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Penetration of surfactant solutions into hydrophobic capillaries

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The initial rise velocity of surfactant solutions in hydrophobic capillaries is independent of time (F. Tiberg, B. Zhmud, K. Hallstensson and M. von Bahr, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5189). By analogy with the hydrodynamics of an overflowing cylinder, we present a steady-state solution for capillary penetration in which the velocity is determined by the adsorption kinetics at the air–water interface. Good agreement between the model predictions and experimental data of Tiberg and coworkers is obtained for the non-ionic surfactant $C_{10}E_6$ under the assumption of diffusion-controlled adsorption. The longer chain homologue, $C_{14}E_6$, shows evidence of kinetic barriers to adsorption.

Introduction

In 2000, Tiberg and co-workers published a paper describing the dynamics of capillary rise of solutions of the non-ionic surfactants, hexaethyleneglycol decyl ether ($C_{10}E_6$) and hexaethyleneglycol tetradecyl ether ($C_{14}E_6$), in hydrophobic capillaries.[1] An interesting feature of this paper is that the initial rise $z(t)$ was linear in t rather than following the $t^{0.5}$ scaling expected from the Lucas–Washburn equation for capillary rise of pure liquids.[2,3] Tiberg and coworkers developed a detailed theoretical model for the experimental observation in which the constant rise velocity was rationalised in terms of the transfer rate of surfactant at the three-phase contact line (tpc). As z increased, $z(t)$ reverted to a $t^{0.5}$ scaling, which Tiberg interpreted as indicative of diffusion-limited adsorption arising from depletion of surfactant near the advancing liquid front.

In this paper, we seek a steady-state solution for the initial linear portion of the capillary rise. We show that such a solution exists and that it can explain the experimental results of Tiberg *et al.* The rate of rise is limited by adsorption of surfactant to the air–water interface. As this is a steady-state solution, no depletion of surfactant at the advancing liquid front occurs with time. The origin of the breakdown in the linear rise velocity at longer times is explored.

Theory

We seek a steady-state solution to the velocity of rise, $V = dz(t)/dt$, of a surfactant solution in a hydrophobic capillary (*i.e.* a capillary for which the advancing contact angle of pure water is $>90°$) under the following conditions:

(i) Gravity may be neglected;
(ii) Viscous dissipation may be neglected;
(iii) Inertia may be neglected;
(iv) There is fully developed parabolic flow in the capillary sufficiently far away from the free liquid surface;
(v) Adsorption of surfactant at the air–water interface is diffusion-controlled;
(vi) Transfer of surfactant across the tpc is fast;
(vii) The solution is below the critical micelle concentration;
(viii) Adsorption at the liquid–vapour and solid–liquid interfaces may be described by the Langmuir isotherm.

Assumptions (i)–(iv) are necessary to obtain a steady-state solution. Assumptions (v)–(vii) allow us to neglect surfactant adsorption kinetics, the difference in diffusion coefficients of monomers and micelles, and micellar break-down processes. Assumption (viii) is the simplest adsorption isotherm for non-ionic surfactants. A detailed discussion of these assumptions and the consequences of their breakdown is provided later in this paper.

The typical internal radius of the capillaries in the Tiberg experiment was $R_0 = 1 \times 10^{-4}$ m. Borosilicate glass capillaries were rendered hydrophobic by reaction with dimethyloctylchlorosilane. The contact angle of pure water, $\theta^0 = 110°$, so in the absence of surfactant, water is depressed in the hydrophobic capillaries. The surfactant concentration used was in the range 0.5–10 mM. Depending on the nature and concentration of the surfactant, the rise velocity, V, in the linear regime ranged from <0.1–40 mm s^{-1}. For the purpose of estimating the magnitude of the dimensionless numbers that characterise the fluid dynamics, we take $V = 2.4 \times 10^{-3}$ m s^{-1} (the value for 1 mM $C_{10}E_8$), viscosity $\mu = 1$ mPa s, density $\rho = 10^3$ kg m^{-3} and temperature $T = 293$ K. For the dynamic surface tension, σ_{lv}, of the solution we take a value $\sigma_{lv} = 0.05$ N m^{-1} intermediate between the equilibrium surface tension and that of pure water, $\sigma^0_{lv} = 0.072$ N m^{-1}. For the diffusion coefficient of the monomeric surfactant, we assume a value of $D = 4 \times 10^{-10}$ m^2 s^{-1}, which lies within the range of those quoted for $C_{10}E_6$ in the literature.

