Effect of a Small Insoluble Surfactant Concentration on the Shape of a Steady Sessile Drop

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Abstract. In this research, we constructed a mathematical model to describe the influence of a surfactant concentration on the shape of a steady sessile drop, more specifically to the alteration of its contact angle. We used the Young-Laplace equation the shape of drop and proposed a model for the distribution of the surfactant at the surface. Both equations are combined and then solved numerically. A constant sessile drop volume is a boundary condition in the model. Results show that a concentration of the surfactant on the drop surface causes the value of the drop's contact angle to be bigger than the free surfactant one. This result corresponds to the fact that the wettability of a substrate can be altered by the surfactant solution.

Keywords: Asymptotic approximation, Drop Shape, Steady State, Surfactant

1 Introduction

Surfactants are typically molecules with two distinct chemical properties [1]. It can influence the properties of surfaces and interfaces [2]. This effect has been utilized in many industrial processes. For example, in the petroleum industry surfactant is used to increase oil production by modifying the wettability of the rock's surface to become more water wet. As a result, the oil becomes less sticky and then imbibes spontaneously from the porous rock [3].

The effect of surfactant on the changing wettability of a substrate has been much studied, both experimentally [3-6] and numerically [7-8]. In general, their results showed that the surfactant leads to an increase in the contact angle of a sessile drop. However, studies of this problem from the analytical mathematical point of view are still very limited [9-10].

The present work concerns with the change of a substrate wettability property due to the presence of surfactant on the drop surface, at the steady condition. Since the wettability is represented by the value of the contact angle between the fluid and the substrate [11], the investigation is carried out on the determination of the shape of a steady sessile drop.

F. Khoerunnisa et al. (eds.), *Proceedings of the 9th Mathematics, Science, and Computer Science Education International Seminar (MSCEIS 2023)*, Advances in Social Science, Education and Humanities Research 860,
https://doi.org/10.2991/978-2-38476-283-5_42

The problem of a steady shape non-surfactant sessile drop has been solved by many researchers. Finn [12] described the capillarity phenomena, including the shape of symmetric sessile drops. Skinner, *et al.* [13] developed a model to measure contact angles using as input parameters the liquid surface tension, the drop volume, and the contact diameter of the drop. They analyzed the drop shape numerically and experimentally. Rienstra [14] derived an asymptotic solution for the non-surfactant-drop shape with small and high bond numbers. Rio and Neumann [15] presented axisymmetric drop shape analysis techniques and advanced numerical methods for the computation of interfacial tensions and contact angle of pendant and sessile drops. Stalder *et al.* [16] presented a drop shape analysis method for measuring contact angles and surface tensions from sessile drop images. They used a first-order approximation of the Young–Laplace equation to provide an analytical solution to the contour of sessile drops at a low computational burden. Prabhala *et al.* [17] developed an approximate analytical solution for the shape of a non-axisymmetric sessile drop using regular perturbation methods to the circular footprint of a spherical cap. Danov, *et al.* [18] used a drop shape analysis approach to determine surface tension of drops with isotropic and anisotropic surface stress distributions. They proposed a method based on processing data for the digitized drop/bubble profile and capillary pressure.

In the present paper, we include a surfactant parameter that decreases the surface tension of drop. We also propose a model for the distribution of the surfactant at the drop's surface. To obtain the shape and the value of the contact angle, the model is then solved numerically.

2 Method

In this paper, we construct a mathematical model for the shape of a steady sessile drop that contains surfactant. First, we outline the full formulations of the problem together with their boundary conditions. We solved the equations numerically in two steps, that is the boundary condition problem and then the initial value problem. The numerical simulation shows the shape of the drop and the value of its contact angle.

3 Results and Discussion

3.1 The Mathematical Model

We consider a steady state sessile drop of densityρ, viscosity μ, and volume V placed on a horizontal plane. An insoluble surfactant is present on the drop surface. To describe the shape of drop, here we use the cylindrical coordinates (r, θ, z), such that the z -axis is vertically directed downward, i.e. in the direction of the gravity. Here are the assumptions:

1. The drop is symmetry to the z -axis.
2. The drop is in stationary condition (or the velocity field does not take place). Consequently, the effect of the drop's viscosity can be neglected, and the drop's pressure gradient is balanced with the gravity force only, i.e.$\nabla p = \rho \boldsymbol{g}$. So:

$$p = p_0 + \rho g z, \tag{1}$$

where the constant p_0 is the pressure at $z = 0$.

