Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Colloid and Interface Science 270 (2004) 180–186
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Spontaneous rise of surfactant solutions into vertical hydrophobic capillaries

Victor M. Starov

Department of Chemical Engineering, Loughborough University, LE11 3TU, UK

Received 7 April 2003; accepted 7 November 2003

Abstract

It has been found earlier (N.V. Churaev, G.A. Martynov, V.M. Starov, Z.M. Zorin, Colloid Polym. Sci. 259 (1981) 747) that aqueous surfactant solutions spontaneously rise in vertical hydrophobized quartz capillaries. A theory of this phenomenon is presented, which connects the experimental observations with the adsorption of surfactant molecules in front of the moving meniscus on the bare hydrophobic interface.

Keywords: Surfactant solutions; Hydrophobic capillaries; Spontaneous rise

1. Introduction

Pure water does not penetrate spontaneously into hydrophobized quartz capillaries. However, surfactant solutions penetrate spontaneously and the penetration rate depends on the concentration of surfactant. Both the air–liquid interfacial tension, γ, and the contact angle of the moving meniscus, θ_A, where a subscript A indicates the advancing contact angle, are concentration-dependent [1].

Adsorption of surfactant molecules behind the moving meniscus results in a decrease of the bulk surfactant concentration from the capillary inlet in the direction of the moving meniscus [1,2]. However, the major process, which determines penetration of surfactant solutions into hydrophobic capillaries or spreading of surfactant solutions over hydrophobic substrates, is the adsorption of surfactant molecules onto a bare hydrophobic substrate in front of the moving three-phase contact line [1–3]. The latter process results in a partial hydrophilization of the hydrophobic surface in front of the meniscus/drop, which, in its turn, determines the spontaneous imbibition/spreading.

Let us consider the very beginning of the imbibition process in order to understand why the adsorption in front of the moving meniscus on a hydrophobic substrate determines the spontaneous imbibition. At this initial moment the meniscus of surfactant solutions touches an inlet of the hydrophobic capillary for the first time. The contact angle, θ_A, at this moment is more than $\pi/2$ and the liquid can not penetrate into the hydrophobic capillary. Solid–liquid and liquid–air interfacial tensions, γ_{SL} and γ, do not vary with time because the adsorption of surfactant molecules onto these surfaces is a fast process as compared with the rate of imbibition into hydrophobic capillaries. The only interfacial tension that can vary is the solid–air interfacial tension, γ_{SV}. If the adsorption on the solid–air interface does not occur then the spontaneous imbibition into the hydrophobic capillary cannot take place spontaneously because the advancing contact angle remains above $\pi/2$. However, if the adsorption of surfactant molecules onto the bare hydrophobic surface in the vicinity of the three-phase contact line takes place then γ_{SV} grows with time. The advancing contact angle reaches $\pi/2$ and the spontaneous imbibition process starts after some critical adsorption is reached.

In the case of partial wetting the capillary imbibition in the horizontal direction proceed according to the dependency [4]

$$l = \sqrt{\frac{R\gamma\cos\theta_A}{2\eta}}t, \tag{1}$$

where l is the length of the part of the capillary filled with the liquid; R is the radius of the capillary; η is the liquid viscosity; the advancing contact angle, θ_A, in Eq. (1) is below $\pi/2$: $0 < \theta_A < \pi/2$; and t is time.

Pure water does not penetrate into hydrophobic capillaries and shows an advancing contact angle $\theta_A > \pi/2$. The

E-mail address: v.m.starov@lboro.ac.uk.

