

Comments on Some Dynamic Surface Tension Measurements by the Dynamic Bubble Pressure Method

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Experiments described in recent papers of M. Rosen and co-workers using the dynamic bubble pressure method for different surfactants are reevaluated using diffusion theory. It is concluded that the results can be described by a diffusion-controlled mechanism except in the case of DESS and that the dynamic bubble pressure method gives reliable data. © 1992 Academic Press, Inc.

In recent papers Hua and Rosen (1, 2) give results of dynamic surface tension measurements of surfactant solutions using the dynamic bubble pressure method. According to data given by these authors, this method operates over a very broad time window, from say 40 ms to minutes, and compares with the time window of our inclined plate method (3) (between 30 ms and 2 s). It is our conviction that the experimental results of Hua and Rosen can be discussed more thoroughly and that this discussion will support the usefulness of the dynamic bubble pressure method.

First, it should be remarked that during the formation of a bubble the surface is continuously renewed and that as a consequence the age of the surface is less than the dropping or bubble time (5, 6). This situation is the same as that for the dropping mercury electrode in electrochemistry (7). Indeed, since the bubble expands during its formation, convective terms must be accounted for in the diffusion equation for the transfer of surface-active material from the bulk to the surface of the expanding surface (6). This point was treated by Miller (8), giving for the absorption Γ with time an equation of the type of Ward and Tordai,

$$\Gamma = 2C_0 \left(\frac{3Dt}{7\pi} \right)^{1/2} - 2 \left(\frac{D}{\pi} \right)^{1/2} \times t^{-2/3} \int_0^{\sqrt{\tau}} C_s(\tau - \lambda) d\sqrt{\lambda}, \quad [1]$$

where C_0 is the bulk concentration, D is the diffusion coefficient, C_s is the subsurface concentration, τ is $\frac{3}{2}t^{7/3}$, λ is a dummy variable, and t is bubbling time.

Equation [1], which is the equation of Ward and Tordai for a constant flow rate, describes the dynamics of the adsorption process over the whole time scale. The convolution integral makes its application difficult. Therefore approximated relaxations which are valid over a limited time scale were derived from it (4). In the very beginning of the adsorption process the subsurface concentration is small and is neglected, yielding

$$\Gamma = 2C_0 \left(\frac{3Dt}{7\pi} \right)^{1/2}. \quad [2]$$

Since the surface tension, and not the adsorption, is measured directly, in order to apply Eq. [2] the relation between the adsorption and the surface tension must be known. In this way the usefulness of Eq. [2] is founded on the reliability of a surface equation of state.

At the end of the adsorption process, when the adsorption has nearly attained its equilib-

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rium value and the subsurface concentration changes little with time, Eq. [1] approximates to

$$\Gamma = 2 \left(\frac{3Dt}{7\pi} \right)^{1/2} \Delta C^s, \quad [3]$$

with $\Delta C^s = C_0 - C_s$.

If the adsorption process is diffusion-controlled, this change in subsurface concentration ΔC^s corresponds with a change in surface tension,

$$\sigma - \sigma_e = \frac{d\sigma}{dC} \Delta C_s, \quad [4]$$

and Eq. [2], using Gibbs equation, results in

$$\sigma = \sigma_e + \frac{RT\Gamma^2}{C_0} \left(\frac{7\pi}{12Dt} \right)^{1/2} \quad [5]$$

for a nonionic surfactant solution and an ionic surfactant with an excess of nonsurfactant-active electrolyte.

For an ionic surfactant without excess electrolyte, Eq. [5] should be written as

$$\sigma = \sigma_e + \frac{2RT\Gamma^2}{C_0} \left(\frac{7\pi}{12Dt} \right)^{1/2}. \quad [6]$$

For obtaining Eq. [5] or [6], it should be emphasized that no use is made of a surface equation of state. Now the question of when the short-time and the long-time approximations should be used arises. The answer is clear: at the beginning of the adsorption process, when the surface tension is near that of the solvent, the short-time approximation should be used, at the end of the process, when the surface tension is near equilibrium values, the long-time approximation should be used. The short-time approximation is expected to become worse with increasing times and the long-time approximation with decreasing times. Because in nature nothing is large or small, one should compare the times with a proper parameter. An adsorption time is considered short compared with the diffusion relaxation time. The simplest way to evaluate the diffusion relaxation time, τ_D , is to set it equal to the time at which adsorption equilib-

rium should be established, assuming that the adsorption is given by the first term of Ward and Tordai:

$$\Gamma_e = 2C_0 \left(\frac{3D\tau_D}{7\pi} \right)^{1/2} \rightarrow \tau_D = \frac{7\pi}{12D} \frac{\Gamma_e^2}{C_0}. \quad [7]$$

