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Surfactant-mediated wetting and spreading: Recent advances and applications

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Abstract

Surfactant-mediated wetting and spreading are ubiquitous. Understanding of these phenomena in-depth allows precise tailoring of wetting performance which can contribute to global challenges in the food supply chain, healthcare, ecology and industrial processes. The first part of this review shows how surfactants can be used to improve the efficacy of fertilisers and pesticides in agriculture, enhanced oil recovery, treatment of lung diseases and extinguishing fires involving flammable liquids. The second part provides analysis of recent studies on wetting and spreading over solid substrates. It includes discussion on the effect of surfactants on the outcome of the impact of liquid drops, the wetting state after impact, autophobic effect and spreading kinetics for both partial and complete wetting, including superspreading. Perspectives of future development in the area of surfactant-assisted wetting and spreading on solid substrates are outlined.

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Introduction

Wetting and spreading are present in many natural phenomena and are an essential part of many industrial processes, for which precise tailoring of wetting behaviour can substantially improve efficacy and minimise ecological impact. There are two complementary approaches to control wetting and spreading. Firstly, the chemistry and structure of wetted surfaces can be adjusted to achieve a required wetting pattern. This approach is invaluable when the properties of the wetting liquid cannot be changed and very often is inspired by the diversity of natural surfaces. The most commonly known example is the class of super-hydrophobic and self-cleaning biomimetic surfaces inspired by the lotus leaf. The considerable progress in 'on-demand' surface design relies on the rapid development of various micromanufacturing techniques. Tailored surface manufacturing is covered by numerous recent reviews [1–7]*. Wetting can be also controlled by electric field in processes known as electrowetting [8] and dielectrowetting [9]. Secondly, when the properties of the wetted surface cannot be manipulated, which is the case for biological surfaces or for industrial applications where a change of the surface properties can affect the product functionality, the only way to control wetting and spreading is by adjusting the composition of the wetting liquid. In many applications, aqueous formulations are used on rather hydrophobic surfaces, and therefore surfactants are necessary to control the process efficacy and environmental impact. Examples of such applications are given below.

Applications

Agriculture

In agriculture, the application of spray droplets to plant leaves is used to deliver fertilisers [10], pesticides [11] and microbial inoculants [12]*. The contact angle of water (CAW) on plant leaves has a very broad range from ∼60° to ∼ 150° [13–16]* and is determined mostly by the chemical composition and especially by the structure of epicuticular wax, although other factors such as trichome density can also contribute to leaf wettability [16,17]*. Spray droplets can bounce and are easily removed by gravity and wind from the leaves (with high CAW). This decreases enormously the treatment efficacy and simultaneously causes contamination of soil and groundwater. Therefore, adjuvants are added to the formulation tanks to provide improved wetting of the leaves leading to better spray retention and penetration of active ingredients (AIs). Because this approach minimises environmental contamination, surfactants are an essential part of adjuvant formulations [10–12]*. In addition, adjuvants allow the concentration of AIs in the formulation to be decreased, which further reduces the environmental impact. The most effective adjuvants used now in agricultural formulations include trisiloxane surfactants, for example, Break-Thru®and Silwet L-77® [18].

Although adjuvants are considered to be biologically inert and therefore are not included in agrochemical risk assessments, there are growing concerns that they can have a negative environmental impact [18–20]. There is also evidence that surfactants can solubilise the protective epicuticular wax layer on the leaf [21,22]. Therefore, for herbicides applied during the vegetation phase, the optimal adjuvant should provide the minimum attachment of spray drops to the plant and maximum attachment to the weeds. For foliar fertilisers, adsorption of AIs stops after drop evaporation; therefore a balance should be found between spread area and time of evaporation to maximise the AI uptake [23]*. In particular, the evaporation can be slowed down by humectants included in the fertiliser composition. Thus, study of surfactant effect on the short-time behaviour of drops deposited on the solid surface, wettability, spreading kinetics and effect of surface structure on these processes as well as development of new adjuvants and testing their performance and ecological impact are of great importance for agriculture. The requirements for adjuvants depend considerably on the formulation and application.

Enhanced oil recovery

Despite the considerable progress in development of renewable energy resources, oil still remains a valuable commodity for energy production and as a chemical feedstock. Therefore, sustainable oil production is of importance at least for the next decade. The oil near the rock walls, especially that in pores, is usually unavailable to primary and secondary (water flooding) oil recovery processes [24]. The chemical method of enhanced oil recovery (EOR) is a tertiary process which uses various additives, including surfactants, to retrieve at least part of the oil remaining in the rock reservoirs. Surfactants assist oil recovery in two different ways: firstly, they decrease the interfacial tension between oil and aqueous phase and therefore decrease capillary pressure of oil in pores; secondly, they induce wettability alteration and therefore decrease the adhesion of oil patches to the rock surface. The latter effect is within the scope of this review.