We will work in a frame of reference in which a capillary with internal radius R_0 is plunging into a solution at a velocity V exactly equal to the capillary rise velocity (See Fig. 1A).[4]

We will show that the free surface (the meniscus) is approximately plane and define the height of the free surface at $r = 0$ to be at $z = 0$. At the free surface, the velocity $v_s(r)$ has radial component v_r and axial component $v_z = 0$. The fluid in contact with the wall ($r = R_0$) has a velocity $-V$ (assuming a no-slip boundary condition) and radial velocity $v_r = 0$. Sufficiently far beneath the free surface, the fluid has a parabolic flow profile

$$v_z(r) = V\left(1 - 2\frac{r^2}{R_0^2}\right) \qquad (1)$$

In the centre of the capillary ($r = 0$) the fluid is rising with velocity $+V$, while at $r = R/\sqrt{2}$, there is a stagnation cylinder where $v = 0$. We will assume that this parabolic flow persists up to a small distance l_h from the free surface.

We now draw an analogy with the hydrodynamics of the overflowing cylinder (OFC), which is an experimental platform

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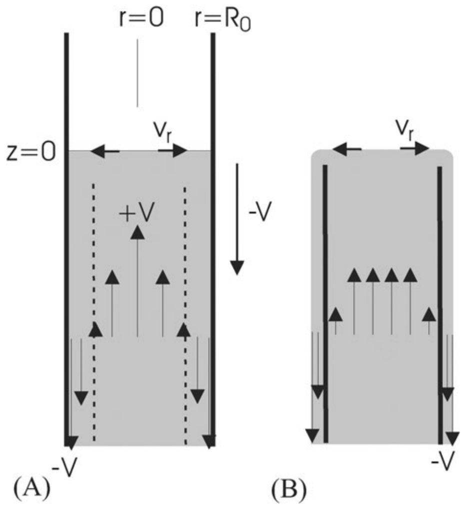

Fig. 1 (A) Flow profile in hydrophobic capillary in the moving frame of reference. The dashed lines show the stagnation cylinder where the flow velocity is zero. (B) Flow profile in an overflowing cylinder in the stationary frame.

with well-defined hydrodynamics for studying expanding liquid interfaces under steady-state conditions (see Fig. 1B).[5–7] The liquid flows up the inner cylinder, overflows the weir and then flows down the outside wall. The free surface of the OFC is planar, except in the immediate vicinity of the weir. In both the capillary and the OFC, there is a stagnation point at (0,0) and radial flow on the free surface. The analogy with the hydrodynamics of the capillary rise (Fig. 1A) and the OFC (Fig. 1B) is clearer if one places a hypothetical solid cylinder within the capillary at a distance $r = R/\sqrt{2}$, terminating at $z = -l_h$. This cylinder will have no effect on the hydrodynamics of the capillary, since the flow velocity is zero at this radius. The flow is therefore very similar to an OFC in which the wetting film on the outside of the cylinder has a velocity $-V$. The flow profile within the capillary differs from that in an OFC (which approximates to plug flow), but it is known that the surface properties of the OFC are insensitive to the bulk flow pattern (*e.g.*, the radial surface velocity is independent of flow rate or cylinder diameter). We will therefore seek a steady-state solution to the capillary rise problem in which the surface velocity has the same form as in the OFC,[6] *i.e.* $v_r \propto r$, except in the immediate vicinity of the capillary wall (where $v_r = 0$).

