Journal of Colloid and Interface Science **227,** 185–190 (2000)
doi:10.1006/jcis.2000.6851, available online at http://www.idealibrary.com on

Spreading of Surfactant Solutions over Hydrophobic Substrates

Victor M. Starov,*[,1] Serguei R. Kosvintsev,†,‡[,2] and Manuel G. Velarde†[,3]

**Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.; †Instituto Pluridisciplinar,*
Universidad Complutense, Paseo Juan XXIII, n.1, 28040, Madrid, Spain; and ‡Department of General Physics,
Perm State University, 15 Bukirev St., 614600, Perm, Russia

Received December 6, 1999; accepted March 15, 2000

The spreading of surfactant solutions over hydrophobic surfaces is considered from both theoretical and experimental points of view. Water droplets do not wet a virgin solid hydrophobic substrate. It is shown that the transfer of surfactant molecules from the water droplet onto the hydrophobic surface changes the wetting characteristics in front of the drop on the three-phase contact line. The surfactant molecules increase the solid–vapor interfacial tension and hydrophilize the initially hydrophobic solid substrate just in front of the spreading drop. This process causes water drops to spread over time. The time of evolution of the spreading of a water droplet is predicted and compared with experimental observations. The assumption that surfactant transfer from the drop surface onto the solid hydrophobic substrate controls the rate of spreading is confirmed by our experimental observations.

Key Words: **surfactant solutions; spreading; hydrophobic surfaces.**

INTRODUCTION

Surfactant adsorption on solid–liquid and liquid–vapor interfaces changes the corresponding interfacial tensions. Liquid motion caused by surface tension gradients on liquid–vapor interfaces (Marangoni effect) is the most investigated process (1). The phenomena produced by the presence of surfactant molecules on a solid–vapor interface have been studied less. In one study (2, 3), the imbibition of surfactant solutions into thin quartz capillaries was investigated. Spreading of surfactant solutions on both hydrophobic and hydrophilic surfaces (4–6) revealed various intriguing phenomena. In the present paper we address the problem of aqueous surfactant solutions spreading over hydrophobic surfaces from both the theoretical and experimental points of view.

THEORY

Let a small water drop be placed on a hydrophobic surface. If the drop is small enough then the effect of gravity can be ignored. Accordingly, the drop radius r has to be smaller than the capillary length, a, and hence, $r \le a = \sqrt{\gamma/\rho g}$, where ρ and γ are the liquid density and liquid–vapor interfacial tension, respectively; g is the gravity acceleration.

Let us assume that in the absence of surfactant the drop forms an equilibrium contact angle above $\pi/2$. If the water contains surfactants then three transfer processes take place from the liquid onto all three interfaces: surfactant adsorption at both (i) the inner liquid–solid interface and (ii) the liquid–vapor interface, and (iii) transfer from the drop onto the solid–vapor interface just in front of the drop. Adsorption processes (i) and (ii) result in a decrease of corresponding interfacial tensions, γ_{sv} and γ. The transfer of surfactant molecules onto the solid–vapor interface in front of the drop results in an increase of a local free energy; however, the total free energy of the system decreases. That is, surfactant molecule transfer (iii) goes via a relatively high potential barrier and, hence, goes considerably slower than adsorption processes (i) and (ii). Hence, they are "fast" processes as compared with the third process.

The transfer of surfactant molecules onto the unwetted (hydrophobic) solid–vapor interface in front of the liquid has been shown (7, 8) to play an important role in the wetting of hydrophobic surfaces.

All three surfactant-transfer processes are favorable to spreading, as they result in both an increase of the spreading power, $\gamma_{\mathrm{sv}} - \gamma - \gamma_{\mathrm{sl}}$, and, hence, a decrease of the contact angle. As it was mentioned above, the transfer of surfactant molecules from the drop onto the solid–vapor interface in front of the drop results in an increase of local surface tension, γ_{sv}. Hence, the slowest process will be the rate-determining step. Let us define the initial contact angle by

$$\cos\theta^0 = \frac{\gamma_{\mathrm{sv}}^0 - \gamma_{\mathrm{sl}}^0}{\gamma^0} \ge \frac{\pi}{2}, \qquad [1]$$

with γ_{sv}^0, γ_{sl}^0, and γ^0 the initial values of solid–vapor, solid–liquid, and liquid–vapor interfaces. The term "initial" means that although the adsorption process on the liquid–vapor and solid–liquid interfaces has been completed (they are fast processes), the solid–vapor interface still has its initial condition as a bare hydrophobic interface without any surfactant adsorption. At this

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[1] To whom correspondence should be addressed. V.M.Starov@lboro.ac.uk.
[2] kosvintsev@psu.ru.
[3] mvelarde@pluri.ucm.es.

