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Kinetics of wetting and spreading by aqueous surfactant solutions

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ABSTRACT

Interest in wetting dynamics processes has immensely increased during the past 10–15 years. In many industrial and medical applications, some strategies to control drop spreading on solid surfaces are being developed. One possibility is that a surfactant, a surface-active polymer, a polyelectrolyte or their mixture are added to a liquid (usually water). The main idea of the paper is to give an overview on some dynamic wetting and spreading phenomena in the presence of surfactants in the case of smooth or porous substrates, which can be either moderately or highly hydrophobic surfaces based on the literature data and the authors own investigations. Instability problems associated with spreading over dry or pre-wetted hydrophilic surfaces as well as over thin aqueous layers are briefly discussed. Toward a better understanding of the superspreading phenomenon, unusual wetting properties of trisiloxanes on hydrophobic surfaces are also discussed.

Contents

1. Introduction

Both wetting and de-wetting play an important role in many natural and technological processes. In many applications, surface wettability is macroscopically described by the equilibrium or, more frequently, by a static advancing contact angle. This description is mostly used to describe wetting properties of liquids on smooth, chemically homogeneous surfaces and pure liquids excluding adsorption and evaporation effects. However, such kind of approach is not sufficient for description of a host of technological processes as the kinetic aspects in the presence of surfactants should be considered. In a number of applications dynamic wetting and de-wetting processes are of crucial importance. The spreading velocity is often an important criterion based on which the efficiency of surface-active substances (surfactants) can be estimated.

The dynamic behaviour of a pure liquid on an ideal solid surface can often be successfully described by the equilibrium contact angle (or rather static advancing/receding contact angles), the dynamic (time-dependent) contact angle as well as the spreading velocity. Such approach [1,2] leads to the spreading force $\gamma_{lv}(\cos\theta_0 - \cos\theta(t))$, where θ_0 is the static advancing or receding contact angle. Note, in the case of spreading θ_0 should be selected as static advancing contact angle, while in the case of de-wetting θ_0 should be selected as static receding contact angle. Work is necessary to expanding the solid–liquid interface, and energy dissipates due to viscous shear in the liquid. The molecular-kinetic theory [3] assumes, however, particular displacements due to the surface diffusion at the three-phase contact line as a possible reason for the spreading force. It completely neglects viscous dissipation in the liquid and, hence, is suitable for describing of very slow velocities of spreading. Its application to predict the

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spreading velocity is rather problematic since the molecular parameters such as the density of the adsorption centres and the distance between them on real surfaces is unknown and generally inaccessible to experiments.

In general, when a liquid drop is placed on a solid surface, either it spreads over the surface, i.e. it completely wets it (Fig. 1a), or it forms a finite contact angle with the surface. If the contact angle is between 0 and 90° the situation is refereed to as partial wetting (Fig. 1b). However, if the contact angle is larger than 90°, the liquid does not wet the surface and the situation is refereed to as non-wetting (Fig. 1c). A more detailed description of advancing, receding, equilibrium and hysteresis contact angles as well as problems of experimental and theoretical verification of equilibrium contact angles have been recently provided [4,7].

A reduction of water surface tension by adsorption of surfactant molecules on a water-vapour interface and adsorption of surfactant molecules on solid–liquid and solid–vapour interfaces alters a non-wetting behaviour of aqueous solutions on hydrophobic substrates into a partial or even complete wetting behaviour. Surfactants have been used for a long time and their influence on surface wettability is well known and widely used. However, employing surfactants to enhance spreading complicates the wetting process through time-dependent diffusion and adsorption processes at the involved interfaces. The same processes are important in the case of water penetration into hydrophobic porous media. Aqueous surfactant solutions can spontaneously penetrate into hydrophobic porous substrates and the penetration rate depends on both the surfactant type and its concentration. Both the liquid–vapour interfacial tension γ_{lv} and the contact angle of moving meniscus, θ_a, (advancing contact angle) become concentration dependent.

The major process determining penetration of aqueous surfactant solutions into hydrophobic porous media or spreading over hydrophobic substrates seems to be the adsorption of surfactant molecules onto a bare hydrophobic substrate in front of the moving three-phase contact (TPC) line. The latter process results in a partial hydrophilisation of the hydrophobic surface in front of the meniscus or drop, which determines a spontaneous imbibition or spreading.

