Supporting Information

<u>For the Paper</u>: The Maximum Bubble Pressure Method: Universal Surface Age and Transport Mechanisms in Surfactant Solutions <u>Authors</u>: Nikolay C. Christov, Krassimir D. Danov, Peter A. Kralchevsky, Kavssery P. Ananthapadmanabhan, and Alex Lips

(The reference numbers are the same as in the main paper; see the reference list therein)

Appendix A. Experimental Supporting Information

One of the main problems with MBPM is that different experimental setups give different experimental curves $\gamma(t_{age})^{24}$ Moreover, the same setup gives different $\gamma(t_{age})$ -curves if different (hydrophilic and hydrophobic) capillaries are used.¹⁷ This is illustrated in Figure A.1 with data obtained by means of two experimental setups. The first one is an apparatus constructed and described in ref 17; data obtained by this setup (the square symbols in Figure A.1) are taken from ref 26. The second MBPM apparatus is the commercial tensiometer Krüss BP2. As usual,^{28,29} the data are plotted as γ vs. $(t_{age})^{-1/2}$. One sees that the experimental curves obtained at the same surfactant and salt concentrations by two different setups are rather different. The main difference is in the shape of the curves, including their slopes at $(t_{age})^{-1/2} \rightarrow 0$. On the other hand the intercept at $(t_{age})^{-1/2} = 0$, which gives the equilibrium surface tension, is not so different for the two setups.

As mentioned in relation to Figure A.1, the data for the dynamic surface tension produced by the MBPM are usually plotted as γ vs. $t_{age}^{-1/2}$, and the equilibrium surface tension, γ_{eq} , is determined from the intercept, while the asymptotic slope (at $t_{age}^{-1/2} \rightarrow 0$) is subjected to theoretical analysis.²⁹ However, as illustrated in Figure A.2, this procedure gives uncertain values of the asymptotic slope and intercept. One sees that the data for $t_{age}^{-1/2} > 1$ s^{-1/2} comply well with a straight line. The same is true for the data for $t_{age}^{-1/2} < 1$ s^{-1/2} (the inset in Figure A.2). The slopes of the two lines are markedly different, whereas the difference between the intercepts is of the order of the experimental error of γ_{eq} , which is typically ±0.1 mN/m. The difference is especially pronounced for the slopes. Because the adsorption rate depends on both surfactant type and concentration, one could not know in advance in which range of bubbling periods the experimental dependence γ vs. $t_{age}^{-1/2}$ reduces to a straight-line asymptotic ally fitted with a straight line.



Figure A.1. Plot of the dynamic surface tension, γ , vs. $(t_{age})^{-1/2}$ for data obtained by means of two MBPM setups, denoted in the figure: (a) 1.5 mM SDS + 128 mM NaCl; (b) 2 mM SDS + 128 mM NaCl.



Figure A.2. Plot of data for γ vs. $t_{age}^{-1/2}$ obtained by MBPM for 12 mM DTAB + 100 mM NaBr. For $t_{age}^{-1/2} > 1 \text{ s}^{-1/2}$, the slope of the linear regression is 0.353 mN.m⁻¹.s^{1/2}, whereas for $t_{age}^{-1/2} < 1 \text{ s}^{-1/2}$ (the inset), the slope is 0.543 mN.m⁻¹.s^{1/2}.

Figure A.3 shows typical dynamic-surface-tension curves, $\gamma(t_{age})$, obtained by means of the two types of capillaries, those hydrophobized by silicone oil and HMDS. We recall that for the Krüss BP2 tensiometer, the surface age, t_{age} , is defined as the time interval between the minimal measured pressure, identified with the bubble formation, and the maximum pressure, which marks the onset of the spontaneous bubble detachment. The registered value of γ corresponds to the latter moment. Each curve $\gamma(t_{age})$ is obtained by variation of the bubbling period. Figure A.3 shows that there is a difference between the experimental $\gamma(t_{age})$ -curves obtained by means of the capillaries treated by silicone oil and HMDS. In the former case (Figure 3 in the main paper), the curves are relatively smooth, while in the latter case (Figure 4 in the main paper) the curves exhibit some undulations, which are probably due to the more complicated regime of bubble release. In our basic experiments (Figures 5–8 in the main paper), we used the capillary hydrophobized by silicone oil, which provides a regular regime of bubble formation (Figures 1b and 3 in the main paper), described by the apparatus function, $A(t_d)$, given by eq 3.1 in the main paper.