The surface of the OFC is characterised by a constant dilational strain rate $s = r^{-1}\partial(rv_r)/\partial r$. The radial surface velocity is

$$v_s(r) = sr/2 \tag{2}$$

Hydrodynamics at the solid/liquid/fluid contact has been analysed by Huh and Scriven[8] within a creeping flow model. For a contact angle of 90°, they find

$$v_s(r \to R_0) = 2V/\pi. \tag{3}$$

However, as the authors note,[8] this flow field is multivalued at the tpc and the dissipation diverges. For the present, we will let the ratio of velocities of the fluid surface and the wall at the tpc, $sR_0/2V$, be κ, where κ is a constant of order unity that will be determined by the detailed flow profile in the vicinity of the tpc.

For the typical parameters of the capillary rise experiment, s is of the order of $10^2\ \mathrm{s}^{-1}$. The hydrodynamic boundary layer at the surface has a thickness $\sqrt{(\mu/\rho s)} \sim 0.1$ mm, which gives us an estimate of l_h.[6] The diffusion layer thickness at the free surface, $l_d \sim \sqrt{(D/s)} \sim 3\ \mu\mathrm{m} \ll l_h$. Mass transport of the surfactant is thus only significant in a region sufficiently close to the surface that $v = v_s$.

The depletion length, l_w, at the wall is the depth of solution that contains enough surfactant to saturate the solid–liquid interface: $l_w = \Gamma_{sl}{}^{eq}/c_b = 1$–$10\ \mu\mathrm{m}$. Since $l_w \ll R_0$, adsorption at the walls can only significantly reduce the bulk concentration very near to the walls. The upward flow of solution in the centre of the capillary continually brings fresh surfactant to the liquid front. Consequently, depletion of the bulk surfactant can play no role in our model, which is a major difference between the model presented here and that of Tiberg *et al*. Other origins for the breakdown in the linear behaviour at large z must therefore be sought.

The mass transport equations can readily be solved within the hydrodynamic boundary layer to obtain a relationship between the strain rate, the concentration gradient and the surface excess, Γ_{lv} at the liquid–vapour interface:[6]

$$\Gamma_{lv} = \sqrt{\frac{2D}{\pi s}}(c_b - c_s) \tag{4}$$

where c_b is the bulk concentration and c_s is the subsurface concentration. Mass balance at the tpc requires that

$$\Gamma_{lv}(R_0)v_s(R_0) = \Gamma_{sl}(z = 0)V. \tag{5}$$

Substituting for $v_s(R_0)$ from eqn. (2) and for Γ_{lv} from eqn. (4) yields

$$\Gamma_{sl}(z = 0) = \frac{(c_b - c_s)R_0}{V}\sqrt{\frac{Ds}{2\pi}}. \tag{6}$$

Substituting for s then gives

$$\Gamma_{sl}(z = 0) = (c_b - c_s)\sqrt{\frac{DR_0\kappa}{\pi V}}. \tag{7}$$

To determine Γ_{sl}, we turn first to Young's equation for the equilibrium contact angle, θ, in terms of the interfacial tensions, σ:

$$\sigma_{lv}\cos\theta = \sigma_{sv} - \sigma_{sl}. \tag{8}$$

For a hydrophobic capillary in pure water, $\cos\theta^0 < 0$ and hence $\sigma^0_{sv} < \sigma^0_{sl}$, where the superscript '0' indicates pure water.