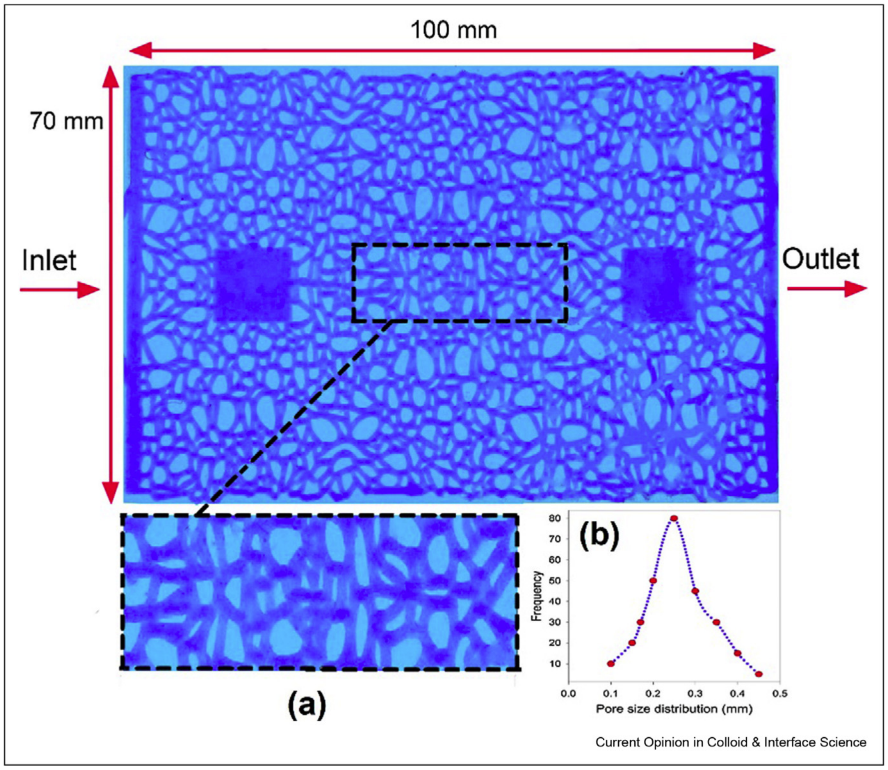
Pristine mineral surfaces are hydrophilic and easily wetted by water. However, when rocks are in contact with crude oil, its amphiphilic constituents irreversibly adsorb on the rock surface, usually because of strong electrostatic interactions, with hydrophobic parts of molecules facing into the oil. This makes the rock surface hydrophobic, and therefore oil displacement by water without surfactant is ineffective. Surfactants, when added to the EOR flooding agent, desorb adsorbed oil components from the rock by forming ionic pairs with them and therefore make the rock surface hydrophilic again [25]. Considering this mechanism and the undesirable adsorption of the surfactant itself onto the rock surface, the choice of surfactant depends primarily on the rock properties. For positively charged rocks, such as carbonates, cationic surfactants are the most effective [24,25], whereas anionic surfactants are used on negatively charged sandstone rocks [24,26–28]*; zwitterionic surfactants can be effective on both types of rocks [29]. The efficacy of the surfactant also depends on the rock structure, the properties of oil and other components included in the flooding liquid, such as salts, polymers or nanoparticles [24,30]. Therefore synthesis and study of new surfactants enabling increase in efficacy and lowering cost and the negative environmental impact of EOR is a very active area of research [26–30]*. Another important research area is the development of new techniques for the study and optimisation of EOR formulations on the laboratory scale to minimise the environmental footprint of this work. A promising approach is the use of reservoirs-on-a-chip: microfluidic models of porous media with relevant wall chemistry (Figure 1) enable direct visualisation of displacement of oil by flooding liquid in rock reservoirs and therefore effective testing of various EOR flooding agent compositions [26,28,31]*.

Medicine

The spreading of surfactant solutions over thin layers of viscous liquid is critical for the treatment of lung diseases such as respiratory distress syndrome (RDS) and cystic fibrosis (CF) [32]*. RDS is a result of the deficiency of pulmonary surfactants produced inside the lungs and is treated by surfactant replacement therapy, which is very effective for paediatric patients, but much less effective for adults. One possible reason for this difference is that the lung area is two orders of magnitude larger and number of airways generations is double in adults when compared with those in neonates. This makes it much more difficult to deliver the therapeutic amount of exogenous surfactants to alveoli of adult patients [33].

CF is a genetically caused thickening of mucus which lines the epithelial surfaces of lungs. This forms highly viscous, adherent mucus plaques [34]. Normally, mucus traps inhaled particles and pathogens which are then removed by cilia [35]. If, as a result of CF, the mucus viscosity increases enormously, then it cannot be removed by cilia and trapped pathogens remain in the lungs and proliferate causing secondary lung infections. In addition, mucus accumulation can obstruct airflow and lead to respiratory failure [34]. A rheological study performed on model samples [36] has shown that application of surfactant can result in a decrease of both loss and the storage modulus of mucus and therefore relieve CF symptoms. The decrease is probably due to surfactant interaction with mucin, which is a gel-forming polymer component; the surfactant is thought to disrupt the process of cross-linking. Even more

Figure 1



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Microfluidic device for study of oil displacement from a porous medium: **(a)** device structure, **(b)** pore size distribution. The thickness of the device is 2 mm. Reprinted from study by Kiani et al. [26]* Copyright 2020 with permission from Elsevier.

importantly, addition of surfactant to drug formulations uses Marangoni flows distributing AIs over the lung surface to enable deeper penetration of drugs and/or exogenous surfactants into affected lung areas and increase the efficacy of treatment of adult RDS, CF and secondary lung infections [32,37,38].

Fire fighting

Aqueous film-forming foams (AFFFs) are used to extinguish fires on flammable liquids, such as hydrocarbon fuels and solvents, and to prevent re-ignition [39]. They work fast and are, for example, very effective at plane crash scenes and in accidents within the hydrocarbon processing industries. When the AFFF is applied to a fuel fire, liquid drains out of the foam and spreads over the fuel surface sealing it. The spread film and the foam layer on the top of it extinguish the fire by preventing access of oxygen, cooling the surface and suppressing fuel evaporation into atmosphere. There are many factors contributing to the AFFF performance, such as foam stability and fuel diffusion rate through the foam [40], but also film formation and spreading over the fuel layer [41]: the faster the film spreading rate, the earlier the fuel surface is sealed and the more effective is the AFFF. Therefore, the kinetics of spreading of surfactant solutions over hydrocarbon liquids is an important parameter for development new AFFF formulations.

Hydrocarbon fuels have low surface tension, mostly in the range of $\gamma_O \sim 22-28$ mN/m [42,43]. To make an aqueous film spread over such a low-energy liquid substrate, an AFFF formulation must have very low water/oil, γ_{WO}, and water/air, γ_W, interfacial tensions to provide a positive spreading coefficient $S = \gamma_O - (\gamma_{WO} + \gamma_W)$. Therefore, usually AFFFs include a combination of fluorocarbon and hydrocarbon surfactants in their composition [39]. A fluorosurfactant adsorbs preferably at the water/air interface decreasing the surface tension up to $\gamma_{WO} \sim 16$ mN/m, whereas a hydrocarbon surfactant adsorbs preferably at the water/oil interface and can decrease the corresponding interfacial tension close to zero [39,44]. Unfortunately, fluorosurfactants with fluorocarbon chain lengths ≥ 8, contain or degrade to perfluorooctane sulfonates. Although used previously in commercial AFFFs, they have been found to be very toxic and prone to bio-accumulation [39,45,46]. Their usage in new products was prohibited in the European Union in 2011 and in Canada in 2013 [46], and it has been agreed by manufacturers to eliminate their use in the USA in 2015 [47]. Therefore, the development of new compositions for AFFFs, including nontoxic short chain fluorosurfactants [43,47,48] and silicone surfactants [40,49], has been a very active area over the last decade. It can be concluded from the analysis of recent publications that the effect of surfactants on fuel diffusion through AFFFs, the stability of foam in presence of fuel molecules in the aqueous phase as well as formation and spreading of a liquid film on the fuel surface are the main challenges in development of environment-friendly AFFFs.