0021-9797/00 $35.00

"initial" instant of time a process of slow transfer of surfactant molecules starts from the drop onto the solid–vapor interface. Let $\Gamma_\mathrm{s}(t)$ be the instantaneous value of surfactant adsorption onto the solid surface in front of the liquid drop on the three-phase contact line, and Γ_e be the equilibrium surface density of adsorbed surfactant molecules which would eventually be reached. The driving force of the process is proportional to the difference $\Gamma_\mathrm{s}(t) - \Gamma_\mathrm{e}$. Hence, the surfactant adsorption behavior with time is described by

$$\frac{d\Gamma_\mathrm{s}(t)}{dt} = \alpha[\Gamma_\mathrm{e} - \Gamma_\mathrm{s}(t)], \qquad [2]$$

with the initial condition that

$$\Gamma_\mathrm{s}(0) = 0 \quad \text{at } t = 0, \qquad [3]$$

and $\tau_\mathrm{s} = 1/\alpha$ is the time scale of surfactant transfer from the drop onto the solid–liquid interface at the three-phase contact line. Let us assume that

$$\alpha = \alpha_\mathrm{T}\,\Xi\,\exp\left(\frac{-\Delta E}{kT}\right), \qquad [4]$$

where the prefactor α_T is determined by thermal fluctuations only; ΔE is an energy barrier for surfactant transfer from the liquid drop onto the solid–liquid interface; k and T are Boltzman's constant and absolute temperature, respectively; Ξ is a fraction of the drop liquid–vapor interface covered with surfactant molecules. Obviously the surfactant molecules' position on a hydrophobic interface is "hydrophobic tails down".

We have assumed that transfer of surfactant molecules onto the hydrophobic solid interface takes place only from the liquid–vapor interface. It is difficult to assess the contribution of surfactant molecule transfer along the solid surface from beneath the liquid. However, as will be seen, our experimental data support this assumption (although they do not prove it decisively). The drop surface coverage Ξ will be an increasing function of the bulk surfactant concentration inside the drop, whose maximum is reached close to the critical micelle concentration (CMC). It follows from Eq. [4] that at low surfactant concentrations inside the drop τ_s should decrease with increased concentration, while above the CMC τ_s should level off and reach its lowest value. Both of these effects are observed in our experimental results (compare Fig. 4).

As the drop adopts a position according to the triangle rule, the contact angle, $\theta(t)$, is determined by the relationship

$$\cos\theta(t) = \frac{\gamma_\mathrm{sv}(t) - \gamma_\mathrm{sl}^0}{\gamma^0}, \qquad [5]$$

where $\gamma_\mathrm{sv}(t)$ is the instantaneous solid–vapor interfacial tension at the three-phase contact line. The latter dependency is determined by $\Gamma_\mathrm{s}(t)$. According to Antonov's rule,

$$\gamma_\mathrm{sv}(t) = \gamma_\mathrm{sv}^\infty \frac{\Gamma_\mathrm{s}(t)}{\Gamma^\infty} + \gamma_\mathrm{sv}^0\left(1 - \frac{\Gamma_\mathrm{s}(t)}{\Gamma^\infty}\right), \qquad [6]$$

where $\gamma_\mathrm{sv}^\infty$ is the solid–vapor interfacial tension of the surface completely covered by surfactants, and Γ^∞ is the total number of sites available for adsorption. Hence, the final value of the contact angle can be determined from Eq. [5] as

$$\cos\theta^\infty = \frac{\gamma_\mathrm{sv}^\infty - \gamma_\mathrm{sl}^0}{\gamma^0}. \qquad [7]$$

According to Eq. [6] the solid–vapor interface in front of the spreading drop changes its wettability with time, from highly hydrophobic at initial stage to partially hydrophilic at the final stage.