The equation of Young and Laplace gives the pressure differential, ΔP, across the meniscus:

$$\Delta P = \frac{2\sigma_{lv}\cos\theta}{R_0} = \frac{2(\sigma_{sv} - \sigma_{sl})}{R_0}. \tag{9}$$

The liquid will rise up the capillary if $\Delta P > 0$ and be depressed if $\Delta P < 0$. (We note the one difference between the model of Fig. 1A and the experiment of Tiberg, namely that in the capillary rise experiment the Laplace pressure must also support the weight of the column of water of height $z(t)$. This factor may be neglected in the early stage of capillary rise, see later.) In the absence of dissipation, only an infinitesimal pressure is required to cause the liquid to rise up the capillary. Therefore capillary rise will occur as soon as $\cos\theta > 0$, *i.e.* when $\theta < 90°$. This deduction is the basis for our assumption that the surface is approximately plane. (Since the capillary number, $Ca = \mu V/\sigma_{lv} \ll 1$, we can assume that the local equilibrium and dynamic contact angles are approximately equal.)

Note that the change in sign of ΔP has nothing to do with σ_{lv} but is determined solely by $\sigma_{sv} - \sigma_{sl}$ and hence by the amount of surfactant adsorbed at the solid–liquid interface. Assuming a Langmuir isotherm, the dependence of σ_{sl} on Γ_{sl} is given by

$$\sigma_{sl} = \sigma^0_{sl} + RT\Gamma^\infty_{sl}\ln\left(1 - \frac{\Gamma_{sl}}{\Gamma^\infty_{sl}}\right) \tag{10}$$

where R is the gas constant and Γ^∞_{sl} is the limiting value of the surface excess at infinite chemical potential (which is larger than the maximum value of Γ^{eq}_{sl} reached at the critical micelle concentration).

The condition $\cos\theta = 0$ (*i.e.* $\theta = 90°$) together with eqn. (8) gives

$$\ln\left(1 - \frac{\Gamma_{sl}}{\Gamma^\infty_{sl}}\right) = -\frac{\sigma^0_{sl} - \sigma_{sv}}{\Gamma^\infty_{sl}RT} = \frac{\sigma^0_{lv}\cos\theta^0}{\Gamma^\infty_{sl}RT}, \tag{11}$$

on the assumption that $\sigma_{sv} = \sigma_{sv}^0$ (*i.e.* no adsorption of surfactant occurs at the capillary surface ahead of the advancing tpc). Rearranging eqn. (11) yields an expression for Γ_{sl}:

$$\Gamma_{sl}^{\infty} = \Gamma_{sl}^{\infty}\left(1 - e^{\sigma_{lv}^0 \cos\theta^0/\Gamma_{sl}^{\infty} RT}\right). \qquad (12)$$

Most surfaces exhibit contact angle hysteresis, *i.e.* the advancing and receding contact angles are different. For the capillary rise problem, it is the advancing contact angle that is important and that should appear in eqn. (12). The contact angle of pure water in the capillary, $\cos\theta^0$, is most readily determined from the capillary depression.

Substituting the value of Γ_{sl} from eqn. (12) into eqn. (7) gives the final expression the capillary rise velocity, V:

$$V = \frac{(c_b - c_s)^2 D R_0 \kappa}{\pi \Gamma_{sl}^{\infty 2}\left(1 - e^{\sigma_{lv}^0 \cos\theta^0/\Gamma_{sl}^{\infty} RT}\right)^2}. \qquad (13)$$

Comparison with experiment

Before making a quantitative comparison with the experimental data, we make a few observations. For the hydrophobic capillaries employed, the initial surface tension difference $\sigma_{sl}^0 - \sigma_{sv} \sim 24$ mN m^{-1}. Within the Langmuir model, Γ_{sl} must reach 90% of Γ_{sl}^{∞} before this difference is reduced to zero. The result is that the velocity is relatively insensitive to the exponential term in eqn. (13), but very sensitive to the value of Γ_{sl}^{∞}. As $\cos\theta^0 \rightarrow 0$, the exponential term $\rightarrow 1$ and the velocity grows rapidly. Consequently, the predicted velocity is sensitive to overestimation of θ^0 as a result of, for example, roughness or contact line pinning. (V does not actually diverge as $\cos\theta^0 \rightarrow 0$, since we have neglected viscous dissipation, which will result in a return to Lucas–Washburn kinetics at high velocities.)