Figure A.3. Comparison of dynamic surface tension curves, $\gamma(t_{age})$, obtained by the two capillaries, one of them hydrophobized by silicone oil (Figure 3 in the main paper), and the other one – by HMDS (Figure 4 in the main paper).



Figure A.4. Plot of the data from the immobile bubble (IB) method in Figure 3 as γ vs. $t^{-1/2}$ in accordance with eq 5.21 ($t = t_{age}$). The SDS concentrations are 0.2 and 0.5 mM, and the NaCl concentration is 100 mM.

As an illustration of the applicability of eq 5.21 in the main paper,

$$\gamma = \gamma_{\rm eq} + \frac{s_{\gamma,0}}{t^{1/2}} \tag{5.21}$$

in Figure A.4 we have plotted the data from the immobile bubble (IB) method in Figure 3 (main paper) as γ vs. $t^{-1/2}$. As seen in Figure A.4, the data comply very well with straight lines. The intercept and the slope of these lines, γ_{eq} and $s_{\gamma,0}$, are listed in Table A.1, where they are compared with the values of γ_{eq} and $s_{\gamma,\gamma}$ for the same SDS concentrations in Table 1 of the main paper (MBPM). One sees that the values of γ_{eq} determined by the MBPM and IB method practically coincide (Table A.1). On the other hand, s_{γ} is systematically greater than $s_{\gamma,0}$. The ratio $\lambda \equiv s_{\gamma}/s_{\gamma,0}$ is about 6. As demonstrated in section 5.3 of the main paper, the quantity λ is, in fact, the apparatus constant of the used MBPM setup.

Table A.1. Comparison of the MBPM and IB Methods for Solutions of SDS + 100 mM NaCl

C _{SDS} (mM)	γ _{eq} [IB] (mN/m)	γ _{eq} [MBPM] (mN/m)	$s_{\gamma,0}$ [IB] (mN.s ^{1/2} .m ⁻¹)	$s_{\gamma} [MBPM] (mN.s^{1/2}.m^{-1})$	$\lambda \equiv s_{\gamma}/s_{\gamma,0}$
0.2	52.78	53.10	4.88	27.7	5.7
0.5	44.13	44.37	2.28	14.0	6.1

Appendix B: Calculation of D in Eqs 5.36 and 5.38 for Ionic Surfactants below the CMC

Here, as usual, the components 1, 2 and 3 are, correspondingly, the surfactant ions, counterions and coions. For example, in the case of SDS + NaCl, these are, respectively, DS⁻, Na⁺, and Cl⁻. In the case of DTAB + NaBr, components 1, 2 and 3 are, respectively, DTA⁺, Br⁻, and Na⁺. The corresponding bulk concentrations and diffusivities are denoted by $c_{1\infty}$, $c_{2\infty}$, $c_{3\infty}$, and D_1 , D_2 , D_3 . Note that because of the solution's electroneutrality, we have $c_{2\infty} = c_{1\infty} + c_{3\infty}$.