0021-9797/$ – see front matter
doi:10.1016/j.jcis.2003.11.018

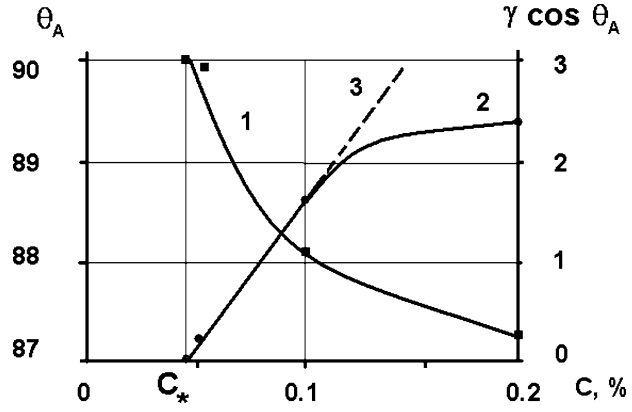

Fig. 1. The influence of the concentration of aqueous surfactant solutions (Syntamide-5, molecular weight of about 420) on the advancing contact angle, θ_A (squares, curve 1), and $\gamma\cos\theta_A$ (filled circles, curve 2), measured on a flat hydrophobized quartz surface [1]. C_* marks the critical surfactant concentration, below which surfactant solutions do not spread. Line 3 is a linear fit according to Eq. (6).

liquid can be only forced into the capillary and does not penetrate spontaneously. However, the advancing contact angle is a decreasing function of the surfactant concentration and at some critical concentration, C_*, is equal to $\pi/2$. At concentrations above C_* surfactant solution penetrates spontaneously into hydrophobic capillaries [1,2]. An experimental procedure for hydrophobization of quartz capillaries has been described in [1,2].

In the case of the imbibition of surfactant solutions into hydrophobic capillaries the penetration is controlled by both surfactant molecule transfer and liquid viscosity according to Eq. (1) [1,2]. In this case the aim is to reveal the mechanism of the penetration and to determine the concentration of surfactant molecules near the meniscus $C_m < C_0$, where C_0 is the surfactant concentration at the capillary inlet. This problem has been discussed from both experimental and theoretical points of view in [1,2].

Fig. 1 shows that the advancing contact angle, θ_A, exceeds 90° above some critical concentration, C_*, which is slightly below 0.05% in the case of surfactant solutions of Syntamide-5 [1].

It is necessary to emphasize that the mechanism investigated below is the opposite of an autophobing event [5].

Below, a spontaneous capillary rise in hydrophobic capillaries is considered and a theory is presented for this case. It is shown that in the case of spontaneous capillary rise the mechanism greatly differs from the case of spontaneous imbibition into hydrophobic capillaries [1,2] because concentration on the moving meniscus cannot remain constant as in the case of spontaneous imbibition.

2. Theory

Let us consider a dependency of $\varphi(C_m) = \gamma(C_m) \times \cos\theta_A(C_m)$ on the concentration of surfactant, C_m, on the moving meniscus. According to the triangle rule it can be calculated as

$$\varphi(C_m) = \gamma_{SV}(C_m) - \gamma_{SL}(C_m), \tag{2}$$

where γ_{SV} and γ_{SL} are solid–vapor and solid–liquid interfacial tensions. According to Antonov's rule the dependency of the latter two interfacial tensions on the concentration can be presented as

$$\gamma_{SV}(C_m) = \gamma_{SV}^0\left(1 - \frac{\Gamma_+}{\Gamma^\infty}\right) + \gamma_{SV}^\infty\frac{\Gamma_+}{\Gamma^\infty},$$
$$\gamma_{SL}(C_m) = \gamma_{SL}^0\left(1 - \frac{\Gamma_-}{\Gamma^\infty}\right) + \gamma_{SL}^\infty\frac{\Gamma_-}{\Gamma^\infty}, \tag{3}$$

where superscripts 0 and ∞ mark zero and complete coverage of hydrophobic sites, respectively; subscripts $+$ and $-$ mark positions just behind and just in front of the moving meniscus, correspondingly; Γ is the surface concentration of surfactant molecules.

Note that adsorption of surfactant molecules results in a decrease of SL interfacial tension; that is, $\gamma_{SL}^0 - \gamma_{SL}^\infty > 0$. However, adsorption of surfactant molecules on the bare hydrophobic surface in front of the moving meniscus results in a local increase of the SV interfacial tension; that is, $\gamma_{SV}^0 - \gamma_{SV}^\infty < 0$. The initial contact angle on the bare hydrophobic interface is bigger than $\pi/2$; that is, $\gamma_{SV}^0 - \gamma_{SL}^0 < 0$.