From Eq. [7] it is clear that the diffusion relaxation time is dependent on the concentration and the surfactant used. For highly surface-active substances requiring a small concentration to produce a significant appreciable depression of the surface tension, τ_D may amount to hours, whereas for a slightly surface-active substance requiring a large concentration, τ_D may be in the millisecond range.

It should also be noted that t in Eqs. [5] and [6] is the bubbling time and not the adsorption time or the age of surface t_a . The relation between both is

$$t_a = \frac{3}{7} t. \quad [8]$$

This allows the time window to be reduced to a somewhat shorter time.

Here it seems fair to say that Garrett and Ward (9) debate Eq. [8] and take $t_a = t$. Following Garrett and Ward's approach the adsorptions obtained from the dynamic data are 1.24 times higher than ours. The argument raised by Garrett and Ward, obtained from photographic evidence, is that the hemisphere is formed as soon as a bubble breaks away. A quiescent period then elapses, during which the hemisphere may move slightly into the capillary. Growth of a new bubble then follows after a period of time t , which is the age of the surface, since the area does not change substantially during drop formation. However, from a practical point of view the approach of Garrett and Ward's approach and our approach are not very different and both give consistent data.

Previously, we have discussed our experimental results of the dynamic drop volume method with Eq. [5] or [6].

We have reevaluated the results of Rosen and co-workers by plotting the dynamic sur-

face tension as a function of $t^{1/2}$. After long times a linear relationship is to be expected. From its slope the adsorption is obtained using a somewhat arbitrary value for the diffusion coefficient, $D = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, of the correct order of magnitude. The correct value of D does not matter seriously since $\Gamma \sim D^{-1/4}$.

All the results of Rosen and co-workers can be understood in this way, giving acceptable values for the adsorption, except in the case of DESS [di(2-ethylhexyl) sulfosuccinate]. This is understandable since it was shown that for some sulfosuccinates the adsorption process is not controlled only by diffusion; a rearrangement of surfactant molecules in the surface occurs also (10–12).

In Fig. 1 (see also Table I), the data of C_{12}BMG (*N*-dodecyl-*N*-methylglycine) are plotted. A linear relation between σ and $t^{-1/2}$ is obtained as expected. From the slopes the

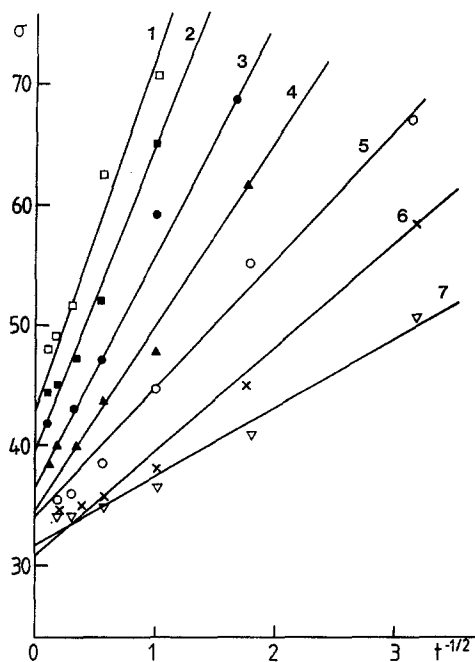


FIG. 1. Dynamic surface tension (σ in mN m^{-1}) plotted as $t^{-1/2}$ (t , time in seconds) for C_{12}BMG . 1(□), $C = 7.8 \times 10^{-8} \text{ mol cm}^{-3}$; 2(■), $C = 1.5 \times 10^{-7} \text{ mol cm}^{-3}$; 3(●), $C = 2 \times 10^{-7} \text{ mol cm}^{-3}$; 4(▲), $C = 3 \times 10^{-7} \text{ mol cm}^{-3}$; 5(○), $C = 3.9 \times 10^{-7} \text{ mol cm}^{-3}$; 6(×), $C = 6 \times 10^{-7} \text{ mol cm}^{-3}$; and 7(▽), $C = 1.02 \times 10^{-7} \text{ mol cm}^{-3}$.