Substituting Eq. [6] in Eq. [5] yields the instantaneous contact angle,

$$\cos\theta(t) = \cos\theta^0 + \lambda\frac{\Gamma_\mathrm{s}(t)}{\Gamma^\infty}, \qquad [8]$$

where $\cos\theta^0$ is given by Eq. [1], and the positive value of λ is $\lambda = (\gamma_\mathrm{sv}^\infty - \gamma_\mathrm{sv}^0)/\gamma^0$.

Equation [2] with initial condition [3] yields the solution

$$\Gamma_\mathrm{s}(t) = \Gamma_\mathrm{e}(1 - \exp(-\alpha t)). \qquad [9]$$

Substituting Eq. [9] in Eq. [8] gives the final expression for the instantaneous contact angle,

$$\cos\theta(t) = \cos\theta^0 + \lambda\frac{\Gamma_\mathrm{e}}{\Gamma^\infty}(1 - \exp(-\alpha t)). \qquad [10]$$

A simple geometrical consideration (Fig. 1) shows that the radius of the wetted spot, $r(t)$, occupied by the drop can be expressed as

$$r(t) = \left(\frac{6V}{\pi}\right)^{1/3} \frac{1}{\left[\tan\frac{\theta}{2}\left(3 + \tan^2\frac{\theta}{2}\right)\right]^{1/3}}, \qquad [11]$$

where V is the drop volume, which is supposed to remain constant and the contact angle, θ, is given by Eq. [10].

Equations [10] and [11] include two parameters: the dimensionless $\beta = \lambda\Gamma_\mathrm{e}/\Gamma^\infty$ and the parameter α with dimension of inverse of time. It follows from Eq. [10] that $\beta = \cos\theta^\infty - \cos\theta^0 > 0$, where θ^∞ is the contact angle after the spreading

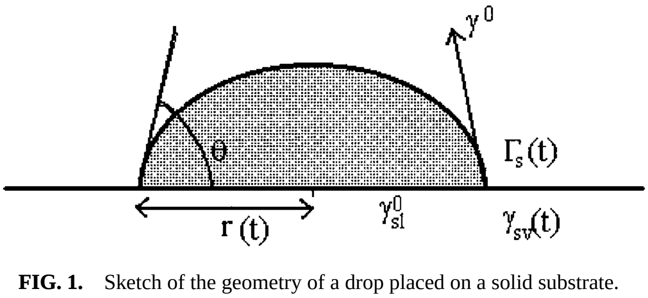

FIG. 1. Sketch of the geometry of a drop placed on a solid substrate.

process is completed. Both values of the contact angle, θ^0 and θ^∞, have been measured and, hence, β can be determined. Only α is used to fit the experimental data.

Let us introduce a dimensionless wetted area, $S(t)$, as

$$S(t) = \frac{r^2(t)}{(6V/\pi)^{2/3}} = \frac{1}{\tan^{2/3}\frac{\theta}{2}\left(3+\tan^2\frac{\theta}{2}\right)^{2/3}} = \frac{1+X}{(1-X)^{1/3}(4+2X)^{2/3}},$$

where $X = \cos\theta$, $(\cos\theta^0 \le X \le \cos\theta^\infty)$, which using Eq. [10] becomes $X = \cos\theta^\infty - \beta e^{-\alpha t}$.

It follows that both $dS(t)/dt$ and $dS(X)/dX$ are always positive, and the second time derivative is

$$\frac{d^2S(t)}{dt^2} = \frac{\alpha^2}{(1-X)(2+X)}(\cos\theta^\infty - X)\frac{dS(X)}{dX} \times [-2X^2 + 3X\cos\theta^\infty - (2-\cos\theta^\infty)] \quad [12]$$

Two different situations are possible: (A) if the second derivative [12] changes sign then the spreading rate can go via a maximum/minimum value, while (B) if the second derivative [12] is always negative then the spreading rate $dS(t)/dt$ decreases with time. Case A corresponds to "high surfactant activity,"

$$\cos\theta^\infty \ge \frac{4}{9}(\sqrt{10}-1) \approx 0.961,$$

while case B corresponds to "a low surfactant activity,"

$$\cos\theta^\infty < \frac{4}{9}(\sqrt{10}-1) \approx 0.961.$$

Using Eq. [7] the latter two conditions can be rewritten as

$$\gamma_{sv}^\infty > 0.961\gamma^0 + \gamma_{sl}^0$$

at "a high surfactant activity," and

$$\gamma_{sv}^\infty < 0.961\gamma^0 + \gamma_{sl}^0$$

at "low surfactant activity."