In ref 53, by analysis of the diffusion of the ionic species across the electric double layer, eqs 5.36 and 5.38 in the present paper were derived. In these equations, D is an effective diffusion coefficient of the ionic surfactant defined as follows:⁵³

$$D = (a_{11} + a_{33} + 2a^{1/2})q^2$$
(B.1)

where

$$q = \frac{(c_{1\infty} + c_{2\infty})a^{1/2}}{(a_{33} - a_{31} + a^{1/2})c_{1\infty} + (a_{33} + a^{1/2})c_{2\infty}}$$
(B.2)

$$a = \frac{2c_{2\infty}}{B}D_1D_2D_3 \tag{B.3}$$

$$B = D_1 c_{1\infty} + D_2 c_{2\infty} + D_3 c_{3\infty}$$
(B.4)

$$a_{11} = D_1 + \frac{D_2 - D_1}{B} D_1 c_{1\infty}$$
(B.5)

$$a_{31} = \frac{D_2 - D_1}{B} D_3 c_{3\infty} \tag{B.6}$$

$$a_{33} = D_3 + \frac{D_2 - D_3}{B} D_3 c_{3\infty} \tag{B.7}$$

In the special case of *high salt* concentration or *low surfactant* concentration, $c_{1\infty}/c_{3\infty} \ll 1$, eq B.1 reduces to:⁵³

$$D_{\rm eff} \approx D_1 \qquad (c_{1\infty} / c_{3\infty} << 1)$$
 (B.8)

In the *absence* of non-amphiphilic electrolyte ($c_{3\infty} = 0$), eq B.1 acquires the form:⁵³

$$\frac{1}{D_{\rm eff}} = \frac{1}{2} \left(\frac{1}{D_1} + \frac{1}{D_2} \right) \qquad (c_{3\infty} = 0)$$
(B.9)

In the general case, one has to calculate D_{eff} from eq B.1, along with eqs B.2 – B.7. The latter equations are applicable for concentrations below the CMC.

Here, in our calculations we used the following values of the diffusion coefficients. For SDS, the surfactant diffusivity is $D_1 = 5.5 \times 10^{-10} \text{ m}^2/\text{s.}^{60}$ Using the Stokes-Einstein formula for the diffusivity of elongated molecules,⁶¹ we estimated the diffusivity of the surfactant ion for DTAB:

$$(D_1)_{\text{DTAB}} \approx \left[\frac{(\Gamma_{\infty}^{-1})_{\text{SDS}}}{(\Gamma_{\infty}^{-1})_{\text{DTAB}}}\right]^{1/2} (D_1)_{\text{SDS}}$$
(B.10)

The values of the excluded area per molecule in the adsorption layer, Γ_{∞}^{-1} , are taken from Table 3 for SDS and DTAB. Thus we obtained $D_1 = 5.0 \times 10^{-10} \text{ m}^2/\text{s}$ for DTAB. The diffusivities of the Na⁺, Cl⁻, and Br⁻ ions were calculated from the radii of the hydrated ions⁶² with the help of the Stokes-Einstein formula, substituting $\eta = 0.852$ mPa.s for the viscosity of

water at $T = 27^{\circ}$ C. Thus, for the system SDS + NaCl we obtain $D_2 = 7.18 \times 10^{-10}$ m²/s and $D_3 = 7.83 \times 10^{-10}$ m²/s, whereas for the system DTAB + NaBr we have $D_2 = 7.83 \times 10^{-10}$ m²/s and $D_3 = 7.18 \times 10^{-10}$ m²/s (the hydrated Cl⁻ and Br⁻ ions have practically the same size). Afterwards, D was calculated by means of eqs B.1 – B.7 as a function of $c_{1\infty}$ and $c_{2\infty}$.

It should be noted also that the total surfactant adsorption, $\tilde{\Gamma}_1 = \Gamma_1 + \Lambda_1$, includes both the ions adsorbed at the interface (Γ_1) and the excess ions in the diffuse electric double layer (Λ_1). The computations show that for not too low ionic strengths, $c_{2\infty} \ge 1$ mM, the diffuse electric double layer is relatively narrow, and then Λ_1 is negligible, so that $\Gamma_{eq} = \tilde{\Gamma}_1 \approx \Gamma_1$. However, at lower ionic strengths ($c_{2\infty} < 1$ mM) one has to substitute $\Gamma_{eq} = \tilde{\Gamma}_1 = \Gamma_1 + \Lambda_1$ in eqs 5.36 and 5.38; see ref 53 for details.