Fig. 2 reproduces data from the Tiberg experiment, showing the linear dependence of z on t for the non-ionic surfactants $C_{10}E_6$ and $C_{14}E_6$ at various bulk concentrations.

The critical micelle concentrations are 10^{-3} M for $C_{10}E_6$ (Fig. 2A) and 10^{-5} M for $C_{14}E_6$ (Fig. 2B). The only data in the Tiberg paper for a surfactant below the cmc are for $C_{10}E_6$ at 1 mM (open circles in Fig 2A). For $C_{10}E_6$, the maximum surface excess at a hydrophobic solid surface has been measured to be 2.8×10^{-6} mol m^{-2}, which we take as a reasonable estimate for Γ_{sl}^{∞}.[9] At the strain rate, $s = 50$ s^{-1} (Fig. 2A), the surface of a 1-mM surfactant solution is far from equilibrium.[10] Penfold *et al.* report[11] an equilibrium value of $c_s = c_b = 0.1$ mM for a surface excess of 2.3×10^{-6} mol m^{-2}, which is a reasonable estimate for Γ_{lv}. Substituting the parameters given above into eqn. (13) gives a value of $V = 1.4\ \kappa$ mm s^{-1}. The Huh and Scriven value of $\kappa = 2/\pi$ gives $V = 0.9$ mm s^{-1}, which is somewhat lower than the experimental value of 2.4 mm s^{-1}. We note, however, that since Γ_{sl}^{∞} and Γ_{lv}^{∞} are of similar magnitude and Γ_{lv} cannot exceed Γ_{lv}^{∞}, a value of κ (= Γ_{sl}/Γ_{lv}, eqn. (5)) significantly less than unity is inconsistent with mass balance at the tpc. A value of $\kappa = 1$ gives better agreement with experiment.

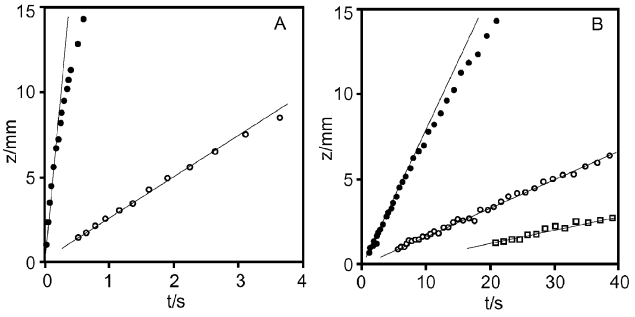

Fig. 2 Rise height as a function of time for (A) $C_{10}E_6$ and (B) $C_{14}E_6$. Bulk concentration is (●) 10 mM (○) 1 mM (□) 0.5 mM. (Redrawn from ref. 1).

Under conditions where $c_b \gg c_s$, eqn. (13) predicts that V should scale as the square of the bulk concentration, c_b. For 10 mM $C_{10}E_6$, V was found experimentally to be about 20 times larger than for 1 mM. With a dilational strain rate, $s \sim 800$ s^{-1}, the liquid–vapour interface will be far from equilibrium even at 10 mM bulk concentration. At this concentration, most of the surfactant is present as micelles. Einaga and coworkers have studied micelles of $C_{10}E_6$ and $C_{14}E_6$ as a function of temperature and concentration.[12,13] These surfactants form rods or worm-like micelles the length of which increases with concentration, temperature and chain length of the hydrophobic tail. They did not study $C_{10}E_6$ under quite the conditions of the experiment, but by extrapolation from their data[11] one can infer that the aggregation number, N, at 10 mM concentration is around 50 and that the micelles have an aspect ratio (length/diameter) of 3. Early work by Corkill and Walker[14] yielded a micellar diffusion coefficient $D_{mic} = 7.6 \times 10^{-11}$ m^2 s^{-1}, which is in line with Einaga's more recent study. (For spherical micelles, $D \propto N^{-1/3}$, so a factor of five difference between the monomer and micellar diffusion coefficients is reasonable). Consequently, $c_b{}^2 D$ is about 20 times higher for 10 mM $C_{10}E_6$ than for 1 mM $C_{10}E_6$, predicting a velocity ratio in good agreement with experiment. This supralinear variation of V with c_b helps to support our model. Micelles of the related surfactant, $C_{14}E_8$, adsorb to the surface of a liquid jet at a diffusion-controlled rate:[15] diffusion-controlled adsorption of the shorter-chain surfactant $C_{10}E_6$ in micellar solutions is therefore not too surprising.

