Colloids and Surfaces A: Physicochem. Eng. Aspects xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Kinetics of spreading of synergetic surfactant mixtures in the case of partial wetting

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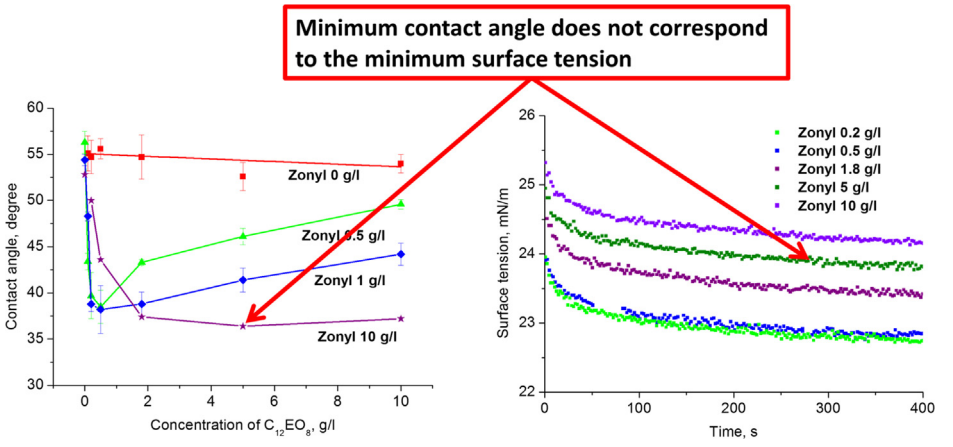
HIGHLIGHTS

- Mixtures of fluoro- and hydrocarbon surfactant show synergism in wetting properties.
- Spreading exponent of mixtures is larger than that of individual solutions.
- The maximum spreading exponent is at the minimum contact angle.
- Spreading kinetics of mixtures depend on experimental protocol.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 September 2015
Received in revised form
12 November 2015
Accepted 14 November 2015
Available online xxx

Keywords:
Oxiethylated alcohol $C_{10}EO_8$
Fluoro-surfactant Zonyl FSN-100
Sylanized glass substrate
Interfacial tension
Equilibrium contact angle
Spreading exponent

ABSTRACT

Spreading kinetics of mixtures of hydrocarbon surfactant, octaethylene glycol monododecyl ether, and fluoro-surfactant, Zonyl FSN-100, on highly hydrophobic substrate was experimentally studied. The mixtures reveal a synergism in their wetting properties with equilibrium contact angle of mixtures being 15–20° lower than that of individual surfactant solutions. The synergism is due to different affinity of the surfactants to the liquid/air and liquid/solid interface. Both individual surfactants and their mixtures demonstrate power law kinetics of spreading over the time span of tens of seconds. The spreading exponent is lower than that for pure liquids, but spreading exponent of mixtures is higher than that of individual solutions. The maximum in the spreading exponent is observed for the mixtures demonstrating the lowest equilibrium contact angles. For these mixtures the spreading exponent is close to that of pure liquids.

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1. Introduction

Spreading kinetics of various liquids on solid surfaces is of great importance in many industrial applications including painting, printing, coating etc. The problem has been studied thoroughly

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http://dx.doi.org/10.1016/j.colsurfa.2015.11.026
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Please cite this article in press as: N. Kovalchuk, et al., Kinetics of spreading of synergetic surfactant mixtures in the case of partial wetting, Colloids Surf. A: Physicochem. Eng. Aspects (2015), http://dx.doi.org/10.1016/j.colsurfa.2015.11.026

for the case of pure liquids. Spreading kinetics in the case of complete wetting consists of two stages. During the first, inertial stage, radius of spread drop increases proportionally to the square root of time, $R \sim \sqrt{t}$ [1,2]. The duration of this stage is in the range of millisecond, with characteristic timescale given by $(\rho R^3/\sigma)^{1/2}$, where ρ is the liquid density and σ is the liquid surface tension. Later viscous dissipation becomes more important than inertia and spreading slows down. In the purely viscous regime, when inertia is negligible $R \sim t^{0.1}$ [3,4]. For the droplets larger than the capillary length $\left(l_c = \sqrt{\sigma/\rho g}\right)$, the spreading exponent increases to $\alpha = 0.125$, due to contribution of gravity [5].

In the case of partial wetting by pure liquids both pre-factor and spreading exponent during the inertial stage of spreading decrease with the increase of the equilibrium contact angle [6]. As usually a static advancing contact angle is referred to below as "equilibrium contact angle". Viscous stage of wetting was observed only for liquids with small contact angles with threshold value of equilibrium contact angle increasing with an increase of the liquid viscosity [2]. According to Ref. [2] for the mixtures of water and glycerol with viscosity below 35 mPa s only inertial stage of spreading was observed on substrates with contact angle 63°. The spreading in those cases was completed within approximately 10 ms. For the mixtures with viscosity of 35 mPa s and above the viscous stage was observed on the same substrate. The spreading exponent was $\alpha \sim 0.1$, i.e. similar to that of complete wetting case [2].