Appendix C: Dynamic Surface Tension of Micellar Solutions: Derivation of Eq 6.1

For concentrations above the CMC, the initial and boundary conditions for the monomer concentration, c_1 , are:

$$c_1 = c_{\text{CMC}} \quad \text{at } t = 0 \text{ and } x > 0 \tag{C.1}$$

$$c_1 = c_{\text{CMC}}$$
 at $t > 0$ and $x \to \infty$ (C.2)

where c_{CMC} is the equilibrium monomer concentration in the considered case. For kinetics of adsorption from micellar surfactant solutions in regimes BC and DE, the diffusion equation and the surfactant mass balance at the interface read:³⁴

$$A_{\rm L}\left(\frac{\partial c_1}{\partial t} - \dot{\alpha}x\frac{\partial c_1}{\partial x}\right) = A_{\rm R}D\frac{\partial^2 c_1}{\partial x^2} \qquad (t > 0, \ x > 0)$$
(C.3)

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} + \dot{\alpha}\,\Gamma = A_{\mathrm{R}}D\frac{\partial c_{1}}{\partial x} \qquad (t > 0, \ x = 0) \tag{C.4}$$

where

$$A_{\rm L} = 1 + \frac{\sigma_{\rm eq}^2}{m_{\rm eq}}\beta, \quad A_{\rm R} = 1 + \frac{\sigma_{\rm eq}^2}{m_{\rm eq}}\frac{D_{\rm m}}{D}\beta \quad (\text{regime BC})$$
(C.5)

$$A_{\rm L} = 1 + \frac{m_{\rm eq}^2 + \sigma_{\rm eq}^2}{m_{\rm eq}}\beta, \quad A_{\rm R} = 1 + \frac{m_{\rm eq}^2 + \sigma_{\rm eq}^2}{m_{\rm eq}}\frac{D_{\rm m}}{D}\beta \quad (\text{regime DE})$$
(C.6)

In terms of the variables (y, τ) defined by eq 5.6, eqs C.3 and C.4 acquire the form:

$$A_{\rm L} \frac{\partial c_1}{\partial \tau} = A_{\rm R} D t_{\rm age} \frac{\partial^2 c_1}{\partial y^2} \qquad (\tau > 0, \ y > 0)$$
(C.7)

$$\frac{\mathrm{d}}{\mathrm{d}\,\tau}(\Gamma\widetilde{A}) = A_{\mathrm{R}}Dt_{\mathrm{age}}\frac{\partial c_{1}}{\partial y} \qquad (\tau > 0, \ y = 0) \tag{C.8}$$

Next, we apply Laplace transform to eq C.7 with respect to τ , and solve the obtained ordinary differential equation:

$$L[c_1] = \frac{c_{\rm CMC}}{s} + L[c_{\rm s} - c_{\rm CMC}] \exp[-\frac{(sA_{\rm L})^{1/2} y}{(A_{\rm R}Dt_{\rm age})^{1/2}}]$$
(C.9)

where *L* denotes Laplace transform; *s* is the Laplace parameter; and $c_s(\tau) \equiv c_1(y=0,\tau)$ is the subsurface concentration of surfactant monomers. Further, we apply Laplace transformation to eq C.8, and substitute eq C.9:

$$L[\Gamma \widetilde{A}] = \frac{\Gamma_0}{s} - \left(D_{\text{eff}} t_{\text{age}} / s\right)^{1/2} L[c_s - c_{\text{eq}}]$$
(C.10)

where $\Gamma_0 = \Gamma(\tau=0)$ and

$$D_{\rm eff} \equiv A_{\rm L} A_{\rm R} D \tag{C.11}$$

Because eq C.10 is analogous to eq 5.11 in the main paper, we arrive again at eq 5.31, where s_{γ} is defined by eq 6.1. In addition, the substitution of eqs C.5 and C.6 into eq C.11 leads to eqs 6.4 and 6.5.

The reference numbers are the same as in the main paper; see the reference list therein.