For $C_{14}E_6$ at 10 mM, the rise velocity for $C_{14}E_6$ was 50 times slower than for $C_{10}E_6$ at the same concentration. Γ_{sl}^{∞} does not differ greatly between the two surfactants, since it is largely controlled by the size of the E_6 head group: Kumar *et al.* report a maximum surface excess of 3.2×10^{-6} mol m^{-2} at the hydrophobic solid–water interface.[9] However, $C_{14}E_6$ forms much longer micelles than $C_{10}E_6$. At 10 mM concentration, $N = 430$ and the aspect ratio is 35.[13] At the lower concentration of 1 mM, $N \sim 230$ and the aspect ratio is $\sim$20. At both concentrations, $D = 1.5 \times 10^{-11}$ m^2 s^{-1}. Eqn. (13) with $\kappa = 1$ predicts $V = 5$ mm s^{-1} for 10 mM $C_{14}E_8$, which is six times larger than the experimental value of $V = 0.8$ mm s^{-1}. Furthermore, one would still expect a quadratic scaling of V with c_b for diffusion-controlled adsorption in micellar solutions. However, the concentration dependence of V for $C_{14}E_6$ was much closer to linear than quadratic (*e.g.* $V = 0.17$ mm s^{-1} for 1 mM and 0.07 mm s^{-1} for 0.5 mM, Fig. 2B). These observations are indicative of an activation-controlled adsorption mechanism in which the flux to the surface is a linear function of the local concentration. The kinetic barrier could be associated either with direct adsorption of micelles to the air–water interface or with breakdown of the micelles into monomers prior to adsorption. In terms of eqn. (13), an activation barrier to adsorption leads to a build up of surfactant beneath the surface and a reduction in the value of the $(c_b - c_s)^2$ term in the numerator.

Analysis of assumptions

In this section, we analyse the assumptions used in the model and consider how the breakdown of these assumptions can lead to the observed deviations in $z(t)$ from linear behaviour at larger z.

(i) Neglect of gravity

The effect of gravity is to decrease the contact angle, θ, at the advancing liquid front since a capillary pressure is required to balance the hydrostatic pressure of the column of liquid. A lower contact angle implies a larger value of $\mathit{\Gamma}_{\mathrm{sl}}$. Since surfactant is supplied by diffusion to the air–water interface, the strain rate will be lower (eqn. (4)) and so will the rise velocity. Balancing the capillary force against the gravitational force gives $\cos\theta = R_0\rho gz/2\sigma$ (where g is the acceleration due to gravity). Gravity may be neglected when z is much less than a length, $l_g = 2\sigma_{\mathrm{lv}}/\rho gR_0 \sim 10$ cm for $R_0 = 0.1$ mm. Work against gravity is a major reason for the slow down in the capillary rise velocity at longer times. Experiments conducted with horizontal capillaries would eliminate this effect.

(ii) Neglect of viscosity

The relative importance of viscous and capillary forces is given by the capillary number multiplied by the dimensionless height, z/R_0. In the linear region of the capillary rise, $Ca \sim 10^{-6}$–10^{-3}, and $z/R_0 < 10^2$. Thus for the steady-state solution, viscosity can safely be neglected. With the possible exception of the 10 mM $C_{10}E_6$ solution, the eventual slow down in V is due to gravity, not viscous dissipation. In horizontal capillaries, where gravitational effects are absent, viscous effects would limit the linear regime of capillary penetration.

