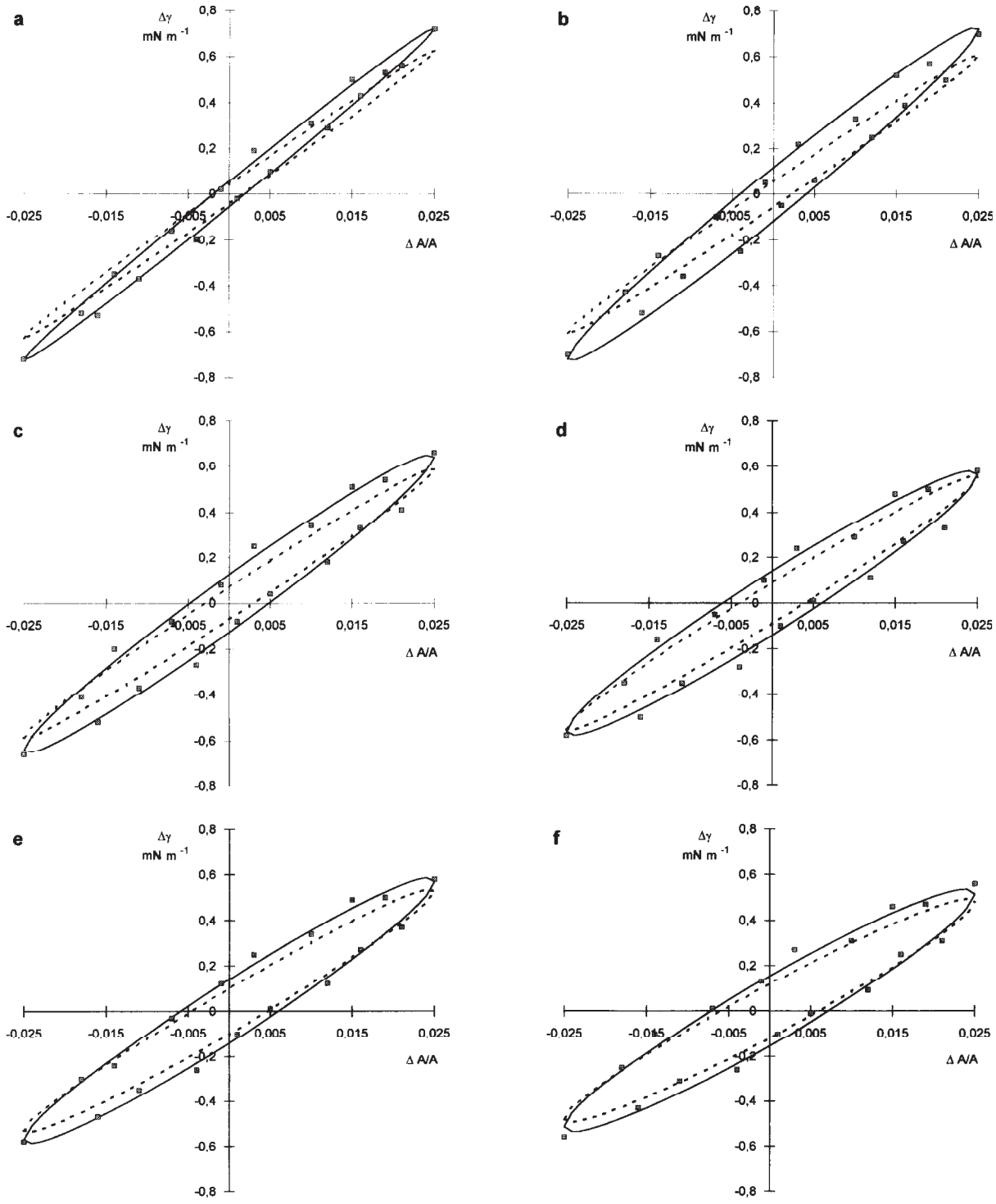

Fig. 2. (Caption opposite.)

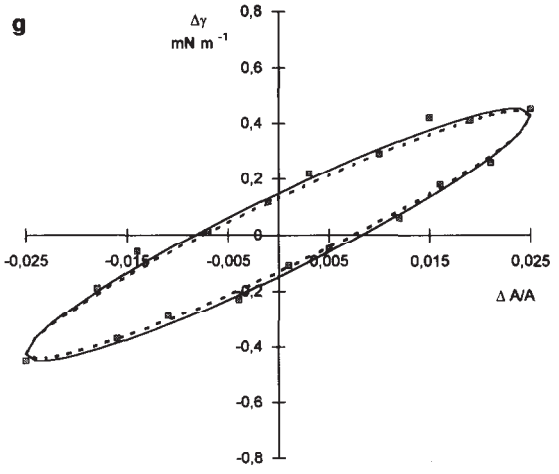

Fig. 2. Hysteresis loops of $\Delta\gamma$-response vs. harmonic $\Delta A/A$-perturbation, at different angular frequencies ω: (a) 0.57; (b) 0.299; (c) 0.165; (d) 0.084; (e) 0.057; (f) 0.029; (g) 0.015 rad s^{-1}. Shaded squares, experimental points; solid line, least-squares fit curve; dotted line, predicted behaviour from transient-response fit parameters.

$$\epsilon'' = \epsilon_0 \frac{\sqrt{\frac{\omega_0}{\omega}}}{1 + 2\sqrt{\frac{\omega_0}{\omega}} + 2\frac{\omega_0}{\omega}}$$

The fit-parameter reliability was assessed from the parameter-retrieval ability of the computer program, from simulated responses affected by random noise.