Under our experimental conditions we have only observed case B and, hence, we seem to have used "low surface activity" surfactants while in Ref. (6) "high surface activity" surfactants were apparently used.

EXPERIMENT

Materials

Two types of substrate were used, a polytetrafluoroethylene (PTFE) film and a polyethylene (PE) wafer. The latter substrate was prepared by crushing granules of the PE composition (softening point is 100°C) between two clean glass plates under an applied pressure of 1 kg/cm^2 at 110°C. Transparent wafers of circular section with radius 1.5 cm and thickness 0.01 cm were used.

The cleaning procedure for PTFE and PE wafers was as follows: the surfaces were rinsed with alcohol and water, then the substrates were soaked in a sulfochromic acid from 30 to 60 min at 50°C. The surfaces then were washed with distilled water and dried with a strong jet of nitrogen. The equilibrium macroscopic contact angles obtained were 105° and 90° for PTFE and PE substrates, respectively (for pure water droplets).

Aqueous solutions of sodium dodecyl sulfate (SDS) from Merck with weight concentration from 0.005% up to 1% (the CMC of the SDS is 0.2%) were used in our spreading experiments.

Monitoring Method

The time evolution of the contact line was monitored by following VCR images of drops. The images were stored using a CCD camera and a recorder at 25 frames/s. The automatic processing of images was carried out using the image-processor Optimas. In the case of spreading over PE the initial contact angle of the drop was less than 90° and the drop was observed from above. The observed wetting area of the drop was monitored and the wetting radius was calculated. For the PTFE substrate we used a side view of the drop and, hence, the wetting radius was determined directly.

Simple mass balance estimations show that time variation of surfactant concentration inside the spreading drops can be neglected in our experiments (though it may become important in experiments of longer duration).

Water adsorption in front of the spreading drops was neglected because of the hydrophobic nature of the substrates used (in contrast to spreading of evaporating drops (9)). In all of our experiments surfactant diffusion in front of the drop was neglected.

RESULTS AND DISCUSSION

According to our observations all the experimental drops were of spherical shape, and no disturbances or instabilities were detected. Immediately after deposition the drops had a contact angle which differs slightly from the equilibrium angle of pure water on the same substrate. After a very short initial time the drops reached a position which is referred to below as the "initial" position. After that, for 1–15 s, depending on the sodium dodecyl sulfate (SDS) concentration, drops remained at the initial position. Then drops started to spread until a final value of the contact angle was reached and the spreading process was completed.

In Fig. 2 the evolution of the spreading radius of a drop over PTFE film at 0.05% SDS concentration is plotted. In Fig. 3 a similar plot is given for 0.1% SDS concentration. In both figures,