Very often a liquid to spread is an aqueous formulation. Surfactants are the common additives improving spreading characteristics of such formulations. In the case of complete wetting surfactant solutions demonstrate initially the same two stages as pure liquids, inertial and viscous [7]. According to Ref. [7] spreading during the inertial stage does not depend on surfactant properties and concentration and is similar to that of pure liquids, whereas during the viscous stage it becomes surfactant depending and spreading exponent may be higher than that for pure liquids [7]. The most important distinction of the spreading of surfactant solutions from that of pure liquids in the case of complete wetting is the third stage, referred to as surfactant enhanced spreading or superspreading [7–15]. During this stage the spreading accelerates again demonstrating spreading exponent up to 0.5. The precise mechanism governing this stage is not completely established yet. The available experimental results and most promising hypotheses on mechanism of surfactant enhanced spreading and superspreading are discussed in recent reviews [16–18].

In the case of partial wetting the spreading of surfactant solutions depends on the equilibrium contact angle similar to pure liquids. For conventional surfactants on highly hydrophobic substrates (large equilibrium contact angles) only inertial stage of spreading was observed [7], whereas for surfactant solutions with small equilibrium contact angle it was followed by the viscous stage with spreading exponent $\alpha \sim 0.1$. For example the viscous stage was observed in Ref. [7] for solution of trisiloxane surfactant TSS 10/2 on polypropylene (equilibrium contact angle ~12°).

The experiments in Ref. [7] have been performed on rather short time scale to catch the early kinetics, maximum time of observation was 10 s. The study presented in Ref. [19] has been devoted the kinetics of partial wetting of surfactant solutions at time scale of tens of seconds. In agreement with [2,7] ionic surfactants on highly hydrophobic surfaces, such as Teflone, Parafilm and polypropylene (advancing contact angle of water CAW ≥ 99°), demonstrated constant value of equilibrium contact angle at $t > 1$ s (i.e. spreading was finished on much shorter time scale). On substrates of higher energy, poly(vinylfluoride), CAW = 78°, and polyetheleneterephthalate, CAW = 77°, spreading continued during much longer, up to 30 s and duration increased with an increase of concentration. Nonionic surfactant, pentaethylene glycol monododecyl ether, $C_{12}EO_5$, demonstrated slow longtime spreading kinetics on all substrates studied in Ref. [19] at concentrations above 0.25 cmc.

It should be emphasized that the spreading exponent at $t > 1$ s according to Ref. [19] was smaller than 0.1, that is surfactant solutions in this case spread slower than pure liquids. This small value have been ascribed in Ref. [19] to adsorption of surfactant onto solid/liquid and solid/air interface. The theoretical basis of the slow spreading of surfactant solutions due to surfactant adsorption on the solid/air interface in the front of contact line was proposed in Ref. [20,21]. Experimental evidence of such adsorption was provided in Ref. [22]. The slow spreading of long duration was found also in Ref. [23], for several surfactant solutions, both ionic and nonionic. Kinetics of spreading in this case was in good agreement with the theory developed in Ref. [20,21].

Despite the numerous studies on the wetting properties of surfactant solutions, and in particular on partial wetting, the precise values of the spreading exponents during the slow stage of spreading and their dependence on the equilibrium contact angle to the best of our knowledge were not addressed in previous studies. Therefore the aim of the present study is to fill this gap.

The wetting performance of any liquid, including surfactant solution can be estimated using the Young equation:

$$\cos\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \quad (1)$$

where θ is the contact angle, σ_{sv} is the solid-vapor surface tension (specific surface energy od solid), σ_{sl} is the solid–liquid surface tension and σ_{lv} is the liquid–vapor surface tension. The partial wetting correspond to the case $1 > \cos(\theta) > 0$ (i.e. $0 < \theta < 90°$) and the larger is $\cos(\theta)$ the better are the wetting properties. It follows from Eq. (1) that the improvement of wetting properties is possible by decreasing σ_{sl} and/or σ_{lv}. The decrease can be achieved by adding surfactants to a wetting liquid. Note, by using of surfactant mixtures the liquid-vapor surface tension cannot be the only criterion to predict spreading performance, because affinity of various components of mixtures to various surfaces can be different. One of such cases is considered below.

To provide the systematic changes in the contact angle we used synergetic mixtures of two surfactants [24], both at concentrations above critical micellar concentration (cmc). One of the surfactants is fluorinated. According to the literature (see Ref. [25] and references herein) fluorosurfactants adsorb readily on water/air interface lowering the surface tension of aqueous solutions to values ~20 mN/m, but their adsorption on hydrocarbon surfaces is much lower. That is why their spreading performance is much worse than it can be expected based on the surface tension value. The wetting properties can be improved by mixing fluorosurfactants with conventional hydrocarbon surfactants. It should be emphasized that despite proven industrial applications of synergetic mixtures of fluoro- and hydrocarbon surfactants (for example, in aqueous film-forming foams used in firefighting [26]) publications on these systems are rather scarce [27]. Therefore another aim of this work is the study of wetting performance of mixtures of fluoro- and hydrocarbon surfactants to provide direct experimental evidence that the synergism in this system is due to their different affinity to the liquid/air and liquid/hydrocarbon interface.

2. Materials and methods

Fluorosurfactant Zonyl FSN-100 (DuPont), octaethylene glycol monododecylether $C_{12}(EO)_8$ (>98%, Sigma), trimethoxy(octadecyl) silane (Sigma–Aldrich, >90%), heptane (HCROMASOLV®, Sigma–Aldrich, >99%), ammonia hydroxide solution (Sigma–Aldrich, 28–30%) are used as purchased. The aqueous solutions of individual surfactants have been prepared in

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