TABLE I

Adsorptions (Γ) Obtained from Dynamic Surface Tension Data (Long-Time Approximation) with $D = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

Concentration (mol cm^{-3}) $\times 10^7$	Slope ($\text{mN m}^{-1} \text{ s}^{-1/2}$)	Γ (mol cm^{-2}) $\times 10^{10}$	σ_e (mN m^{-1})
$\text{C}_{12}\text{EOSO}_4\text{Na}$			
3	16.5	3.85	41.4
3.7	16.4	4.25	38.2
4.95	6.7	3.16	34.1
7.4	6.6	3.80	35.0
C_{12}BMG			
0.78	25.4	2.40	42.6
1.5	16.0	2.71	33.4
2	17.9	3.25	36.5
3	15.2	3.70	34.4
3.9	10.5	3.50	34.0
6	9.45	4.10	30.6
10.2	5.6	4.10	31.6
C_8PY			
65	0.6	3.40	28.5
C_{12}SNa			
30	0.775	1.86	59.5
60	0.65	2.40	48.9
$\text{C}_{12}\text{SO}_3\text{Na} + 0.1 \text{ N NaCl}$			
3	8.2	2.70	54.3
3.7	6.1	2.60	50.7
5.3	5.45	2.93	48.6
6.3	4.85	3.00	45.8
12.7	2.95	3.35	43.8
C_{10}PY			
1.5	81.0	6.0	45.0
2.95	38.6	5.8	39.5
4.35	14.4	4.3	31.0
C_{12}EO_8			
0.6	41.3	2.5	38.9
1.0	21.2	2.1	37.3
1.9	10.8	2.1	36.0

adsorptions are calculated and plotted in Fig. 2. These data can be described by a Langmuir equation,

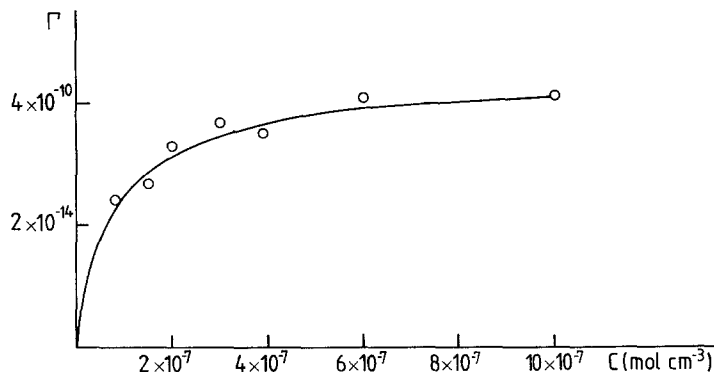


FIG. 2. Adsorption data, Γ , for $C_{12}BMG$ from Fig. 1 plotted as a function of the concentration and compared using a Langmuir equation.

$$\Gamma = \Gamma^\infty \frac{c}{a + c} \quad [9]$$

with $\Gamma^\infty = 4.4 \times 10^{-10} \text{ mol cm}^{-2}$ and $a = 8 \times 10^{-8} \text{ mol cm}^{-3}$. However, plotting the extrapolated equilibrium surface tensions as a function of the concentration and applying Gibbs' equation give an adsorption of $\Gamma = 2.5 \times 10^{-10} \text{ mol cm}^{-2}$. This value is too low, although it is of the correct order of magnitude. It should be emphasized that our Eq. [5] is an approximation, applicable for long times, which allows us to describe dynamic surface tensions for a diffusion-controlled adsorption process. The extrapolated surface tensions may be different from the true equilibrium surface tensions. Indeed, our Eq. [5] is at variance with that of Hansen (4), which applies to surface tensions very close to equilibrium [13]:

$$\sigma = \sigma_e + \frac{RT\Gamma^2}{C_0} \left(\frac{7}{3\pi Dt} \right)^{1/2} \quad [10]$$