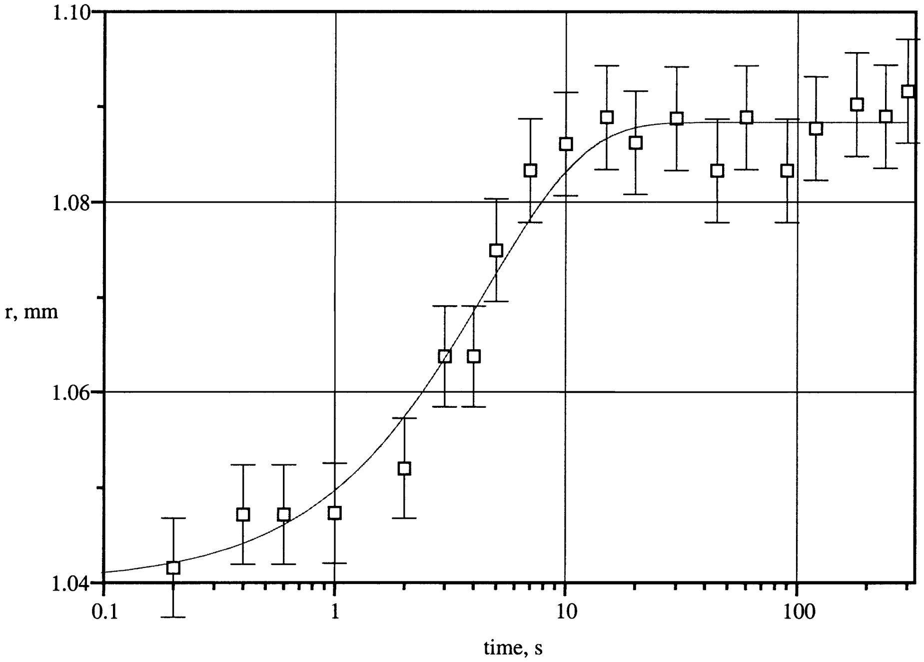

FIG. 2. Time evolution of the spreading of a water drop (aqueous solution $C = 0.05\%$ SDS; 2.5 ± 0.2 μl volume) over a PTFE wafer. Error bars correspond to the error limits of video evaluation of images (pixel size).

the solid lines correspond to the fitting of the experimental data by Eqs. [10] and [11], with $\tau_s = 1/\alpha$ used as a fitting parameter.

Figure 4 shows that qualitatively the τ_s dependency agrees with the theoretical prediction and tends to support our assumption concerning the mechanism of surfactant molecule transfer onto the hydrophobic surface in front of the drop.

Similar results were obtained for the spreading over the polyethylene substrate for concentrations below CMC.

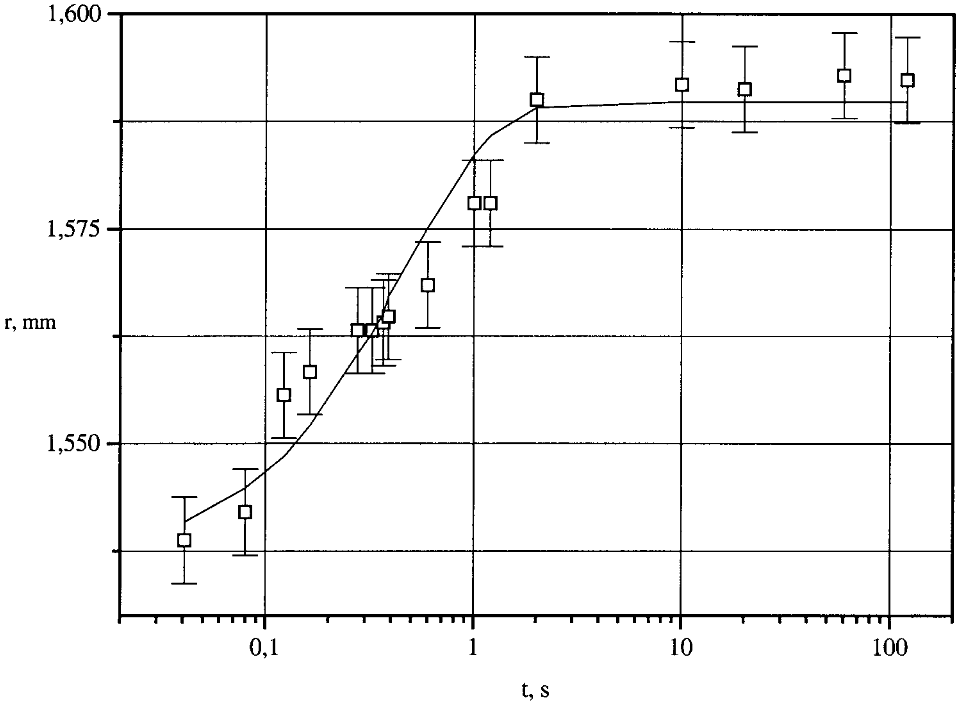

FIG. 3. Time evolution of the spreading of a water drop (aqueous solution $C = 0.1\%$ SDS; 2.5 ± 0.2 μl volume) over a PTFE wafer. Error bars are the same as in Fig. 2.