Let us assume that surfactant molecules do not adsorb in front of the moving meniscus. In this case the interfacial tension of the SL interface remains constant and equal to γ_{SV}^0; hence, from Eqs. (2) and (3),

$$\varphi(C_m) = \gamma_{SV}^0 - \left[\gamma_{SL}^0\left(1 - \frac{\Gamma_-}{\Gamma^\infty}\right) + \gamma_{SL}^\infty\frac{\Gamma_-}{\Gamma^\infty}\right]$$
$$= \gamma_{SV}^0 - \gamma_{SL}^0 + \frac{\Gamma_-}{\Gamma^\infty}(\gamma_{SL}^0 - \gamma_{SL}^\infty).$$

The lowest value of the right-hand site in the latter equation is equal to $\gamma_{SV}^0 - \gamma_{SL}^0 < 0$, while the maximum value is reached at $\Gamma_- = \Gamma^\infty$ and is equal to $\gamma_{SV}^0 - \gamma_{SL}^\infty$. If the latter value is negative, then the contact angle remains bigger than 90° at any bulk surfactant concentration and the spontaneous imbibition of surfactant solutions into hydrophobic capillaries does not takes place at any surfactant concentration.

It is assumed below that both adsorption isotherms are linear functions of the surfactant concentration below CMC (which is the only case considered below) and remain constant above CMC. The latter means that

$$\Gamma_- = G_{SL}C_m \tag{4}$$

at concentrations below CMC.

Spontaneous imbibition and spontaneous capillary rise into hydrophobic capillaries are sufficiently slow processes; that is, we assume below a condition of local equilibrium

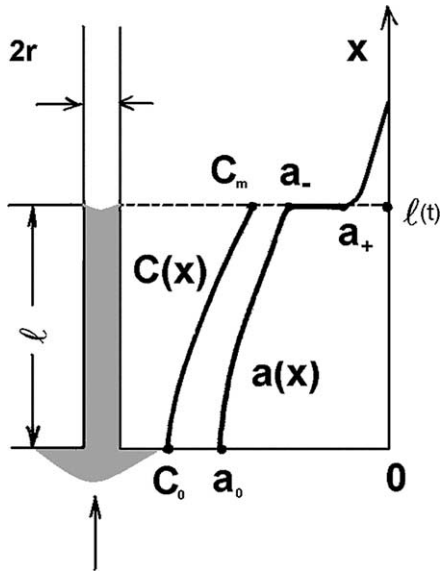

Fig. 2. Bulk volume concentration, C, and surface adsorption, a, distributions along the capillary height during a spontaneous capillary rise in hydrophobic capillaries.

on the moving three-phase contact line. According to this assumption the equality of chemical potentials of adsorbed surfactant molecules should be satisfied across the three-phase contact line; that is,

$$\ln \Gamma_- + \Phi_{SL} = \ln \Gamma_+ + \Phi_{SV},$$

where Γ_- and Γ_+ are jumps of surface concentration across the meniscus surface (Fig. 2), and Φ_{SL}, Φ_{SV} (in kT units) are corresponding values of the energy of surfactant molecules at solid–liquid and solid–air interfaces, respectively. There is no reasons to assume that Φ_{SV} is infinite; that is, adsorption in front of the moving meniscus should take place. From the latter equation we conclude that

$$\Gamma_+ = \frac{\Gamma_-}{\exp(\Phi_{SV} - \Phi_{SL})}.$$

It is obvious that Φ_{SV} is higher than Φ_{SL}, and, hence, $\Gamma_+ < \Gamma_-$. The latter relation can be rewritten using Eq. (4) as

$$\Gamma_+ = G_{SV} C_m, \quad G_{SV} = \frac{G_{SL}}{\exp(\Phi_{SV} - \Phi_{SL})}. \tag{5}$$

Substituting Eqs. (3)–(5) into Eq. (2) and having in mind the latter inequalities, we can conclude after simple rearrangements that

$$\varphi(C_m) = \alpha(C_m - C_*), \tag{6}$$

where

$$\alpha = \left[\frac{G_{SV}}{\Gamma^\infty}\left(\gamma_{SV}^\infty - \gamma_{SV}^0\right) + \frac{G_{SL}}{\Gamma^\infty}\left(\gamma_{SL}^0 - \gamma_{SL}^\infty\right)\right] > 0,$$

$$C_* = \frac{\alpha^0}{\alpha}, \qquad \alpha^0 = \gamma_{SL}^0 - \gamma_{SV}^0 > 0.$$

According to Eq. (6), $\varphi(C_m)$ dependency should be a linear function of concentration at $C_m > C_*$, which is in agreement with experimental observations (Fig. 1).

