Experimental study of the contact line friction coefficient

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Abstract. Industrial applications use surfactants to control surface tension and wettability of surfaces. Instead of studying prepared solutions, we focus on the movement of the contact line after adding the surfactant. We placed the pedant drop with surfactant to a sessile drop of pure water and filmed the spreading process to obtain friction coefficient of the contact line. Our results confirmed that adding surfactants to sessile droplets drives the contact line movement. Small concentrations of LHS and SDBS as well as high concentrations of SDBS pin droplet and increase the hysteresis. Friction coefficient for cationic CTAB and zwitterionic LHS drops with the concentration increase. Anionic SDBS decreases contact angle, making the surface more hydrophilic and intensifying hysteresis.

1. Introduction

The contact line in liquid-liquid- or liquid-vapor-solid systems plays a significant role in many natural and industrial processes, such as irrigation of plants, staining and coating. The industry, from oil production to agriculture, wants to control the speed of the contact line. To increase oil recovery or improve pesticide treatment, engineers need to calculate the dynamics of the interface and control its movement. To achieve this, researchers use many types of additives, such as polymers, surfactants, and nanoparticles that modify the properties of liquids or solid surfaces. The most common additives are surface-active substances (surfactants) used in oil production or in washing powders.

For the contact line movement, an unbalanced force must occur at the interface

\[ F = \sigma_{sv} - (\sigma_{lv} \cos \alpha + \sigma_{sl}), \]

where \( \sigma \) is interfacial tension coefficient, indexes \( s, l, v \) refer to solid surface, liquid and vapor, respectively.

Until now, the paradigm in hydrodynamics is zero velocity near a wall. But such a model predicts that no force, arbitrarily large, can set the contact line in motion. However, from experiments and everyday life, we know that this is not so. An alternative to this postulation in numerical calculation is the assumption of a constant or “viscous” friction force that occurs at the phase boundary [1].

Simple model from molecular kinetic theory (MKT) assumes that liquid particles at temperature \( T \) (Boltzmann constant \( k_B \)) jump from one adsorption site to another at average distance \( \lambda \) with frequency \( K^0 \) with average concentration on the solid interface \( n \sim \lambda^{-2} \). The velocity depends on instant contact angle:

\[ v = 2K^0 \lambda \sinh \left( \frac{\sigma_{lv} (\cos \theta_v - \cos \theta_l)}{2nk_BT} \right) \]
Although the dynamics of the contact line is a rather complex phenomenon, which strongly depends on the scale [2,3], at low speeds and deviations of the contact angle, the equations of motion become linear.

\[ \sigma_l v (\cos \theta_i - \cos \theta_e) = \xi v \]

where \( \theta_i \) is the instant contact angle, \( \theta_e \) is the equilibrium angle, \( \xi \) is friction coefficient of the contact line, \( v \) is the velocity.

Friction coefficient is proportional to liquid viscosity \( \eta_l \) and molecular flow volume \( v_l \) [4]:

\[ \xi = \frac{\eta_l v_l}{\lambda^3} \exp\left(\frac{\sigma(1 + \cos \theta_e)}{nk_B T}\right) \]

In the case of two-fluid systems, when one liquid moves along the surface and displaces the other, the coefficient of friction of the contact line correlates with the value of the same coefficient for the same liquid when it spreads in air [5]. Friction coefficient is proportional to viscosities product [6]:

\[ \xi = \frac{\eta_1 v_1 \eta_2 v_2}{h\lambda^3} \exp\left(\frac{\sigma(1 + \cos \theta_{e12})}{nk_B T}\right) \]

The main way to study and measure \( \xi \) is spreading a drop of one liquid in the medium of another [7]. Although it is possible to study the dynamics of droplets with surfactants [8, 9], this does not allow predicting the behavior of the contact line after adding surfactants to sessile droplets [10].

In this paper, we study the dynamics immediately after the addition of surfactants. To do this, we put a drop of pure water on a substrate immersed in the decane and let it come into balance. Then, add a drop of water with a surfactant and monitor the change in the contact angle and radius of the drop.

2. Methods

2.1. Setup

We used KRUSS Drop Shape Analyzer (DSA 100) and its software. DSA captures droplet wetting diameter, volume and contact angles. Software approximates the drop shape by ellipse, finds the intersection between baseline and approximation, and calculates the properties (Fig. 1). We set time zero when the pendent drop touches the sessile and the KRUSS automatically made measurements every 0.5 or 1 second. For each substrate and surfactant concentration we performed 3-5 tests, placing the drops at different places on the glass, to obtain statistically significant results.