A pure water does not spontaneously penetrate into hydrophobic capillaries and shows the advancing contact angle larger than 90°. The latter means that water can be only forced into the capillary using an applied excess pressure or much easier by adding surface-active agents. Let us consider in more details a very beginning of the imbibition process into a hydrophobic capillary, when a surfactant solution touches the capillary inlet. The advancing contact angle at this moment is larger than 90° and the liquid can not penetrate into the capillary. Solid–liquid and liquid–vapour interfacial tensions do not vary with time on the initial stage, because the adsorption of surfactant molecules onto these surfaces is a relatively fast process compared with the imbibition rate. Only solid–vapour interfacial tension, γ_{sv}, can vary. If the adsorption of surfactant molecules at the bare hydrophobic surface in the vicinity of the TPC line takes place, the solid–vapour interfacial tension increases with time. After reaching some critical value, Γ_{sv}^{cr}, the advancing contact angle reaches 90° and the spontaneous imbibition process can start. The latter consideration shows that there is a critical bulk concentration, c_*, below which Γ_{sv} remains below it's critical value Γ_{sv}^{cr} and the spontaneous imbibition process does not take place.

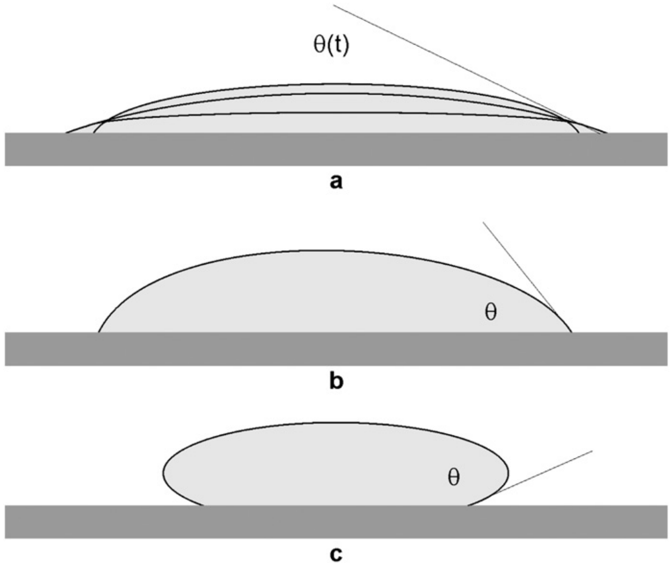

Fig. 1. Different wetting situations: (a) complete wetting case: a droplet completely spreads out and only dynamic contact angle can be measured, which tends to zero over time; (b) partial wetting case: the contact angle is in between 0 and 90°; non-wetting case: the contact angle is larger than 90°.

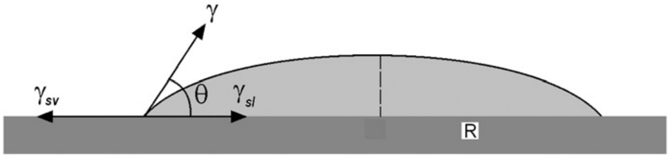

Fig. 2. Schematic of a droplet placed on a solid surface; γ, γ_{sl} and γ_{sv} are liquid–vapour, solid–liquid and solid–vapour interfacial tension, respectively, at the three-phase contact line; R is the radius of the droplet base. The droplet is small enough and the gravity action can be neglected.

The excess free energy Φ of the droplet deposited on a solid substrate Fig. 2 is as follows:

$$\Phi=\gamma S+PV+\pi R^2(\gamma_{sl}-\gamma_{sv}), \tag{1}$$

where S is the area of the liquid–vapour interface; $P=P_a-P_l$ is the excess pressure inside the liquid, P_a and P_l are the ambient air pressure and pressure inside the liquid, respectively; R is droplet base radius; γ, γ_{sl} and γ_{sv} are the liquid–vapour, solid–liquid and solid vapour interfacial tensions, respectively. The last term in the right hand site of Eq. (1) gives the difference between the energy of the surface covered by the liquid drop and the energy of the same solid surface without the droplet. Eq. (1) shows that the excess free energy decreases if (a) the liquid–vapour interfacial tension decreases; (b) the solid–liquid interfacial tension decreases; and (c) the solid–vapour interfacial tension increases. The latter very important conclusion is often overlooked.

In the absence of surfactants, the drop forms a contact angle above 90° with a hydrophobic substrate. In the presence of surfactants the following three transfer processes take place from the liquid onto all three interfaces: surfactant adsorption at both (i) the inner solid–liquid interface and (ii) the liquid–vapour interface, and (iii) transfer of surfactant molecules from the drop onto the solid–vapour interface in front of the drop on the bare hydrophobic substrate. As mentioned above, all three processes lead to a decrease of the excess free energy of the system. However, adsorption processes (i) and (ii) result in a decrease of corresponding interfacial tensions γ_{sl} and γ, but the transfer of surfactant molecules onto the solid–vapour interface in front of the drop results in an increase of a local free energy, however, the total free energy of the system decreases according to Eq. (1). 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, processes (i) and (ii) are "fast" processes compared with the "slow" third process (iii).

Despite the enormous technical importance of spreading of aqueous surfactant solutions over solid surfaces, information on possible spreading mechanisms is still limited in the literature. Disjoining