Other applications of surfactant-mediated wetting/spreading include usage of surfactant herding to localise marine oil spillages [50—52], gravure [53], and inkjet printing [54], in particular, the topology of deposit formed after drop evaporation/solidification [55,56]. Note that surfactant-assisted deposit formation is of importance not only in printing, but also, for example, in agriculture [57] and the production of photonic materials [58]. Wetting of skin [59,60] and hair [61,62] are of great importance for development of new products in dermatology and cosmetics. In the food industry, wetting is important both for technological processes and the quality of consumer products, for example, in food coatings [63,64] or in rehydration behaviour of dry products [65].

The following discussion addresses recent developments in the spreading of surfactant solutions over rigid solid surfaces. Spreading on soft solid substrates has been covered in recent reviews [66,67] mostly including results for pure liquids, whilst spreading over porous solid substrates is addressed in the study by Johnson et al. [68]* including spreading of surfactant solutions. Spreading over liquid layers is discussed in the study by Stetten et al. [32]*.

The outcomes for a drop impact on a solid substrate

When a liquid drop impacts a solid substrate it initially spreads over it because of inertia, but its further fate depends on many parameters, the most important being the drop size, velocity, surface tension and the substrate wettability. In particular, if the contact angle at the end of the inertial part of spreading is larger than the advancing contact angle, the drop will continue to spread, but if the contact angle is smaller than the receding contact angle, the drop will recede under the action of capillary force and the spread area will decrease. A very detailed discussion of the forces acting and the phenomena accompanying a drop impact on a solid substrate and on thin liquid layers, although mostly without surfactant effect, is given in the sudy by Yarin [69]. A comprehensive study [70] identified six possible outcomes of drop impingement on a solid surface:

- ***deposition*** (homogeneous wetting) means that drop deforms on impact but remains attached to the surface and does not break up;
- ***a prompt splash*** is observed only on rough surfaces, small droplets are ejected from the main drop at the three-phase contact line (TPCL) at the beginning of spreading;
- ***a corona splash*** is similar to that observed for a drop impact on the liquid surface and is characterised by droplets formed at the top of the liquid rim near the TPCL;
- ***receding break*** up where small drops are formed behind the receding TPCL;
- ***partial rebound*** where the receding part of the drop is detached from the substrate;
- ***rebound*** (bouncing off) where the whole drop detaches from the substrate.

The rebound phenomena are usually observed on poorly wetted surfaces, in particular when water impacts onto superhydrophobic surfaces, that is those with CAW $>150°$, with small contact angle hysteresis. The contact time of the bouncing drop with the substrate does not depend on the impact velocity in the broad range of drop sizes, but increases with an increase of drop radius, R, as $\sim R^{3/2}$ and is of order of 10 ms for a mm-size drop [71]. Superhydrophobicity can be only achieved on structured surfaces and corresponds to the Cassie—Baxter wetting state on these surfaces. At large enough impact velocities a transition from the Cassie—Baxter to the Wenzel wetting state can be achieved. Under these conditions, drop impingement can result in impalement, when the drop adheres to the surface with a pinned TPCL [72].

The addition of a surfactant can dramatically change the outcome of a drop impact on a solid substrate. A study of aqueous drop impact on a leaf of *Brassica oleracea* L. characterised by a CAW $\sim$156° has shown [73]* that at a chosen impact velocity, a drop of pure water on this substrate splashes and on receding breaks up into numerous drops, most of which rebound. Addition of sodium dodecyl sulfate (SDS) or a trisiloxane surfactant (not specified) to the aqueous phase results in transition to the receding break up, when by receding the main drop breaks into smaller drops, but those remain on the substrate. Addition of Aerosol OT (AOT) results in transition to impalement, when the receding flow is suppressed and the drop remains pinned covering the relatively large surface area (Figure 2). Bouncing can also be prevented by using another surfactant, Tween 80, in concentrations ≥0.06% [74] or by adding a flexible polymer to less concentrated solution of AOT [75]. The last approach works well also on wired and curved leaves.