We now try to solve theoretically the problem of a spontaneous rise of surfactant solutions into vertical hydrophobic cylindrical capillaries, taking into account the transfer and the surface diffusion of surfactant molecules, as well as adsorption onto the bare hydrophobic surface in front of the moving meniscus. The location of the moving meniscus in the capillary is $l(t)$ (Fig. 2).

The transfer of surfactant molecules in the filled portion of the capillary is described by the equation

$$\frac{\partial C(t,x,r)}{\partial t} = D\frac{\partial^2 C(t,x,r)}{\partial x^2} + D\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C(t,x,r)}{\partial r}\right) - \frac{\partial}{\partial x}\big(v(r)C(t,x,r)\big),$$

where $C(t,x,r)$ is the local concentration of surfactant; D is the diffusion coefficient; t, x, r are time, axial, and radial coordinates, respectively; and $v(r)$ is the axial velocity distribution.

Integration of the last equation over radius from 0 to R, where R is the capillary, radius, results in

$$\frac{\partial}{\partial t}\left(\int_0^R rC(t,x,r)\,dr\right) = D\frac{\partial^2}{\partial x^2}\left(\int_0^R rC(t,x,r)\,dr\right) + R\left(D\frac{\partial C(t,x,r)}{\partial r}\right)_{r=R} - \frac{\partial}{\partial x}\left(\int_0^R rv(r)C(t,x,r)\,dr\right).$$

The second term on the right-hand side of the last equation is equal to

$$-D\frac{\partial C(t,x,r)}{\partial r}\bigg|_{r=R} = \frac{\partial \Gamma}{\partial t} - D_{SL}\frac{\partial^2 \Gamma}{\partial x^2},$$

where D_{SL} is the surface diffusion coefficient over the filled portion of the capillary. Hence, the last two equations result in

$$\frac{\partial}{\partial t}\left(\int_0^R rC(t,x,r)\,dr\right) = D\frac{\partial^2}{\partial x^2}\left(\int_0^R rC(t,x,r)\,dr\right) - R\left(\frac{\partial \Gamma}{\partial t} - D_{SL}\frac{\partial^2 \Gamma}{\partial x^2}\right) - \frac{\partial}{\partial x}\left(\int_0^R rv(r)C(t,x,r)\,dr\right).$$

The characteristic time scale of the equilibration of the surfactant concentration in a cross section of the capillary $\tau \sim R^2/D \approx 0.1$ s, if we use for estimate $R \sim 10$ μm and $D \sim 10^{-5}$ cm^2/s. The characteristic time scale of the spon-

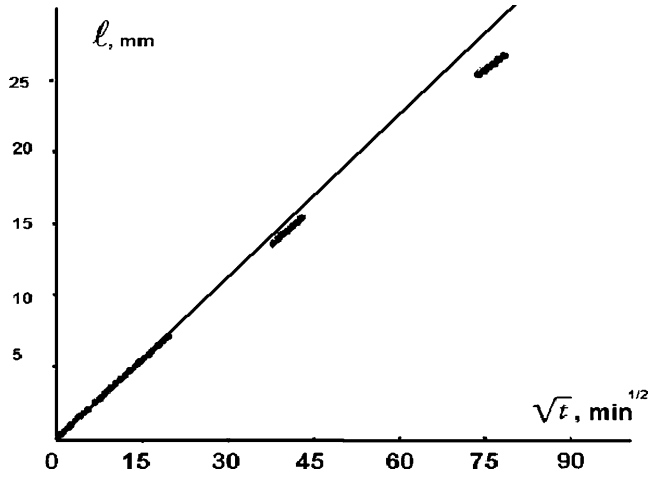

Fig. 3. Spontaneous capillary rise in a vertical hydrophobized quartz capillary ($r = 11$ μm), Syntamide-5 surfactant solution ($C_0 = 0.1\%$). Time evolution of the capillary rise height, l (mm), with time, t (min) [1].