(iii) Neglect of inertia

The relative importance of inertial to capillary forces is given by the Weber number, $We = \rho V^2R_0/\sigma_{\mathrm{lv}}$. In Tiberg's experiments, $We \sim 10^{-8} - 10^{-4}$. The work done in time Δt by the meniscus is $2\pi a\sigma_{\mathrm{lv}}\cos\theta V\Delta t$, while the work done in accelerating an element of fluid from rest to speed V is $\pi a^2\rho V^3\Delta t/2$. Equating these two expressions gives $\cos\theta = We/4$. The decrease in contact angle due to inertial effects is thus entirely negligible.

(iv) Poiseuille flow

The lead-in length is of the order of $0.12\ ReR_0$,[16] where the Reynolds number $Re = \rho VR_0/\mu$. In the experiments of Tiberg, $Re < 4$ so the lead-in length is of the order of $R_0 = 0.1$ mm. Since the linear part of the capillary rise occurs over a distance of 1 cm, non-Poiseuille flow may be neglected except at the very beginning of the capillary rise.

(v) Surfactant effects

In the limit of fast micelle breakdown, micellar transport can be included by established methods.[17] Kinetic barriers would reduce the rate of adsorption. V would be reduced from its diffusion-controlled value, but a steady-state solution would still be possible giving a linear rise with time. Given the large strain rates achievable in capillary rise experiments, such measurements might provide a useful means of studying adsorption kinetics on short timescales. More complicated adsorption isotherms can readily be incorporated in the model, if the isotherms are known.

(vi) Transport across the three phase contact line

If transport across the tpc were rate-limiting, then V and s would have lower values than those given by eqn. (13), and hence $\mathit{\Gamma}_{\mathrm{lv}}$ would be larger (eqn. (4)). Since $\mathit{\Gamma}_{\mathrm{sl}}$ is still determined by eqn. (12), $\mathit{\Gamma}_{\mathrm{lv}} > \mathit{\Gamma}_{\mathrm{sl}}$. Conservation of mass at the tpc means that $v_s(R_0) < V$ and there is a velocity mismatch at the tpc ($\kappa < 1$). This mismatch is not large, since the maximum values of $\mathit{\Gamma}_{\mathrm{lv}}$ and $\mathit{\Gamma}_{\mathrm{sl}}$ will be similar for a hydrophobic solid and, as we have argued above, $\mathit{\Gamma}_{\mathrm{sl}}$ is approaching its maximum coverage. If transport across the tpc is sufficiently slow compared to the diffusion time, then the free liquid surface will be very close to chemical equilibrium ($c_s \approx c_b$) and surfactant can be supplied to the solid surface at the tpc by diffusion from the bulk. The hydrodynamic model proposed here would then no longer apply.

Conclusion

In this short paper, we have presented a steady-state model for the rate of capillary rise of surfactant solutions in a hydrophobic capillary. The simplifying hydrodynamic assumptions are shown to be valid over the linear part of $z(t)$ observed experimentally. Within the model, there is an unknown hydrodynamic parameter, κ, which represents the ratio of the velocities of the fluid at the free liquid surface and at the wall near the three-phase contact line. For a value of $\kappa = 1$, good agreement is obtained with the data of Tiberg *et al.* for $C_{10}E_6$, while $C_{14}E_6$ shows evidence of kinetic barriers to adsorption.

If the kinetics of transport of surfactant across the three phase contact line are slow, the hydrodynamics are likely to deviate markedly from those described in this paper. Consequently, the steady-state model proposed here for the linear rise velocity and the model of Tiberg *et al.* should not be seen as contradictory, but as alternative models whose range of validity depends on the kinetics at the tpc.

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