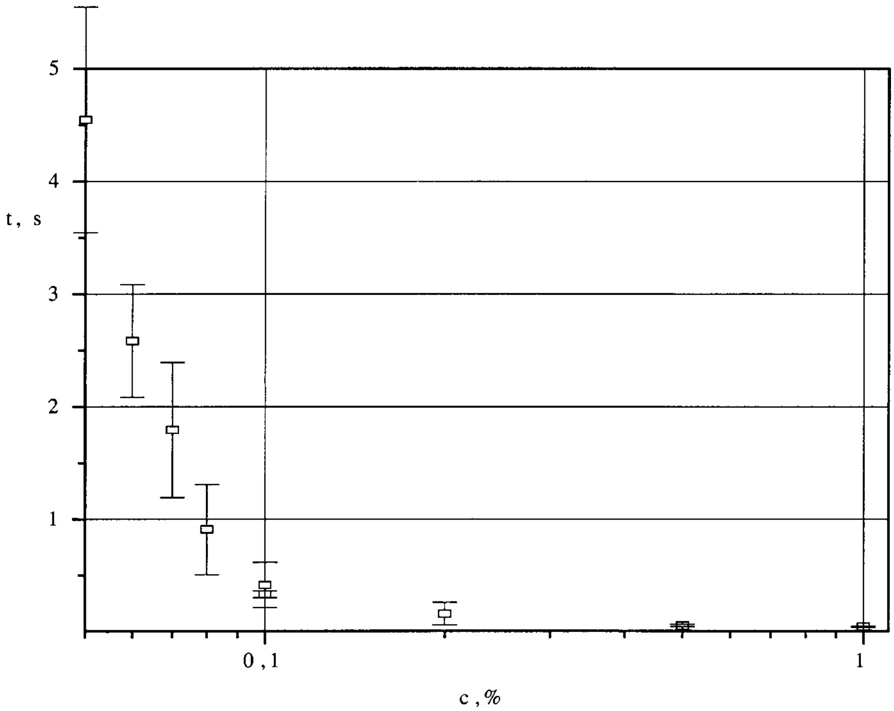

FIG. 4. Fitted dependency of τ_s on surfactant concentration inside the drop (spreading over PTFE wafer). Error bars correspond to the experimental points scattering in different runs; squares are average values.

However, in this case the spreading behavior of drops at concentrations above CMC is drastically different with increasing SDS concentration (Fig. 5). The rate of spreading is increased so much that at 1% concentration the power law with the exponent 0.1 (solid line) fits experimental data reasonably well. This clearly shows a transition to a different mechanism of spreading, which can be understood in the following way. In our previous considerations the influence of the viscous forces was ignored. It

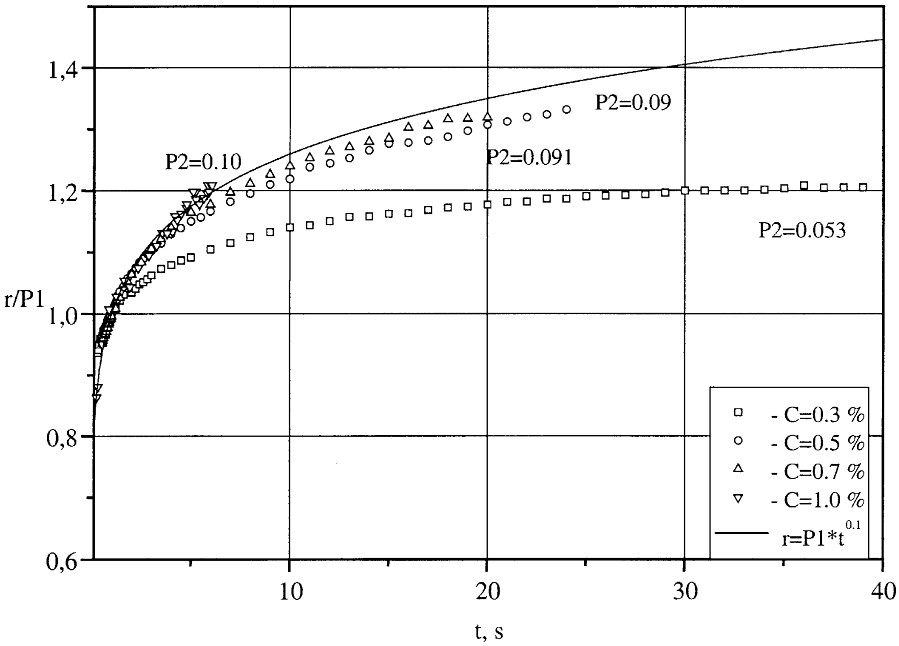

FIG. 5. Spreading of SDS solution over polyethylene substrate, concentration above CMC. Dependency of spreading radius on time ($r/P1$, where $P1$ and $P2$ are fitted parameters in $r = P1t^{P2}$). Only the case $P2 = 0.1$ is shown by a solid line.

was assumed that $\tau_s \gg \tau_{vis}$, where τ_{vis} is a time scale of viscous spreading. In the latter case τ_s decreases so considerably that the mentioned inequality becomes invalid and now rather $\tau_s \sim \tau_{vis}$ becomes valid.