taneous capillary rise into hydrophobic capillaries is around 10^5 s (see Fig. 3), which is much bigger than 0.1 s. That is, the surfactant concentration is constant in any cross section of the capillary and depends only on the vertical position, x (Fig. 2); that is, $C = C(t, x)$. Taking this into account, the latter equation can be rewritten after both sides are divided by $R^2/2$ as

$$\frac{\partial(a + C)}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + D_{\mathrm{SL}}\frac{\partial^2 a}{\partial x^2} - v\frac{\partial C}{\partial x}, \quad 0 < x < l(t), \tag{7}$$

where

$$v = \frac{2}{R^2}\int_0^R r v(r)\, dr$$

is the averaged velocity (the same symbol is used for the averaged velocity as for the local one),

$$a(x, t) = \frac{2}{r}\Gamma = \frac{2}{r}G_{\mathrm{SL}}C(x, t) = F_{\mathrm{SL}}C(x, t), \tag{8}$$

and $F_{\mathrm{SL}} = (2/r)G_{\mathrm{SL}}$. In Eq. (8) local equilibrium between surface and bulk concentrations is assumed.

Substitution of Eq. (8) into Eq. (7) results in

$$(1 + F_{\mathrm{SL}})\frac{\partial C}{\partial t} = D_{\mathrm{ef}}\frac{\partial^2 C}{\partial x^2} - \frac{dl}{dt}\frac{\partial C}{\partial x}, \quad 0 < x < l(t), \tag{9}$$

where $D_{\mathrm{ef}} = (D + F_{\mathrm{SL}}D_{\mathrm{SL}})$ is the effective diffusion coefficient. On the unwetted portion of the capillary surface, $l(t) < x$, only surface diffusion takes place; that is,

$$\frac{\partial a}{\partial t} = D_{\mathrm{SV}}\frac{\partial^2 a}{\partial x^2}, \tag{10}$$

where D_{SV} is the diffusion coefficient of surfactant molecules on the unwetted hydrophobic capillary surface.

Equations (9) and (10) are solved below using the following boundary and initial conditions:

$$C(0, t) = C_0, \qquad a(\infty, t) = 0, \tag{11}$$

$$l(0) = 0, \qquad a(x, 0) = 0. \tag{12}$$

The following condition of the mass balance on the moving meniscus surface should be satisfied,

$$\left(D_{\mathrm{SV}}\frac{\partial a}{\partial x}\right)_{l_+} - \left(D_{\mathrm{ef}}\frac{\partial C}{\partial x}\right)_{l_-} = (a_- - a_+)\frac{dl}{dt}, \tag{13}$$

where l_- and l_+ represent two points located on two opposite sides of the meniscus: on the liquid phase side, l_-, and on the unwetted side in front of the moving meniscus, l_+ (Fig. 2). Condition (13) expresses the conservation of mass at the moving meniscus and three-phase contact line. In order to deduce the latter boundary condition the following procedure should be undertaken: (i) local coordinates should be introduced in a narrow region close to the moving meniscus; (ii) local transport equations should be integrated over this narrow region; (iii) limits from the filled and empty portions of the capillary should be calculated, which gives exactly condition (13). In mathematical terms condition (13) means limits of outer solutions from both sides on the moving meniscus.