![Figure 1](image-url) 

**Figure 1.** Picture of the experiment made with KRUSS DSA 100. The implemented software captures contact angle and radius of the droplet.
2.2. Materials
We used hydrophilic quartz surface. The hysteresis of the surface is important in the experiments with moving contact line, since only after overcoming it the contact line starts moving. Table 1 gives the wettability of the substrate in air and in decane and hysteresis of water in decane.

| Table 1. Contact angle of the substrate. |
|-----------------------------------------|
| Purewater | Decane | Water in decane | Water in decane | Water in decane |
| Advancing | Receding | Advancing | Receding | Advancing | Receding |
| 32.92±0.15 | ≤3.7 | 58.16±0.95 | 61.98 | 41.94 |

We used the anionic surfactant sodium dodecyl benzene sulfonate (SDBS, purity>=95%), the cationic surfactant cetyl trimethyl ammonium bromide (CTAB, purity>=99%), and the zwitterionic surfactant Lauramidopropyl Hydroxy SulfoBetaine (LHS, active matter purity 30%) as surfactants. In this work we obtain the interfacial tension with different concentration of surfactants, presented in the supplement. From economic and environmental considerations, the industry applies only low concentration solutions, so we chose the concentrations from zero to slightly higher than CMC.

3. Results
To obtain the friction coefficient, we calculated instant spreading speed using central differences:

\[ v_n = \frac{r_{n+1} - r_{n-1}}{t_{n+1} - t_{n-1}} \]

and fitted the dependence contact angle vs velocity by linear function. (Fig. 2)

![Figure 2](image)

Figure 2. Dependence of the contact angle times interfacial tension on the contact line velocity. For small velocities the dependence is fitted by linear function.

M is mol per liter.

After the coalescence the surfactant pins the drop for 1–10 seconds and then spreading starts. We measured friction coefficient at the end of the spreading process. CTAB and LHS increase the contact
angle, making the surface more hydrophobic, and vice versa for SDBS. Friction coefficient of CTAB solutions is high for low concentration and drops for high concentrations (Fig. 3).

![CTAB Friction Coefficient](image)

**Figure 3.** Dependence of the friction coefficient on the concentration of CTAB. Friction coefficient is obtained by fitting the velocity vs contact angle dependence. M is mol per liter.

LHS shows similar behavior. The friction coefficient decreases with the concentration increase (Fig. 4). It is worth noting that we obtained significant movement of the contact line only for concentrations over 0.05 g/L. For small concentrations the surfactant pins the contact line [11, 12]. Shrinking rate of LHS is smaller than that of CTAB; therefore, experimental errors are larger.

![LHS Friction Coefficient](image)

**Figure 4.** Dependence of the friction coefficient on the concentration of LHS. Friction coefficient is obtained by fitting the velocity vs contact angle dependence.

Similarly with LHS, small concentrations of SDBS (less than 0.37 M) pin the drop, preventing spreading. However, unlike two previous solutions, SDBS friction coefficient increases as we increase concentration. Moreover, concentrations higher than 1 mM also pin the droplet, resulting in huge hysteresis [12] and long and unstable spreading [11].
Figure 5. Dependence of the friction coefficient on the concentration of SDBS. Friction coefficient is obtained by fitting the velocity vs contact angle dependence. M is mol per liter.

Conclusions
Our results confirmed that adding surfactants to sessile droplets drives the contact line movement. Small concentrations of LHS and SDBS as well as high concentrations of SDBS pin the droplet and increase the hysteresis.

Friction coefficient for cationic CTAB and zwitterionic LHS drops with the concentration increase. Both surfactants decrease the contact angle, making the surface hydrophobic. For high concentrations of CTAB (>1mM) we even saw detachment of the drops and their free moving along the quartz substrate after 10 minutes of waiting. We explain this behaviour by enhancement of spreading by the Marangoni flow [13, 14].

Anionic SDBS decreases contact angle, making the surface more hydrophilic and intensifying hysteresis. Friction coefficient for SDBS increases with concentration. Moreover, for >1 mM hysteresis pins the contact line.

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