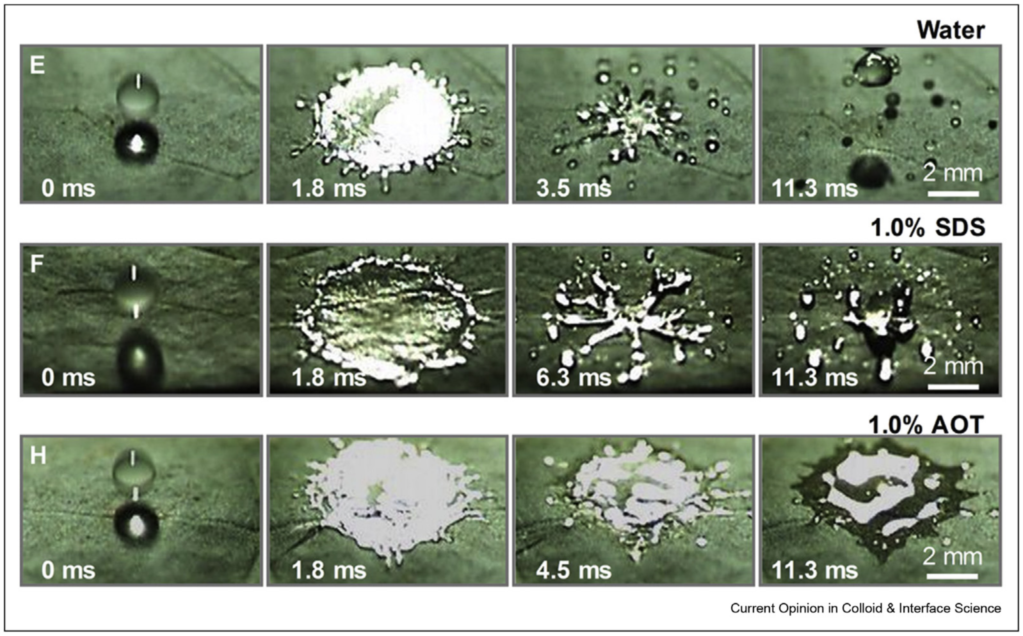
According to Song et al. [73]* the distinctive behaviour of AOT solution is related to its much faster adsorption than that of two other surfactants and the different type of self-assembled structures formed in the bulk liquid: vesicles versus micelles in two other surfactants. The characteristic time scale for the inertial spreading after impact is in the range of 1—10 ms. Therefore dynamic rather than equilibrium surface tension governs the spreading behaviour. Because of faster adsorption, the AOT solution has a much lower surface tension at the end of inertial stage of spreading, that is much lower capillary force causing retraction and a much smaller receding contact angle on the substrate. Therefore, the retraction is suppressed, and the drop of the AOT solution ends up in the impalement state. This mechanism is confirmed in the study by Song et al. [73]* by a study of the concentration dependence of the impingement state for OAT solutions. A decrease in concentration slows down surfactant mass transfer and result in transition from the impalement to the receding break up and further to rebound. It is suggested in the study by Song et al. [73]* that an increase in AOT concentration results in decrease of the area of air pockets under the spreading drop and the transition to impalement corresponds to the transition to the Wenzel wetted state. This suggestion is corroborated by the results of cryo-SEM (Scanning Electron Microscopy) [73]*. These transitions in wetting behaviour of AOT with concentration can be used for the cleaning of superhydrophobic surfaces [76].

Impalement of an aqueous drop after impingement on the superhydrophobic substrate with CAW ∼156° has been reported in the study by Luo et al. [77]**. The aqueous phase contained a mixture of diethylenetriamine and SDS, which form oligomers in aqueous solutions because of electrostatic interactions. Formation of a uniform circular shape after impact was ascribed to lower equilibrium surface tension of the mixture, fast surfactant equilibration and formation of wormlike micelles in solution and their entangling in bulk and with micro/nanostructural features of the substrate.

Contact angle

If a drop impinges a substrate in the deposition mode, then after the short-time inertial spreading it spreads further in the viscous regime until the contact angle reaches an equilibrium value of advancing contact angle. Note, the characteristic time of surfactant adsorption can be considerably larger than the characteristic time of equilibration of a partially wetting drop with constant surface tension. In this case, a surfactant-laden drop will continuously spread until the surface tension at the TPCL reaches its equilibrium value. Therefore, the

Figure 2



Effect of surfactants on the outcome of impact of an aqueous drop on the superhydrophobic leaf surface. Adapted from study by Song et al. [73]* © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0/. AOT, Aerosol OT; SDS, sodium dodecyl sulfate.

equilibrium advancing contact angle for surfactant solution means that the surfactant is in adsorption equilibrium. The time scale for surfactant equilibration can vary over a broad range depending on its concentration, activity and diffusion coefficient. On rough substrates, surfactant dynamics can also affect the wetting state (Cassie—Baxter or Wenzel) on the time scale of observation.

The contact angle of a surfactant solution on a solid substrate depends upon surfactant adsorption on both liquid/air and solid/liquid interfaces which not necessarily follow the same rules. For example, it was reported in the study by Kovalchuk et al. [78] that because of difference in the affinity of hydrocarbon and fluorocarbon surfactants to water/air and water/solid interfaces, a mixture of these surfactants providing the minimum contact angle has different composition from the mixture demonstrating the minimum surface tension. It was shown in the study by Wang et al. [79]* that one of two trisiloxane surfactants of the same surface tension wets a propylene substrate completely, whereas another demonstrates only partial wetting. Moreover, most real substrates are not smooth but rough with different surface topology and possible chemical heterogeneity which can have considerable effect on surfactant adsorption [80]*. Therefore, surfactant solutions with the same surface tension can have different contact angles on the same substrate, and the data on surface tension only are not sufficient to predict contact angle. Thus, studies aimed at characterisation of equilibrium wetting properties of surfactant solutions on various substrates have been actively pursued over the last few years, especially for surfactant mixtures [81,82] and newly synthesised surfactants [83,84].

Motivated by practical applications in agriculture, many studies have focused on the wetting properties of surfactant solutions in combination with fertilisers or pesticides on plant leaves [85,86] or even insects [87]*. Although most of studied surfactants provided only a partial wetting on the surfaces of interest, some of them, especially nonionic surfactants, significantly improved the AI intake and therefore can be recommended as adjuvants for agrochemical applications.

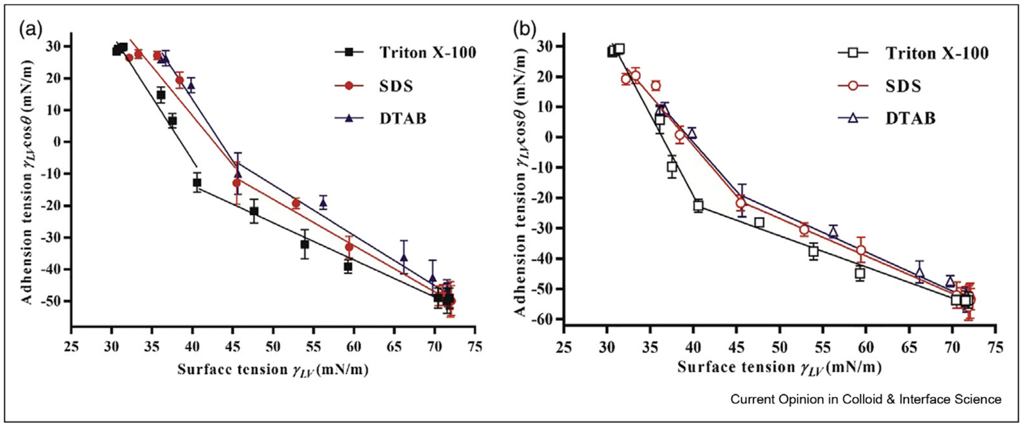
If both, surface tension, γ_{LV}, and contact angle, Θ, are known, the ratio of adsorption on solid/liquid and liquid/air interface, Γ_{SL}/Γ_{LV}, under the assumption of negligible adsorption at the solid/air interface can be estimated from a simple model proposed by Lucassen-Reynders more than 50 years ago [88,89]:

$$\frac{d(\gamma\cos\theta)}{d(\gamma)} = -\frac{\Gamma_{SL}}{\Gamma_{LV}} \tag{1}$$

