Surfactant effects on contact line alteration of a liquid drop in a capillary tube

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Abstract. In this paper, the effect of an insoluble surfactant on the moving contact line of an interface between two fluids filling a capillary tube is studied. The governing equations are the incompressible Navier-Stokes equations with the couple of Eulerian fluid variables and Lagrangian interfacial markers. In our model, capillary force plays a role in the fluids motion. Here, we propose that besides lowering the interfacial tension which affects the capillary force, the surfactant also decreases the surface tension between fluids and a solid surface. That condition is applied to the unbalanced Young condition at the contact line. The front-tracking method is used to solve numerically the free boundary motion of the interface. Results show that the surfactant has a significant effect on the motion of the contact line.

1. Introduction

In the petroleum industry, it is well known that surfactants have significant potential for improved oil recovery purposes. There are some evidences and studies that surfactants solution can imbibe into the oil-wet matrix and displace the oil, for example Kralchevsky et. al. [1], Zhang [2], Chang [3], Wu [4], Gupta and Mohanty [5], Mwangi [6].

A surfactant is a substance that, when present at low concentration in a system, has property of adsorbing onto the interfaces of the system and of altering to a marked degree the interfacial free energies of those surfaces [7]. It causes a non-uniform normal (capillary) and tangential (marangoni) stresses which can significantly affect the dynamic of multi-phase flow [8]. In particular for drop on a substrate, the influence is observed in the changes of the contact angles and the contact lines. The surfactant can remove the drops on the substrate by increasing the contact angles (measured from inside the drop) [9].

There are some previous studies with various methods to simulate the contact angle alteration due to surfactant. Since the main focus is on the change of the contact angle, then the boundary conditions at this point pay need attention. Yon and Pozrikidis [10] used the semi-implicit finite volume method to investigate the influence of an insoluble surfactant to the deformation of a viscous drop attached to a plane wall and subjected to an overpassing simple shear flow. They observed the alteration of the contact angle caused by the surfactant, for the case without movement of the contact line. Lai et al. [9] implemented an immersed boundary method for simulating the motion of a drop on a solid substrate under the influence of insoluble surfactant. They considered two immiscible fluids with equal density and viscosity in which the gravity and the van der Waals forces were neglected. For the dynamics of the contact line, they applied the unbalanced Young’s force to the contact line directly. Klinteberg et al. [11] introduced a domain decomposition approach for the interface to simulate the two-phase flow with...
insoluble surfactants and contact line dynamics in two dimensions. To drive the movement of the contact line, they defined the tangential velocity in the vicinity of the contact line and used the Navier slip condition on the wall away from the contact line. Model and numerical explorations based on the Front-Tracking method to investigate the influence of the insoluble surfactant on the motion of an oil drop on a substrate [12]. They used the unbalanced Young’s force at the contact point and the Navier slip condition along the substrate. They stated that the slip coefficient is a crucial factor for the magnitude of the contact line movement.

In this paper we simulate the effect of surfactant to the alteration of the contact angles in a microsystem, which is the capillary effect dominates the inertia of the fluids. At the contact line, we apply the unbalanced Young’s force which is influenced by the surfactant. Here, we propose that the surfactant besides lowering the interfacial tension between fluids, also decreasing the surface tension between solid and fluids.

2. Methods
In this section, we model the motion of two immiscible fluids separated by an interface \( \Sigma \), the boundary conditions, and the dynamics of surfactant at the interface \( \Sigma \) and at the contact line. The fluids with different viscosity \( (\mu) \) and density \( (\rho) \), labelled 1 and 2, are placed in a capillary tube, which is represented by a fixed two-dimensional domain \( \Omega = [0,1] \times [0,h] \). We assume that both fluids are incompressible viscous Newtonian fluids. The motion of the fluids can be formulated by the Navier-Stokes equation [9, 13] and the continuity equation.

\[
\rho_i \frac{\partial u_i}{\partial t} + \rho_i \nabla u_i = -\nabla p_i + \nabla \cdot (\nabla u_i + \nabla^T u_i) + f, \quad i = 1,2
\]

(1)

\[
\nabla u_i = 0,
\]

(2)

where \( p \) is the pressure, \( u \) is the velocity field, \( t \) is the time, and \( f \) is the capillary force, as defined in eq (3). Since we consider a microsystem, throughout this paper we neglect the gravity force.