Table 1 presents a set of results for transient and oscillatory experiments. The apparent fit parameters were not corrected for the above-mentioned systematic errors. As a consequence, the parameter values are scattered in a rather large interval.

Figs. 1 and 2 display the experimental points and the fit curves for the trapezoidal-pulse response and for the harmonic responses, respectively. Also, Fig. 2 depicts the comparison between observed behaviour in the frequency domain and predicted behaviour from transient-response fit parameters. Inspection of panels a–g in Fig. 2 shows a good agreement between observed and predicted hysteresis loops, despite the large discrepancies reported in Table 1. At the lowest frequencies, observed and predicted behaviours practically coincide.

Eqs. (1) and (2), derived within the framework of the theory for distributed systems [1], have in common the surface dilational modulus

$$\epsilon^*(i\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$$

that is the transfer function of the interfacial system, expressed in the functional form for the simple diffusion model. Then, the agreement illustrated in Fig. 2 supports the statements (1) $\epsilon^*(i\omega)$ is a physical quantity governing all interfacial dynamic behaviours; (2) diffusion is the dominating relaxation mechanism for small-amplitude disturbances of surface equilibrium (convective motion takes place only at larger surface deformations [8]).

3.2. Linearity approximation

The recording of Fig. 3 shows measurement of trapezoidal-pulse responses, $\Delta\gamma(t)$, to $\Delta A/A$-perturbations of different amplitude, in the range $\Delta A/A = 0.02$–0.10. In the figure, each successive response (at intervals $\Delta t \approx 900$ s) has been shifted back to be superimposed on the previous ones. The evidence of a linear relationship between responses and surface disturbances is apparent, within the instrumental systematic errors.

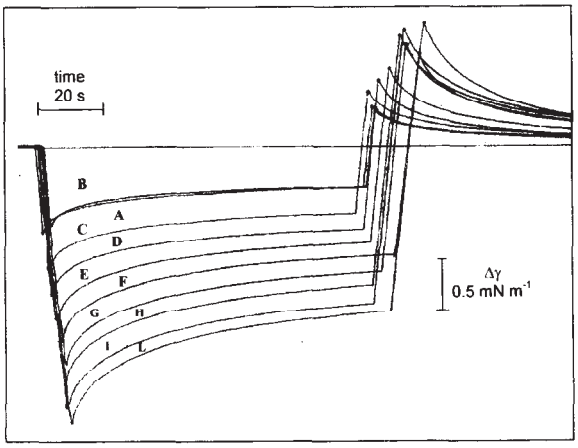

Fig. 3. Representative experimental plot for (superimposed) $\Delta\gamma(t)$-responses, resulting from $\Delta A/A$-trapezoidal pulses of different amplitude: (A) 0.02 (first run); (B) 0.02 (last run); (C) 0.03; (D) 0.04; (E) 0.05; (F) 0.06; (G) 0.07; (H) 0.08; (I) 0.09; (L) 0.1. The experiments were conducted in succession on the same sample, at time intervals $\Delta t \approx 900$ s.

3.3. Measurement repeatability

An example of measurement repeatability is shown in the recording of Fig. 4. A pulse sequence disturbed the surface equilibrium state (the pulse duration was $\Delta t_p = 2t_1 + t_2 \approx 100$ s and the intervals between pulses $\Delta t_i \approx 900$ s). The $\Delta\gamma(t)$ responses were coincident.

Measurement repeatability involves the re-establishment of the equilibrium state both in the surface and in the bulk system. The experiment illustrated in Fig. 4 supports the theoretical prediction that the spatial distribution of the perturbing effect practically vanishes after 8 times the pulse duration [1].

4. Conclusions

An overall examination of the results suggests that the present experimental investigation supports the relevant aspects of the theory. Then, the observed behaviour lets us assert the truth of the following sentences.

(1) The formalism of distributed systems theory can be applied to nonequilibrium thermodynamic properties of adsorption layers.

(2) The diffusion model is suitable for describing, interpreting and predicting the surface phenomena for simple surfactant solutions, subjected to small-amplitude perturbations. In other words, diffusion is the rate controlling mechanism of adsorption processes both for transient and for harmonic disturbances of surface equilibrium, under the described conditions.

(3) The surface dilational modulus is a constitutive property of a liquid solution, independent of the type of perturbation.

(4) A linearity range in the perturbation–response relationship exists.

(5) Trapezium-pulse responses are repeatable, which means that surface and bulk equilibrium states are reproducible within a short time interval after a trapezium pulse.

(6) Time resolved techniques are complementary to periodic techniques and appear useful for characterizing the dynamic properties of adsorption layers.

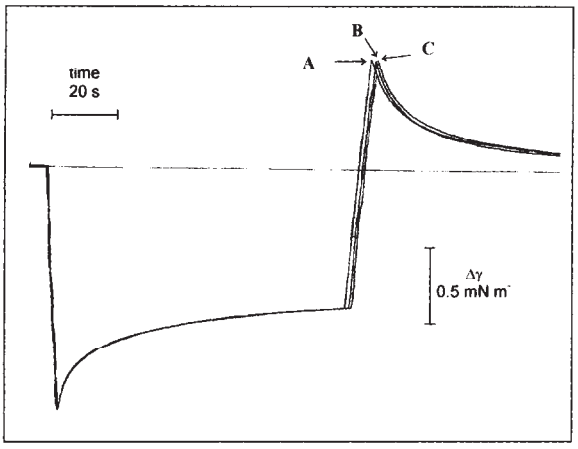

Fig. 4. Plot of three (superimposed) successive $\Delta\gamma(t)$-responses (at time intervals $\Delta t \approx 900$ s), observed on the same sample under exactly the same experimental conditions.

Acknowledgements

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