Studies performed on various smooth interfaces with common low-molecular-weight surfactants, such as SDS, hexadecyltrimethylammonium bromide, CTAB, Triton X-100 and so on and their binary mixtures demonstrated good linear dependence between $\gamma cos\Theta$ and γ with slope depending on the substrate [90,91]. However, for surfactant solutions on bio-interfaces, a more complicated dependence was observed [85,87]* as shown in Figure 3.

Bio-interfaces have a complicated hierarchical surface structure. Surfactant adsorption on the solid/liquid interface changes the surface energy of this interface, which can result in a transition from the Cassie—Baxter wetting state, characteristic of highly hydrophobic

Figure 3



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Dependence of $\gamma cos\Theta$ on γ for housefly wing **(a)** and **(b)** notum surfaces. Reproduced from the study by Wan et al. [87]* with permission from John Wiley and Sons. DTAB, dodecyl trimethyl ammonium bromide; SDS, sodium dodecyl sulfate.

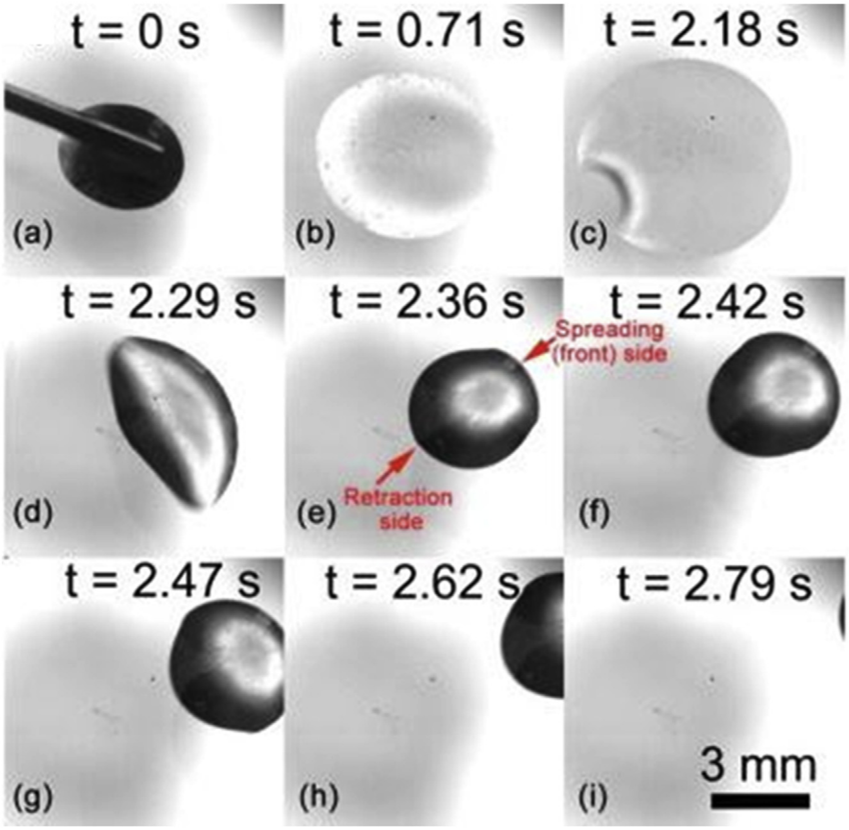
surfaces, to the Wenzel state which applies for less hydrophobic surfaces [92,93]. Such an explanation for the kink in the data shown in Figure 3 was proposed in studies by Zhang et al. [85] and Wan et al. [87] *. The slope of dependence of $\gamma cos\Theta$ on γ for larger surfactant concentrations (smaller surface tension) becomes higher because of the sharp increase in the solid area available for surfactant adsorption in the Wenzel state than in the Cassie–Baxter state. Note, identification of this transition is important for practical applications because Cassie–Baxter states demonstrate much smaller contact angle hysteresis than Wenzel states.

Another available approach enabling calculation of contact angles of surfactant solutions on the rough surface in both wetting states and therefore identifying wetting transitions was proposed by Milne et al. [94] and requires knowledge of dependence of the contact angle on surfactant concentration for a smooth substrate of the same chemistry. Considering that such dependence is usually unknown for bio-interfaces, using the Lucassen-Reynders approach can be very useful for identifying the wetting state of surfactant solutions on these interfaces. Very instructive in this respect would be a study verifying the transition found from the dependence of $\gamma cos\Theta$ on γ by direct microscopic observation, as was carried out in Shardt et al. [95] for the Milne approach.

Autophobic effect

As discussed in the early passages, surfactants generally decrease the contact angle of aqueous solutions on low energy (hydrophobic) substrates. On highly hydrophilic substrates completely wetted by water, such as silica or mica, electrostatic interactions between surfactant and substrate can result in an increase of the contact angle of aqueous solution with an increase of surfactant concentration [89] and in a reversal of spreading (autophobic effect). The last was observed, for example, for spreading of a tetradecane drop containing octadecylamine surfactant on freshly cleaved mica [96]**. Retraction of the drop after initial spreading was caused by an increase of the contact angle from that corresponding to clean mica surface to one on an adsorbed

Figure 4



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Movement of a 4 μL drop of 98 mM octadecylamine in tetradecane placed on a mica surface due to authophobic effect. Reprinted from the study by Tadmor et al. [97]* Copyright 2020 with permission from Elsevier.

surfactant layer. The drop can just retract and stay still, or it can move along the substrate in the direction of the initial retraction as shown in Figure 4. If the drop has been placed on the vertical or inclined surface, the first retraction occurs in the thicker (i.e. lower related to gravity) part of the drop and drop moves upward, climbing the wall [97]*. The distinctive features of the phenomenon described are that the self-propulsion occurs on the uniform solid surface with surface tension gradients created by the moving drop itself and that direction of motion is determined not by surface properties of the substrate, but by a body force (gravity). Note, the movement results in an increase of the drop potential energy in the gravity field by the cost of chemical energy due to surfactant adsorption.