Fig. 3 shows the results of one of the capillary rise experiments using Syntamide-5 surfactant solution in a vertical hydrophobized quartz capillary [1]. The observed time evolution of the imbibition length, $l(t)$, follows $l(t) = K\sqrt{t}$ dependency at the initial stage of the process and deviates from this dependency at the end of the experiment. The value of K determined using the slope of the $l/\sqrt{t}$ dependence corresponds to the advancing contact angle, θ_A, being only a few seconds less than 90°. At such θ_A values the capillary rise would be expected to stop as soon as the liquid reached a height of $\sim 10^{-3}$ cm. However, it does not stop at this height but goes up to a height of 3 cm. The only explanation of this phenomenon is that the spontaneous rise in the hydrophobic capillary is determined by the adsorption of surfactant molecules, which hydrophilize the bare hydrophobic capillary surface in front of the moving meniscus.

At each position, 1, the meniscus curvature must satisfy the following equilibrium condition,

$$\frac{2\varphi(C_m)}{R} = \rho g l(t), \tag{14}$$

where $\varphi(C_m)$ is given by Eq. (6), ρ is the density of the solution, and g is the acceleration of gravity. Since θ_A is close to $\pi/2$, and, hence, C_m is close to C_*, we can safely use Eq. (6). Using the latter equation we can rewrite Eq. (14) as

$$l(t) = \frac{2\alpha}{\rho g R}(C_m - C_*). \tag{15}$$

The last equation can be rewritten as

$$C_m = C_* + Al, \quad A = \frac{\rho g R}{2\alpha}. \tag{16}$$

Equation (16) shows that the case under consideration is governed by the completely different mechanism as compared with the case of the horizontal imbibition, where C_m remains constant in time [1]. In the case of the spontaneous capillary rise $C_m(t)$ must increase as the capillary rise progresses.

The maximum height of the capillary rise, $l_{\max}$, is reached after the concentration on the moving meniscus, C_m, becomes equal to the concentration at the capillary inlet, C_0. After that the process stops. Using Eq. (16), $l_{\max}$ is determined as

$$l_{\max} = \frac{2\alpha(C_0 - C_*)}{\rho g R}; \tag{17}$$

that is, it decreases with the capillary radius increase. The latter shows that the experimental observation presented in Fig. 3 corresponds to $l(t) < l_{\max}$, that is, the initial and intermediate stages of the capillary rise. Below, using Eqs. (9), (10), boundary conditions, (11)–(13), and Eq. (16), we show that $l(t)$ dependency on time can be calculated and it is proportional to square root of time at the initial stage of the process (see Appendix A for details).

The solution in Appendix A shows that at the initial stage of the capillary rise, $l(t)$ develops as

$$l(t) = K\sqrt{t}, \quad K = l_{\max}\sqrt{\frac{2\kappa}{\omega}}, \tag{18}$$

where κ and ω are defined in Appendix A. The latter dependency agrees with experimental observations in [1] at the initial stage of the capillary rise (see Fig. 3). At the final stage of the capillary rise $l(t)$ levels off as

$$l(t) = l_{\max}\left(1 - \frac{\omega + 1}{\kappa t}\right). \tag{19}$$

According to Eq. (17) and Fig. 1, $l_{\max}^{\exp} \sim 35$ mm in the experiment presented in Fig. 3. The experimental value of $K^{\exp}$ in Eq. (18), calculated according to Fig. 3, is $K^{\exp} \sim 5 \times 10^{-3}$ cm/s$^{1/2}$. In experiments presented in Fig. 3, $\omega \sim 1$. The comparison of the latter estimations gives $\kappa \sim 10^{-5}$ s^{-1}, which coincide with the value calculated according to Eq. (A.11), if we assume that $F_{\mathrm{SV}} \ll F_{\mathrm{SL}}$, $D \sim 10^{-5}$ cm^2/ s, and use the estimate $G_{\mathrm{SL}} \sim 10^{-5}$ cm [1] and the value of α is taken directly from Fig. 1.

3. Conclusion

It has been found earlier [1] that aqueous surfactant solutions spontaneously rise in vertical hydrophobized quartz capillaries. A theory of this phenomenon is presented, which connects this phenomenon with the adsorption of surfactant molecules in front of the moving meniscus on a bare hydrophobic interface. The developed theory predictions are in agreement with experimental data [1].

Acknowledgments

The author expresses his gratitude to Professor M.G. Velarde and Dr. S. Kosvintsev for discussions. This research was supported by the Royal Society, UK, as a joint project with Spain, Grant 15544.