Following to our previous work in Yulianti, et al [12], the interface \( \Sigma \) is parameterized by \( X(\alpha, t), \quad 0 \leq \alpha \leq L_{\rho} \). The capillary force from the interface is expressed by:

\[
f(x, t) = \int_{\Sigma} \frac{\partial}{\partial \alpha} (\sigma(\alpha, t) \tau(\alpha, t)) \delta(x - X(\alpha, t)) d\alpha,
\]

(3)

where \( \delta(x) \) is the two-dimensional dirac delta function, \( \sigma \) is the interfacial tension, and \( \tau \) is a unit tangent to the interface:

\[
\tau(\alpha, t) = \frac{\partial X}{\partial \alpha} \left( \frac{\partial X}{\partial \alpha} \right)^{-1}.
\]

The movement of the interface follows the velocity fields:

\[
\frac{\partial X(\alpha, t)}{\partial t} = u(X(\alpha, t), t) = \int_{\Omega} u(x, t) \delta(x - X(\alpha, t)) dx.
\]

(4)

The interfacial tension \( \sigma \) decreases proportional to the surfactant concentration \( \Gamma \), which is can be stated by the simplified nonlinear Langmuir equation [7]:

\[
\sigma(\Gamma) = \sigma_c (1 + \ln(1 - \xi \Gamma)),
\]

(5)

where \( \sigma_c \) is the interfacial tension of the clean interface, and \( \xi \) is a parameter that measures the sensitivity of interfacial tension due to the change in surfactant concentration [9, 14].

We assume that the surfactant is insoluble. The changes in the surfactant concentration at the interface are governed by a convection equation:

\[
\frac{\partial \Gamma}{\partial t} + (\nabla_s \cdot u) \Gamma = 0,
\]

(6)

where \( \nabla_s \) is the gradient of the interface.

Kralchevsky [1] stated that there were many experimental indications that surfactant solution may dissolve or diffuse into glass substrate. It was been detected in surface-force measurements. Based on
that study, we argue that those facts implies to the alteration of the values of the two superficial tension $\sigma_{s1}, \sigma_{s2}$, where $\sigma_{s1}$ and $\sigma_{s2}$ are the surface tension between the solid surface to the fluid 1 and the fluid 2, respectively. Here we define that the decrease of $\sigma_{si}$ also satisfy the Langmuir equation (2):

$$\sigma_{si}(\Gamma) = \sigma_{ci}(1 + \ln(1 - \xi \Gamma)), \quad i = 1, 2. \quad (7)$$

The condition (7) affects the surface forces acting at the contact lines, which is expressed by the dynamic Young equation:

$$\sigma_{s2}(\Gamma) = \sigma_{s1}(\Gamma) - \sigma(\Gamma) \cos(\theta), \quad (8)$$

where $\theta$ is the contact angle measured from fluid 1.

At the boundaries $x = 0, x = l, y = 0, \text{and} \ y = h$, we assume that there is no penetration of fluid through the solid surfaces. Furthermore, to avoid a non-integrable singularity on the moving contact line problems, at the solid surfaces, i.e. $y = 0$ and $y = h$ we apply the slip condition:

$$v = 0, \quad u = u_* - \beta \frac{\partial u}{\partial y}, \quad (9)$$

where $u_*$ is the horizontal velocity near the solid surface. Here, $\beta$ acts as the slip length which may represent the friction coefficient and measures how large the velocity near the solid surface decreases.

3. Results and Discussion

In this section we report the numerical results. The equation (1)-(6) together with boundaries (7)-(9) are solved numerically by the Front Tracking Method, which available at Tryggvason, et al [15]. We chose the method because the spurious flow problem that may arise in the simulation at low capillary number is less pronounced [15].

3.1. Convergence Test

To validate our numerical scheme, here we demonstrate the convergence of velocity, area of fluid 1, and total of surfactant concentration. The sequence size of Cartesian mesh that we used for the test is $dx = dy = \frac{1}{10^p}, \frac{1}{20^p}$ and $\frac{1}{10^p}$. Here we use the domain $\Omega = [0, 1] \times [0, 0.5]$. As an illustration, we use parameters $\mu_1 = 0.15, \mu_2 = 0.1, \rho_1 = 1, \rho_2 = 0.9, \sigma_c = \sigma_{csi} = 1$, and $\beta = 0.33 \ dy$. The initial condition for the velocity field are $u = 0, \ v = 0$. In this simulation, we set the fluid 1 is more-wet than the fluid 2. So, the contact angle of the fluid 1 is no more than $90^\circ$. The initial shape for the interface is presented in Figure 1.