Autophobic effect demonstrated by solutions of cationic surfactants on glass modified by zwitterionic sulfobetaine silane (SBSi) was used to switch the wettability of the SBSi surface [98]*. Water was found to wet completely a pristine surface of SBSi, but if the surface was treated with the surfactant solution, for example CTAB, and then dried, only partial wetting with water was possible. Washing the substrate with water returned it to the pristine state. Most interestingly, treatment of the substrate with AOT, fatty acid or perfluorodecanoic acid solution in hexadecane resulted in (reversible) transition from complete to partial wetting for oil drops on SBSi. Note, these partially wetted with oil substrates were completely wetted by water. The contact angle of partially wetting oil (water) on the treated substrate depended on the surfactant of choice and its concentration [98]*. Similar approach using perfluorotetradecanoic acid enabled switching between partial and compete wetting for oil drops on a range of substrates such as metals, ceramics and polymers [99] and transition from small to large contact angles for water drops on these substrates. Furthermore, the treatment resulted in transition from complete wetting for both water and oil drops to superhydrophobicity/oleophobicity on the microstructured aluminium alloy surface [99].

Wetting kinetics

Inertial regime

When a drop of radius R approaches a solid surface at a small velocity u (Weber number, $We = \rho u^2 R/\gamma_{LV} \ll 1$, where ρ is the liquid density) and impacts it in the deposition mode, the area, S, covered by the drop increases with time, t, until the equilibrium state of partial or complete wetting is reached. In the very early stages, capillarity is a driving force of spreading opposed by the drop inertia. For pure liquids, spreading during the inertial stage follows the power law $S \sim R^2 \left(\frac{t}{\tau_I}\right)^{\alpha}$, with $\tau_I = \sqrt{\rho R^3/\gamma_{LV}}$ being the characteristic time scale of inertial spreading. The power law exponent, $\alpha = 1$ for the case of complete wetting and decreases to 0.4 with an increase of the equilibrium contact angle [100,101]. Note, the spreading exponent used here is related to the spread area and is not to be confused to exponent related to radius of the spread drop, which is two times smaller. For a water drop of mm size the characteristic inertial time scale is of order of milliseconds; therefore inertial spreading can be observed for $t < 10$ ms.

The kinetics of inertial spreading of solutions of SDS, CTAB in concentration range of 0.1—3 critical micelle concentration and two different trisiloxane surfactants in the concentration range 0.05—1 wt % (all above critical micelle concentration) was studied in study by Wang et al. [79]* on a polypropylene substrate. Solutions of one of trisiloxane surfactants wetted the substrate completely, whereas solutions of other surfactants demonstrated only partial wetting. It was found that the spreading exponent remained constant within the stage of inertial spreading, that is the dynamic of surfactant adsorption did not affect the inertial spreading kinetics in the considered case [79]*. For all surfactant solutions the spreading exponent was larger than that of pure water and increased with concentration because of decrease of the contact angle.

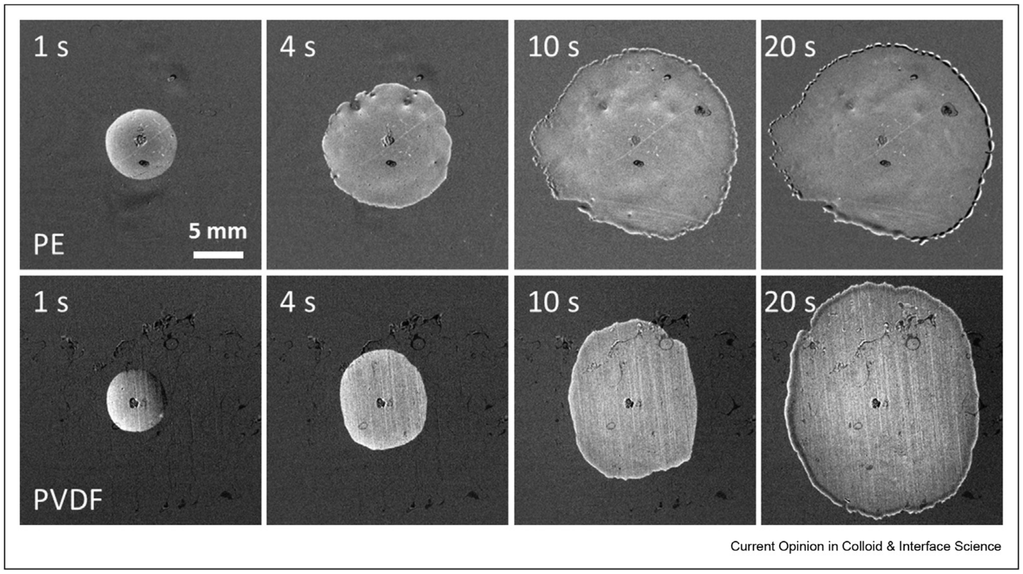
Surprisingly, much larger spreading exponent in inertial regime (up to two times) was observed for saponin surfactant β-aescin, adsorption of which resulted in a considerable increase of surface shear viscosity [102]**. Such fast spreading was ascribed in James et al. [102]** to relaxation of a crumpled surface film and to energy release following its rupture.

Viscous regime, superspreading

Solutions of SDS and CTAB in the study by Wang et al. [79] achieve equilibrium within the inertial spreading stage. For other surfactant solutions wetting proceeds further to viscous stage, when viscous dissipation becomes more important than inertia. For pure liquids, spreading kinetics in the viscous stage follows a power law with a different spreading exponent of $\alpha = 0.2$ [103], that is, it is much slower than the kinetics of the inertial stage. For the partially wetting surfactant solutions, spreading during the viscous regime is slower than that forpure liquids, and the spreading exponent can reach $\alpha = 0.2$ only at large concentrations when surfactant replenishment is fast enough to support close to equilibrium surface tension near the TPCL [79,86]. Spreading exponents smaller than 0.2 were observed also for surfactant solutions with nanoparticles [56,104].