3. The surfactant is insoluble. Its concentration is sufficiently small and affects only the decrease of the surface tension, without any rheological effects.

Following the work of Rienstra [14], the shape of the drop is determined by the Young-Laplace Equation, which is the condition that at the surface the pressure difference with the outside is proportional, by a factor γ (the surface tension), to $\nabla.\boldsymbol{n}$ (equal to the sum of the principal curvatures of the surface), where $\boldsymbol{n}$ denotes vector field, (outward) normal to the surface at the surface. We define ψ is the azimuthal tangent angle of the surface ($tan\,\psi = dz/dr$), parameterized by arc length s (see Figure 1), such that

$$\boldsymbol{n} = (sin\,\psi, -cos\,\psi),\;\; r = \int_0^s cos\,\psi\, ds',\;\; z = \int_0^s sin\,\psi\, ds'$$

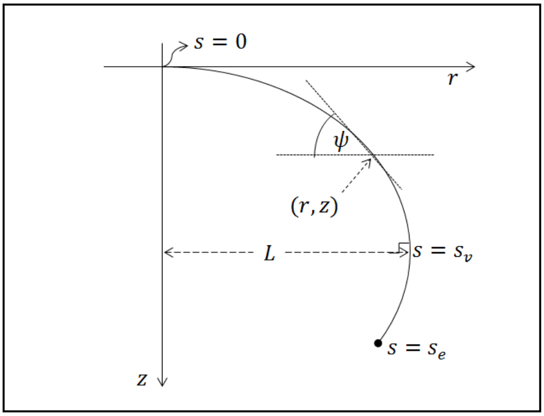

Fig. 1 Geometrical interpretation of the model.

Then, we have

$$\nabla.\boldsymbol{n} = \frac{\partial n_r}{\partial r} + \frac{\partial n_z}{\partial z} + \frac{n_r}{r} = \frac{d\psi}{ds} + \frac{\sin\psi}{r}, \tag{2}$$

where $s \in [0, s_e]$, s_e is the right end point for the domain interval, which is determined by the value of a fixed cross section area L_d:

$$\int_0^{s_e} r \sin\psi\, ds = L_d. \tag{3}$$

The presence of the insoluble surfactant at the drop surface was known to decrease the surface tension [1, 2]. So, here we assume that the decline satisfies:

$$\gamma(s) = \gamma_0 - E_1 \bar{\Gamma}(s) \tag{4}$$

where E_1 is the elasticity, $\bar{\Gamma}$ is the concentration of the surfactant along the drop surface, and γ_0 is the value of the surface tension correspondence to the absence of the surfactant. For distribution of the surfactant $\bar{\Gamma}(s)$, due to the lack of experimental data, we refer to Lai, *et al*. [7], where the distribution of the surfactant concentration on the surface was a non-decreasing function with the maximum value at the contact angle. Therefore, here we propose that the distribution of the surfactant concentration satisfies:

$$\bar{\Gamma}(s) = \bar{A} + As^2 \tag{5}$$

where $\bar{A}$ is the surfactant concentration at the apex of the drop, and A is a positive constant. The even function of (5) is also chosen due to our first assumption. Hence, Equation (4) can be written as:

$$\gamma(s) = \gamma_c - E_2 s^2 \tag{6}$$

with $\gamma_c = \gamma_0 - E_1\bar{A}$, and $E_2 = E_1 A$. Note that the positivity of the surface tension value implies a limitation for the value of E_2 .

Considering (1), (2), and (6), we obtain an equation for the shape of the drop given by:

$$\frac{d\psi}{ds} + \frac{\sin\psi}{r} = \frac{p_0}{\gamma_c - E_2 s^2} + \frac{\rho g z}{\gamma_c - E_2 s^2} \tag{7}$$

with boundary conditions: $\psi = 0$ at $s = 0$; $\psi = \frac{\pi}{2}$ at $r = L$ or some $s = s_v$, where L is the largest radius of the circular horizontal cross section, and $s \in [0, s_e]$ where s_e satisfies (3).