Appendix A

To simplify a mathematical treatment of the problem we neglect below the diffusion of surfactant molecules in front of the moving meniscus and only the adsorption in front of the moving meniscus is taken into account. Under this simplification the process of the capillary rise in a hydrophobic capillary is governed by Eq. (9) with boundary conditions (11)–(13).

The concentration of surfactant molecules changes considerably only in close proximity to the moving meniscus. That means the surfactant concentration differs from the concentration at the capillary inlet, C_0, in a narrow region between $l(t) - \delta(t)$ and $l(t)$, where $\delta(t)$ to be determined. At the boundary $l(t) - \delta(t)$ the concentration is equal to the concentration at the capillary inlet, C_0, and the derivative of the concentration at this point is zero (a smooth transition).

Let us introduce for convenience a new unknown function, $Z = C_0 - C$, which satisfies the following equation and boundary conditions:

$$(1 + F_{\mathrm{SL}})\frac{\partial Z}{\partial t} = D_{\mathrm{ef}}\frac{\partial^2 Z}{\partial x^2} - \frac{dl}{dt}\frac{\partial Z}{\partial x}, \quad 0 < x < l(t). \tag{A.1}$$

The boundary condition (13) takes the following form using Eq. (16):

$$D_{\mathrm{ef}}\left(\frac{\partial Z}{\partial x}\right)_{x=l} = (F_{\mathrm{SL}} - F_{\mathrm{SV}})(C_* + Al)\frac{dl}{dt}. \tag{A.2}$$

Other boundary conditions are

$$Z(l - \delta) = 0, \qquad Z(l) = C_0 - C_* - Al, \tag{A.3}$$

$$\left(\frac{\partial Z}{\partial x}\right)_{x=l-\delta} = 0. \tag{A.4}$$

Integration of Eq. (A.1) after simple manipulations using boundary conditions (A.3) and (A.4) results in

$$\frac{d}{dt}\int_{l-\delta}^{l} Z\,dx = \frac{D_{\mathrm{ef}}}{1 + F_{\mathrm{SL}}}\left(\frac{\partial Z}{\partial x}\right)_{x=l} + \frac{F_{\mathrm{SL}}}{1 + F_{\mathrm{SL}}}(C_0 - C_* - Al)\frac{dl}{dt}. \tag{A.5}$$

Below we find a solution which satisfies the integral balance, Eq. (A.5), and boundary conditions (A.2)–(A.4). The simplest solution, which satisfied boundary conditions (A.3) and (A.4), is

$$Z = (C_0 - C_* - Al)\left(\frac{x - l + \delta}{\delta}\right)^2, \tag{A.6}$$

where both $l(t)$ and $\delta(t)$ dependencies are to be determined. Substitution of the latter expression into the boundary condition (A.2) and Eq. (A.5) gives, after some rearrangements, a system of two ordinary differential equation for determination of two unknown dependencies, $l(t)$ and $\delta(t)$,

$$\frac{d}{dt}\big[(C_0 - C_* - Al)\delta\big] = \frac{6D_{\text{ef}}}{1 + F_{\text{SL}}}\frac{(C_0 - C_* - Al)}{\delta} + \frac{3F_{\text{SL}}}{1 + F_{\text{SL}}}(C_0 - C_* - Al)\frac{dl}{dt},$$
$$\frac{dl}{dt} = \frac{2D_{\text{ef}}}{\Delta F}\frac{(C_0 - C_* - Al)}{\delta(C_* + Al)}, \tag{A.7}$$

where $\Delta F = F_{\text{SL}} - F_{\text{SV}} > 0$. The following initial conditions should be satisfied:

$$l(0) = \delta(0) = 0. \tag{A.8}$$

If the first equation in (A.7) is divided by the second equation then an equation for $\delta(l)$ dependence can be obtained. The latter equation can be solved. After that the solution should be substituted into the second equation in system (A.7), which results in the following equation for $l(t)$ determination,

$$\frac{du}{dt} = \lambda\frac{(1-u)^2}{u(\omega + u)(2 + \chi - u)}, \qquad u(0) = 0, \tag{A.9}$$

where

$$u = l/l_{\max}, \qquad l_{\max} = \frac{C_0 - C_*}{A}, \qquad \omega = \frac{C_*}{C_0 - C_*},$$
$$\lambda = \frac{4D_{\text{ef}}(1 + F_{\text{SL}})}{3\Delta F F_{\text{SV}} l_{\max}^2}, \qquad \chi = \frac{2\Delta F C_0}{F_{\text{SV}}(C_0 - C_*)}. \tag{A.10}$$