The trend is quite the opposite in the case of complete wetting: surfactant solutions in the viscous regime always spread faster than pure liquids. This phenomenon is called surfactant-enhanced spreading. The spreading exponent for surfactant-enhanced spreading varies, but for some surfactants spreading can be as fast as during the inertial

Figure 5



Spreading of the solution of the trisiloxane surfactant BT-278 in 30% glycerol/water mixture on polyethylene (top row) and polyvinylidenefluoride (bottom row) substrate. Initial drop radius ~1 mm. PE, polyethylene; PVDF, polyvinylidenefluoride. Reprinted from the study by Kovalchuk et al. [105]** with permission from MDPI.

stage with the spreading exponent being $\alpha \geq 1$. Such fast spreading is called superspreading. It is important to note that the duration of the superspreading stage is around three orders of magnitude longer than duration of the inertial stage, and therefore it can achieve spread areas which are hundreds of times larger than the size of the initial drop as shown in Figure 5 [105]**. Characteristic features of superspreading are the maximum in the spreading rate over surface wettability and surfactant concentration. The last means that after a certain point an increase in surfactant concentration results in slower spreading. There are also evidences that the spreading rate depends on ambient humidity.

There are a lot of hypotheses attempting to explain the superspreading mechanism and its regularities, as discussed in numerous review papers [106–110]*, but a consistent and generally accepted explanation is still to be developed. Possible factors contributing to superspreading mechanisms are the surfactant architecture, type of self-assembled structures formed in the bulk phase, formation of surface aggregates, nonuniform surfactant distribution and Marangoni flow, direct transfer of the surfactant from the liquid/air to solid/liquid interface through the TPCL and caterpillar motion at the TPCL.

Numerical simulations on superspreading

Numerical simulations contribute to understanding of the superspreading mechanism providing a closer look into processes inside the spreading drop, but the problem is very complicated to model, first of all because of multiple scales involved. Molecular dynamics simulation can achieve a good description of the drop in the vicinity of the TPCL, molecular interactions inside the drop, surfactant aggregation and adsorption on the solid/liquid and liquid/air interface. Results of such simulations are discussed in the comprehensive recent review [109]*, which suggests that the T-shaped surfactant architecture and the ability to form bilayer aggregates facilitate superspreading, but the most crucial parameter is the surfactant chemistry. According to Theodorakis et al. [109]* the ability of a surfactant to replenish quickly at interfaces by adsorption from the bulk is the main difference between superspreading and nonsuperspreading surfactants. At the same time, molecular dynamics simulations are carried out on the time scale of microseconds and the length scale of micrometres and below [109]*. At such scales, it is, for example, impossible to take into account the contribution of convective mass transfer to account for the effect of Marangoni flow on spreading.

To consider the time and length scales of real experiments on spreading, computational fluid dynamics (CFD) simulations are coming into play. Considerable progress was made in this research area enabling the modelling of surfactant-laden flows with moving deformable interfaces. However, there are still difficulties, in particular, related to description of dynamics in the vicinity of the TPCL and especially in modelling of real soluble surfactants. A promising research direction is the coupling of molecular dynamics with continuum-scale models [111]. Another approach is to couple numerical studies with extensive experimental studies providing reliable parameters for the model, such as surfactant adsorption/desorption coefficients for the liquid/air and solid/liquid interface, or the contribution of self-assembled structures present in the bulk into surfactant transfer. These parameters are not available for the most cases considered in numerical studies. For example in the study by Badra et al. [112], the surfactant bulk diffusion coefficient and adsorption/desorption coefficients for the liquid/air interface were used as fitting parameters of the model, whereas adsorption on the solid/liquid interface was not considered. The parameters obtained in the study by Badra et al. [112] from the fitting of numerical results to the experimental data on spreading kinetics are in reasonable agreement with available experimental data [113], except for the surfactant diffusion coefficient. The much smaller value of the diffusion coefficient obtained in the study by Badra et al. [112] is probably related to the fact that the model does not take into account adsorption on the solid/liquid interface.

The possible contributions to the superspreading mechanism are not discussed in the study by Badra et al. [112], whereas a theoretical model developed in the study by Wei [114] explores the contribution of transfer of surfactant molecules from the liquid/air to solid/liquid interface in the vicinity of the contact line. Importance of such transfer for superspreading was first indicated in the most thorough the CFD study to date on the subject [115]. Any specific surfactant properties are not included in the model developed in the study by Wei [114]; instead it introduces a small surfactant leakage from the liquid/air to the solid/liquid interface. It is shown in the study by Wei [114] that such leakage, when not balanced by the surfactant bulk transfer, creates a surfactant-devoid microscopic zone in the vicinity of the TPCL and provides strong Marangoni stresses in the direction of the TPCL resulting in the accelerated spreading kinetics. If the leakage is too large, the depletion zone increases in size and the Marangoni stresses decrease resulting in a slower spreading kinetics.

Experimental studies on surfactant-enhanced spreading

A recent experimental testing of the possible contribution of Marangoni flow to the superspreading mechanism [105]** was based on the dependence of the spreading rate on concentration. If Marangoni flow contributes to superspreading, then the surfactant concentration corresponding to the maximum spreading rate provides the optimum surfactant distribution with maximum attainable surface tension gradients. The surfactant fluxes to the surface are proportional to both the diffusion coefficient and bulk concentration gradients. Therefore, if Marangoni effect is important, a decrease in the surfactant diffusion coefficient should result in the shift of surfactant concentration corresponding to the maximum spreading rate to larger values. The variation of the diffusion coefficient in the study by Kovalchuk et al. [105]** was achieved by addition of small amounts of glycerol to the aqueous phase which resulted in an increase of solution viscosity up to 3.7 times and thus a proportional decrease of diffusion coefficient. It was shown that such an increase in viscosity does not change the spreading rate of pure liquids, but for surfactant solutions the spreading rate was changed considerably with the maximum spreading rate shifted to larger concentrations in more viscous solutions (smaller diffusion coefficient). This confirms the importance of Marangoni flow for the superspreading mechanism.