![Figure 1. The initial condition.](image)

We choose $A_{\text{ref}}$ and $I_{\text{ref}}$ are initially the area of fluid 1 and total surfactant concentration, respectively. For the velocity component $u$, we use the values obtained from the finest grid as our reference solution. The mesh refinement result of the velocity component $u$, area of fluid 1, and the total surfactant concentration is shown in Table 1. Based on the table, the error of velocity component $u$ and area of drop decrease when the mesh is refined. The total of surfactant concentration is absolutely remaining constant. These results suggest that our constructed numerical schemes are quite accurate.
Table 1. The mesh refinement values of velocity component \( u \), area of fluid 1, and total surfactant concentration

| \( dx=dy \) | \( \frac{|u-u_{ref}|}{u_{ref}} \times 100\% \) | \( \frac{|A-A_{ref}|}{A_{ref}} \times 100\% \) | \( \frac{|\Gamma-\Gamma_{ref}|}{\Gamma_{ref}} \times 100\% \) |
|---|---|---|---|
| \( \frac{1}{10} \) | 22.84 | 1.36 | \( 6.66 \times 10^{-14} \) |
| \( \frac{1}{20} \) | 12.69 | 1.10 | \( 4.44 \times 10^{-14} \) |
| \( \frac{1}{40} \) | - | 0.86 | \( 4.44 \times 10^{-14} \) |

\( u_{ref}=0.09, A_{ref}=0.26, \Gamma_{ref}=1. \)

3.2. Solution

We compare the motion of the contact line for clean and contaminated-surfactant interface. Based on the equation (5), \( \xi=0 \) implies no surfactant. For the contaminated case, here we use \( \xi=0.45 \). The solutions are computed up to time \( t=0.2 \), where at that time the trend of the drop shape change can be described.

Figure 2 shows the velocity field of two-phase fluids for clean interface at \( t=0.2 \). Because of the density and the viscosity of the two fluids are different, the capillary force drives the fluids to move. The slip condition (equation (9)) and the curvature of the interface causing the contact line at the bottom \(( y=0 \) moves in the direction to previous curvature. It can be observed that the shape of the interface is not changing much from the initial shape. The fluid 1 is still more-wet than the fluid 2.

![Figure 2: The shape of interface without surfactant at \( t=0.2 \).](image)

The dynamic of two-phase fluids with surfactant on the interface is shown in Figure 3. Decreasing of the \( \sigma_{sl} \) causing the unbalanced young condition at the contact line. As a result, the contact line gradually moves toward the area fluid 1. The upper contact point moves ahead of the lower contact point, due to a greater unbalanced Young’s force there. Furthermore, due to the conservation of mass principle, the movement of the two contact lines toward the fluid 1, causing the velocity field between of the two contact lines flow to the fluid 2. Therefore, the contact angles of fluid 1 become larger than the fluid 2. In other words, fluid 1 becomes less wettable. This result is in accordance with others previous experimental studies that the surfactant solution reversing the wettability of a substrate.
Figure 3. The dynamic of the interface contain surfactant at $t = 0.05$, $t = 0.1$, $t = 0.15$, and $t = 0.2$.

Distribution of the surfactant concentration and its correspondence value of the surface tension are given in Fig. 4. We present it in polar coordinate to conform the position of each point of the interface. Initially, surfactant concentration is uniformly distributed along the interface, $\Gamma(\alpha,0)=1$. Based on simulation shown in the Figure 3, the contact line at $y = 0$ moves into direction of fluid 1. Because the dynamics of surfactant follows the velocity field at the interface, and the velocity field dominantly flow toward into the fluid 1 at the bottom area, then the surfactant concentration at that area is larger than others area.

Figure 4. The distribution of surfactant concentration at $t = 0$ and $t = 0.2$, and the value of the surface tension at $t = 0.2$
4. Conclusion
In this paper we present a mathematical model of two-phase flow with insoluble surfactant and contact line dynamics in a capillary tube. Here we argue that surfactant besides lowering the interfacial tension between fluids, also decreasing the surface tension between solid and fluids. The argument is expressed in terms of Langmuir equation, and then is applied to the unbalanced Young equation as a boundary condition at the contact line. From the simulations, we found that the presence of surfactant at the interface significantly affect the contact line dynamics; it reverse the wettability of a substrate.

5. References
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Acknowledgments
This research was supported by funding of DIPA (DIKTI) 2017.