Similarly, the results for $C_{12}EOSO_4Na$ in 0.1 N NaCl (sodium salt of sulfated polyoxyethylated *n*-dodecyl alcohol) are given in Fig. 3, and the adsorptions obtained from the slopes are given in Table I. The extrapolated equilibrium surface tensions give an adsorption, using Gibbs' equation, of about $\Gamma \approx 3.2 \times 10^{-10} \text{ mol cm}^{-2}$, comparable with the data listed in Table I. In Fig. 4 the data for $C_{12}SO_3Na + 0.1 \text{ N NaCl}$ (sodium dodecyl

sulfonate) are plotted. The extrapolated equilibrium surface tensions plotted as a function of the concentration (Fig. 5) give an adsorption of $\Gamma \approx 3.1 \times 10^{-10} \text{ mol cm}^{-2}$, in reasonable

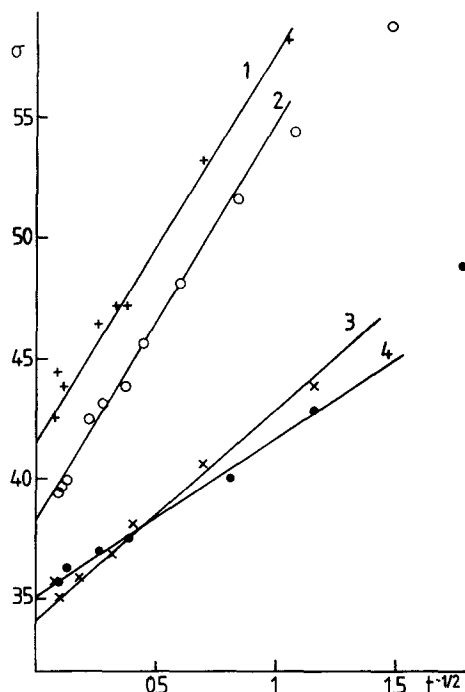


FIG. 3 As. for Fig. 1 for $C_{12}EOSO_4 Na + 0.1 \text{ N NaCl}$. 1(+), $C = 3.0 \times 10^{-7} \text{ mol cm}^{-3}$; 2(O), $C = 3.7 \times 10^{-7} \text{ mol cm}^{-3}$; 3(×), $C = 4.95 \times 10^{-7} \text{ mol cm}^{-3}$; and 4(●), $C = 7.4 \times 10^{-7} \text{ mol cm}^{-3}$.

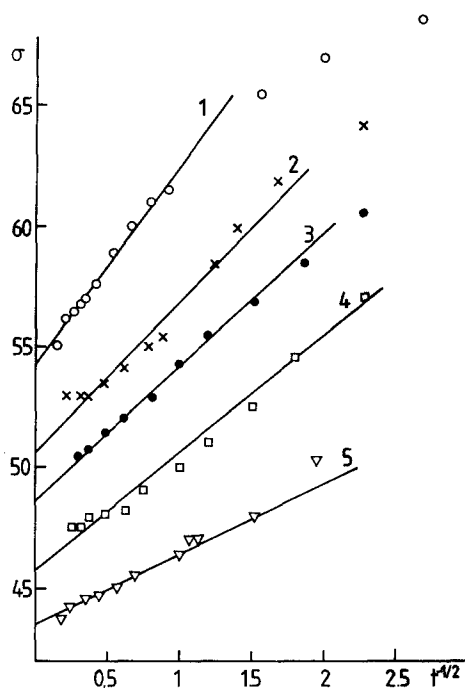


FIG. 4. As for Fig. 1 for $C_{12}SO_3Na + 0.1 N NaCl$. 1 (○), $C = 3 \times 10^{-7} \text{ mol cm}^{-3}$; 2 (×), $C = 3.7 \times 10^{-7} \text{ mol cm}^{-3}$; 3 (●), $C = 5.3 \times 10^{-7} \text{ mol cm}^{-3}$; 4 (□), $C = 6.3 \times 10^{-7} \text{ mol cm}^{-3}$; and 5 (▽), $C = 1.27 \times 10^{-7} \text{ mol cm}^{-3}$.

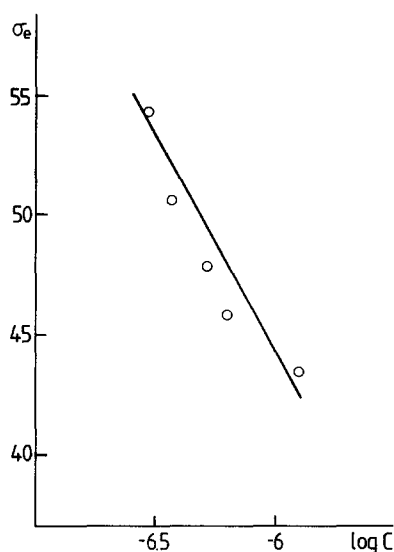


FIG. 5. Extrapolated equilibrium surface tension (σ_e) for $C_{12}SO_3Na$ vs $\log C$.