Equation (7) and its boundary conditions are made into dimensionless form by applying the following scaling: $t = s/L, \tilde{\xi} = r/L, \tilde{\eta} = z/L$. Then, we have

$$(1 - Et^2)\left(\frac{d\psi}{dt} + \frac{\sin\psi}{\tilde{\xi}}\right) = \tilde{\beta} + B\tilde{\eta}, \quad t \in [0, t_e] \tag{8}$$

$$\psi(0) = 0, \tag{9}$$

$$\psi(t_v) = \pi/2 \quad \text{at } \tilde{\xi} = 1. \tag{10}$$

$$\int_0^{t_e} \tilde{\xi} \sin\psi \, dt = \widetilde{L_d}, \tag{11}$$

with $\tilde{\beta} = \frac{p_0 L}{\gamma_c}, t_v = \frac{s_v}{L}, t_e = \frac{s_e}{L}, \widetilde{L_d} = \frac{L_d}{L^2}, B = \frac{\rho g L^2}{\gamma_c}$ which is known as the Bond number, and $E = \frac{E_2 L^2}{\gamma_c}$ is a parameter representing the presence of surfactant. Notice that the values t_v, t_e, and $\tilde{\beta}$ are parts of the solution.

3.2 The Solution

To study the influence of the surfactant on the alteration of the drop's contact angle, we solve (8) - (11) numerically. For our numerical solutions, we refer to the work of Rio and Neumann [15]. We solve Equation (8) - (11) as follows: First, we use the finite difference method by applying the Matlab bvp4c code to solve the boundary value problem (8) - (10) in $[0, t_v]$. As the results, we obtain the profile shape in $[0, t_v]$, the constant value $\tilde{\beta}$, and the area of drop along $[0, t_v]$. Using those obtained values in domain $[0, t_v]$, we then solve the initial value problem in $[t_v, t_e]$ by the explicit Runge-Kutta method (Matlab ode45 code). The value of t_e is determined such that the Equation (11) is satisfied.

As an illustration, we use $B = 4$, $\widetilde{L_d} = 0.6$, and drag the results such that the contact angle at $z = 0$. The shape profile for the contained-surfactant drop ($E = 0.05$) and the free-surfactant drop ($E = 0$) are shown in Figure 2. From the figure, we observe that there is a slightly different between the two shapes of drops. When we zoom-in, the contact angle for the contained-surfactant drop is bigger than the free-surfactant one. The numerical solution for the values of $\tilde{\beta}, t_v, t_e$, and $\psi(t_e)$ are shown in Table 1. From the table, it is observed that the value of contact angle $\psi(t_e)$ for the contained-surfactant drop is bigger than the free one. These results clarify that the surfactant has an effect to increase the contact angle value of the sessile drop [8, 19].

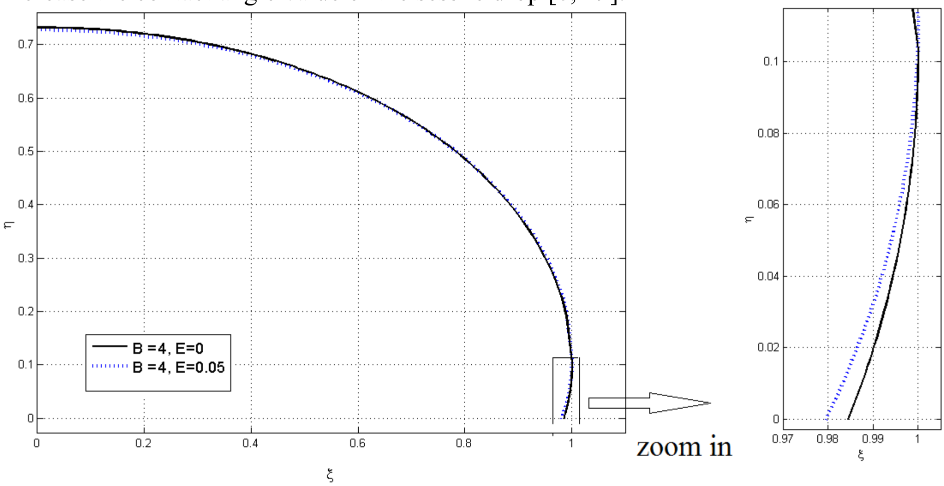

Fig. 2. The shape of drop for $B = 4$.

Table 1 The numerical results.

	$\tilde{\beta}$	t_v	t_e	$\psi(\tau_e)$
$E = 0$	1.174	1.298	1.403	1.876
$E = 0.05$	1.153	1.289	1.404	1.943

4 Conclusions

The influence of an insoluble surfactant concentration to the alteration of the shape of a steady sessile drop was studied. The investigation was emphasized on the changes in the value of the drop's contact angle. The equation for the shape of drop which is combined with the surfactant distribution was solved numerically. Results showed that a concentration of the surfactant was able to increase the value of the drop's contact angle.

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