The latter definitions show that $\chi \gg 1$; hence, Eq. (A.9) can be rewritten as

$$\frac{du}{dt} = \kappa\frac{(1-u)^2}{u(\omega + u)}, \quad \kappa = \frac{\lambda}{\chi} = \frac{D_{\text{ef}}(1 + F_{\text{SL}})(\rho g R)^2}{6\alpha^2\Delta F^2 C_0(C_0 - C_*)},$$
$$u(0) = 0. \tag{A.11}$$

The last equation shows that $1/\kappa$ is a characteristic time scale of the process. It is easy to see that $1/\kappa$ is proportional to $1/R^2$; that is, the duration of the process is longer in thinner capillaries.

Equation (A.11) can be easily solved and the solution is as follows:

$$u + \frac{(\omega + 1)u}{1 - u} + (\omega + 2)\ln(1 - u) = \kappa t. \tag{A.12}$$

If $u \ll 1$ (initial stage of the process), then from Eq. (A.12) we conclude that

$$u = \sqrt{\frac{2\kappa}{\omega}t}. \tag{A.13}$$

At the final stage of the process, $1 - u \ll 1$, Eq. (A.12) gives

$$u = 1 - \frac{\omega + 1}{\kappa t}. \tag{A.14}$$

Appendix B. Nomenclature

Roman

A	$= \rho g R/(2\alpha)$
a	$(= 2\Gamma/R)$, adsorption
C	concentration
D	diffusion coefficient
F	$= 2G/R$
G	adsorption constant (in a linear law)
g	gravity acceleration
K	proportionality coefficient in $l(t) = K\sqrt{t}$
k	Boltzmann constant
l	length of the capillary filled with liquid
r	radial coordinate
R	capillary radius
T	absolute temperature in K
t	time
v	velocity of the moving meniscus
x	upward vertical coordinate
Z	$= C_0 - C$ (see Appendix A)

Greek

α	see Eq. (6)
Γ	surface concentration
δ	size of a region close to the moving meniscus, where concentration considerably changes
γ	interfacial tension
η	dynamic viscosity
Φ	interaction energy in kT units
θ	contact angle
κ	$1/\kappa$ is the time scale of the capillary rise (see Appendix A (after Eq. (A.9))
λ	see Appendix A (after Eq. (A.9))
ρ	density
τ	time scale on diffusion relaxation in a capillary cross section
φ	$= \gamma\cos\theta_A$
Φ	interaction energy in kT units
χ	see Appendix A (after Eq. (A.9))
ω	see Appendix A (after Eq. (A.9))

Subscripts

A	advancing
ef	effective
m	meniscus
max	maximum height
SL	solid–liquid interface
SV	solid–vapor interface

0 capillary inlet
$+$ in front of the moving meniscus
$-$ behind the moving meniscus
$*$ corresponding to $\pi/2$ contact angle

Superscripts

0 bare hydrophobic interface
∞ covered all hydrophobic sites available for the surfactant

References

[1] N.V. Churaev, G.A. Martynov, V.M. Starov, Z.M. Zorin, Colloid Polym. Sci. 259 (1981) 747.
[2] P.P. Zolotarev, V.M. Starov, N.V. Churaev, Colloid J. 38 (1976) 895.
[3] V.M. Starov, S.R. Kosvintsev, M.G. Velarde, J. Colloid Interface Sci. 227 (2000) 185.
[4] E.W. Washburn, Phys. Rev. 17 (1921) 273.
[5] D. Qu, R. Suter, S. Garoff, Langmuir 18 (2002) 1649.