TABLE II

Estimated Adsorptions Γ from the Extrapolated Surface Tensions Compared with Mean $[\Gamma]$ of Dynamic Adsorption

Surfactant	Γ (mol cm^{-2}) $\times 10^{10}$	$[\Gamma]$ (mol cm^{-2}) $\times 10^{10}$
$C_{12}EOSO_4Na$	~ 3.2	3.75
$C_{12}BMG$	~ 2.5	3.4
$C_{12}SO_3Na$	~ 3.1	2.85
$C_{10}PY$	~ 4.3	5.40
$C_{12}EO_8$	~ 0.8	2.2
$C_{12}SNa$	~ 2.8	2.1

Note. For $C_{12}SNa$ only two points are available.

agreement with that obtained from the dynamic data listed in Table I. The other components C_8PY (*N*-octyl-2-pyrrolidone), $C_{10}PY$ (*N*-decylpyrrolidone), $C_{12}SNa$ (sodium dodecylpyrrolidone), and $C_{12}EO_8$ (polyoxyethy-

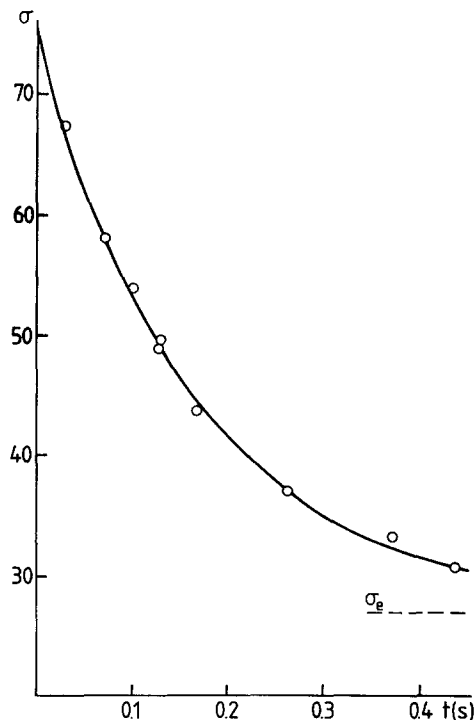


FIG. 6. Dynamic surface tension of DESS ($C = 5.84 \times 10^{-6} \text{ mol cm}^{-3}$) as a function of time and showing exponential decay.

lenated *n*-dodecyl alcohols with eight ethoxy groups) are considered in the same way. Where sufficient data are available, the adsorptions using Gibbs' equation are calculated and the results are given in Table II. Only the adsorption for C₁₂EO₈ seems to be too low. The other data are comparable. All these data indicate that the adsorption process is diffusion-controlled and that the dynamic bubble pressure method gives reliable data.

For DESS (Fig. 10 of Ref. (2)), the results are not in agreement with a diffusion-controlled adsorption process; as seen from Fig. 6, exponential decay is observed,

$$\sigma = \sigma_e + \Delta\sigma_0 e^{-kt}, \quad [11]$$

with $\Delta\sigma = \sigma_0 - \sigma_e$, where σ_0 is the surface tension of the pure solution and σ_e is the equilibrium surface tension.

For the results shown in Fig. 6, $\Delta\sigma = 46 \text{ mN m}^{-1}$ and $k = 5.65 \text{ s}^{-1}$.

As we have previously indicated, for some sulfosuccinates rearrangement at the surface may occur. It was shown (12) that the dynamic surface tension for such a situation is approximately described by

$$\sigma = \sigma_e + \left[\Delta\sigma_{01} \exp\left(-\left(\frac{4t}{\pi\tau_D}\right)^{1/2}\right) + \Delta\sigma_{02} \right] e^{-kt}. \quad [12]$$

The first term accounts for the diffusion, $\Delta\sigma_{01}$ being the amplitude and τ_D the diffusion relaxation time; the other term accounts for the surface reorientation, k being the rate constant. If the diffusion is now slow (τ_D is large), Eq. [12] approximates to Eq. [11].

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