Considering that the best superspreaders are trisiloxane surfactants, several studies were focused on extending this family. Synthesis of gemini-type trisiloxane surfactants was reported in the study by Lin et al. [116] and the glucamine-based trisiloxane surfactant was synthesised and studied in the study by Li et al. [117]. In both these studies, the surfactants were called superspreaders, but kinetics of spreading was studied only in the study by Lin et al. [116], reporting the spreading exponents for the best-performing surfactant solution of $\alpha \sim 1$ on a mango leaf and $\alpha \sim 0.9$ on a more hydrophobic rice leaf.

It is well-known that fluorosurfactants usually do not provide a complete wetting of low-energy hydrocarbon substrates despite their low surface tension due to low adsorption on the solid/liquid interface [44]. However, the synthesis of a fluorinated surfactant, perfluoropolyether amide propyl betaine, enabling complete wetting of parafilm was reported in the study by Shen et al. [118]. Spreading kinetics was not studied in the study by Shen et al. [118] for the case of complete wetting; therefore it is not known whether this surfactant is a superspreader. Such a kinetic study for fluorosurfactant in the case of complete wetting would contribute greatly to an understanding of the superspreading mechanism.

Spreading of a new branched trimethylsilyl surfactant, Mg $(AOTSiC)_2$, was studied in the study by Kovalchuk et al. [119]*. Comparison with results reported in the study by Kovalchuk et al. [105]** for traditional trisiloxane superspreaders has shown that Mg $(AOTSiC)_2$ is a superspreader with a spreading rate similar to trisiloxanes on the same substrate. This study confirms that the surfactant architecture is not a crucial parameter for the superspreading mechanism. Interestingly, Mg $(AOTSiC)_2$ required around a 10 times faster equilibration than trisiloxane surfactants to provide the maximum spreading rate. This highlights the important role of adsorption on the solid/liquid interface for superspreading performance.

The presence of a surfactant in the oil phase can accelerate its spreading on the hydrophilic substrate [96]**. Being in the oil phase, a surfactant does not adsorb on the liquid/air interface, but only on the liquid/solid interface, in which case Marangoni flow is not possible. Therefore, a more detailed study on spreading surfactant—laden oil drops, with a quantitative account on spreading kinetics would be very advantageous for understanding mechanisms of surfactant-enhanced spreading including superspreading.

It is well-known that humidity can affect spreading of surfactant solutions on solid substrates [106], but the exact mechanism of this is still under discussion with essential contribution from the recent work on spreading of pure surfactants over a broad range of humidity values [120,121]. In the study by Ivanova et al. [120]* drops of three different surfactants were deposited on two different hydrophobic substrates at relative humidity (RH) = 45% and were allowed to equilibrate. After the equilibration of the drops (constant contact angle), humidity was gradually increased to nearly 100%. Initially, the drops remained unchanged, but after the humidity increases above a threshold value of 70—80% depending on the surfactant, they begin to spread again. The kinetics of humidity-driven spreading obeyed the power law with exponents depending on the pair surfactant/substrate. For the pairs demonstrating a high contact angle ($>30^\circ$) the exponent was close to 0.2, equal to the exponent of capillary-driven viscous spreading for pure liquids, whereas for the pairs demonstrating a low contact angle ($\leq 20^\circ$) the exponent was between 0.4 and 0.5 indicating contribution of Marangoni flow in the spreading kinetics. Humidity-driven spreading was attributed in the study by Ivanova et al. [120]* to formation of an adsorbed water film on the solid/vapour interface. In the study by Kubochkin and Ivanova [121] periodical transitions between wetting states of surfactant drops were observed in response to cyclic change of humidity in the range 20—85%.

Conclusions and outlook

Surfactants have a great potential to control various aspects of wetting and spreading and therefore to increase efficacy of related processes and improve ecological impact. Considering the fundamental scientific challenges, existing and potential applications and fast development of such research techniques as high speed video recording, atomic force microscopy, electron microscopy, 3D printing, maskless lithography and computer numerical control machining, it can be suggested that the following areas of surfactant-assisted wetting and spreading on solid substrates will receive an increasing attention.

Wetting and spreading on patterned substrates including surfactant adsorption on micro and nanostructures. A lot of work in this area is bio-inspired, whereas huge progress in micromanufacturing techniques enables design of surfaces with sophisticated hierarchical morphology and length scales going down to those characteristic of surfactant self-assembled structures. Development in this area will enable considerable progress in the fundamental understanding of interactions of the surfactant with solid surfaces, especially under confined conditions. It also will result in design of new surfactants with properties precisely tailored for specific applications.

Effect of surfactants on wetting in water/oil/solid configurations, including effect of the partition coefficient. This work is mainly motivated by the applications in the oil industry and a large demand in water/oil separation techniques. Better understanding of fundamental science governing these processes will provide a road map for new material design.

Spreading and evaporation of surfactant solutions including solutions containing nanoparticles and deposit formation. Progress in this area will enable creation of on-demand patterned surfaces, for example, for various analytical tools or electronics.

Surfactant-enhanced spreading in the case of complete wetting; mechanisms contributing to superspreading behaviour; the role of the precursor film and vapour condensation on the substrate on wetting and spreading kinetics. Elucidating the mechanisms responsible for surfactant-enhanced spreading and superspreading enables the formulation optimisation and therefore reducing the ecological impact of many applications. It will also contribute to development of new drug delivery systems for lung therapy and topical applications as well as new solutions in cosmetic industry.

Self-propelled drops, instabilities accompanying spreading and dewetting. These are examples of self-organisation in the systems far from equilibrium and direct transformation of chemical energy in mechanical motion. Along with the fundamental scientific value, progress in this area will contribute to development of new stimuli-responsive micromotors and actuators.

Synthesis of new, more effective and environment-friendly surfactants. Synthesis of new, more effective and environment-friendly surfactants tailored for specific application is of huge importance for tackling ecological problems and securing a sustainable future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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