CONCLUSIONS

The spreading of surfactant solutions over hydrophobic surfaces has been considered from both theoretical and experimental points of view. It has been shown that the transfer of surfactant molecules from a water droplet onto a hydrophobic surface changes the wetting characteristics in front of the drop on the three-phase contact line. This leads to an increase of the surface tension of the hydrophobic solid substrate and its hydrophilization. This process causes the spreading of the water droplet. The spreading rate with time has been predicted and compared to our experimental observations. Spreading of aqueous solutions of the sodium dodecyl sulfate on two types of hydrophobic substrates (a PTFE film and a PE wafer) was studied. Droplets do not wet an initially bare solid hydrophobic substrate. The assumption that surfactant transfer goes from the drop surface onto the solid substrate in front of the drop agrees with our observations. Qualitatively the τ_s dependency on surfactant concentration agrees with the theoretical prediction and tends to support our assumption concerning the mechanism of surfactant molecule transfer onto the hydrophobic surface in front of the spreading drops.

LIST OF SYMBOLS

r	radius of drop base
a	capillary length
g	gravity acceleration
t	time
V	drop volume
C	concentration of surfactant
k	Boltzman's constant
T	absolute temperature

Greek

ρ	liquid density
γ	interfacial tension
θ	contact angle
Γ	adsorption
α	determined in Eq. [4]
λ	$=(\gamma_{sv}^{\infty} - \gamma_{sv}^{0})/\gamma^{0}$
β	$=\lambda\Gamma_e/\Gamma^{\infty}$
Ξ	surface fraction (liquid surface)
τ	time scale

Subscripts

s	solid
v	vapor
l	liquid
e	equilibrium
T	thermal
vis	viscous

Superscripts

0	initial value
∞	after complete coverage

ACKNOWLEDGMENTS

The authors acknowledge fruitful discussions with Dr. A. Nikolov and Dr. N. Denkov. S.R.K. expresses his gratitude to the Spanish Ministry of Education and Culture and to the CSIC (Spain) for a postdoctoral fellowship. This work was sponsored by the EU under Network Grant No. FRB FM RX-CT96-10 and by DGIGYT (Spain) under Grant PB 96-599. V.M.S. was supported by the Royal Society (Grant ESEP/JP/JEB/11159).

REFERENCES

1. Starov, V. M., de Ryck, A., and Velarde, M. G., *J. Colloid Interface Sci.* **190,** 104 (1997).
2. Zolotarev, P. P., Starov, V. M., and Churaev, N. V., *Colloid J. (Russ. Acad. Sci. English Transl.)* **38,** 802–807 (1976).
3. Churaev, N., Martynov, G., Starov, V., and Zorin, Z., *Colloid Polym. Sci.* **259,** 747–752 (1981).
4. Starov, V. M., Maslov, A. Yu., and Iskanderyan, G., *Colloid. J. (English Transl.)* **54,** 410 (1993).
5. Cachile, M., Cazabat, A. M., Bardon, S., Valignat, M. P., and Vandenbrouck, F., *Langmuir* **15,** 1515 (1999).
6. Stoebe, T., Lin, Z., Hill, R. M., Ward, M. D., and Davis, H. T., *Langmuir* **12,** 337 (1996); **13,** 7270 (1997); **13,** 7276 (1997).
7. Berezkin, V. V., Derjaguin, B. V., Zorin, Z. M., Frolova, N. V., and Churaev, N. V., *Dokl. Akad. Nauk SSSR* **255,** 109 (1975).
8. Berezkin, V. V., Zorin, Z. M., Iskandeyan, G. A., and Churaev, N. V., *Trans. 7th Int. Congr. Surfactants B* (Moscow) **2,** 329 (1978).
9. Reyes, R., and Wayner, P., *J. Heat Transfer* **118,** 822–830 (1996).