

SURFACTANT EFFECTS ON THE MOTION OF A DROPLET IN THERMOCAPILLARY MIGRATION

Y. S. CHEN, Y. L. LU, Y. M. YANGt and **J. R.** MAA

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 701, China

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Abstract--A nearly density matched system (water/n-butyl benzoate) was used to study the effects of surfactants (sodium dodecyl sulfate and Triton X-100) on the motion of droplet in thermocapillary migration under earth gravity. The thermal coefficient of interfacial tension over a temperature range of $20-50^{\circ}$ C was determined for water/n-butyl benzoate by a method which is suitable for both equal and unequal density liquids, and consequently the theoretical prediction for the motion of water droplet in n -butyl benzoate in the presence of a temperature gradient can then be made. Experimental results of thermocapillary migration for the clean interface were found to be 19-30% less efficient than the theoretical predictions. This is attributed to the thermal convection effect and/or the trace surface active impurities effect which are neglected in the theory. On the other hand, the experimental results reveal that thermocapillary migration of droplet is significantly depressed by the deliberately introduced water soluble surfactants. Seven hundred parts per million SDS and 1600 ppm Triton X-100 were both shown to inhibit the thermocapillary effect completely. No theoretical model, however, is available in the literature for describing this effect of soluble surfactants. © 1997 Elsevier Science Ltd. All rights reserved.

Key Words: thermocapillary migration, density matched system, surfactant effect

1. INTRODUCTION

The motion of liquid drops (and gas bubbles) under earth gravity has generated a lot of interest for many years. The earliest investigations of the motion of a liquid drop in another immiscible liquid were carried out in the early part of this century. The question about the effect of a third component as an impurity has been addressed by numerous investigators. It is well known that in the presence of trace impurities, a dramatic reduction occurs in the terminal velocity of the droplet as compared to the predicted Hadamard-Rybczynski formula (Levich 1962). The commonly accepted picture involves the surface active impurity being swept by the motion along the interface to the rear of the drop, leading to gradients of interfacial tension on the drop surface. The resulting tangential stress opposes motion along the interface with a consequent increase in the hydrodynamic drag exerted on the drop. The limiting situation would be that corresponding to a rigid surface of the same radius. Several fluid mechanical descriptions of the motion of drops under isothermal conditions in the presence of surfactants have been developed and the literature on this subject is discussed in Quintana (1992).

With the advent of space flight, the study of flows under microgravity conditions was strongly motivated by practical considerations. When a liquid drop is placed in another liquid in the presence of a temperature gradient, the drop will usually move in the direction of warmer fluid. This motion is a consequence of the variation of the interfacial tension with temperature, and is termed thermocapillary migration. Because of the predominance of buoyancy forces on earth, the motion caused by interfacial tension is often neglected. In the absence of gravity force, however, interfacial forces play an important role in determining the thermocapillary flows driven by a temperature gradient. One might note that interracial tension gradients can also be important in the presence of a gravitational field as well in the case of very small drops or when the densities of the drop and the continuous phase are very close to each other. Since the first illustration of the concept by Young *et al.* (1959), much has been written on this subject. The literature on the motion of drops and bubbles due to thermocapillary has been reviewed by Subramanian (1992).

tAuthor to whom correspondence should be addressed.

A few experiments on liquid drops have revealed that it is quite possible for surfactant to play a role in influencing thermocapillary motion. Barton and Subramanian (1989) observed that ethylsalicylate drops suspended in diethylene glycol migrated properly as expected in a temperature gradient. With the addition of relatively small quantities of Triton X-100, however, they found the effect to be retarded. Nallani and Subramanian (1993) reported the results from experiments on the motion of methanol drops in a silicone oil under the combined action of gravity and thermocapillarity. Their data were not consistent with the predictions of the classical model of Young *et al.* (1959) even though convective heat transport effects were quite negligible in the experiments and virtually all of the assumptions made in the model were fulfilled. The authors attributed this discrepancy to the violation of the crucial assumption of a clean interface. Although it was difficult to identify the impurity species that might be acting as a surfactant, they interpreted the data by using the simplest possible model incorporating surfactant effects, namely the stagnant cap model, which was developed by Kim and Subramanian (1989a).

For insoluble surfactants which remain on the interface and do not diffuse or otherwise get transported to the bulk, two principal models have been developed for theoretical description of thermocapillary drop motion in the presence of them. The first is the so-called stagnant cap model in which the surfactants are assumed to collect at one end of the spherical droplet, forming a cap on which a no-slip boundary condition is imposed (Kim and Subramanian 1989a). On the other hand, for insoluble surfactants which do diffuse along the interface, a different model is used in which the surfactant concentration is obtained by solving an interfacial convective-diffusion equation, and the surface tension is taken to be a function of surfactant concentration (Kim and Subramanian 1989b, Nadim and Borhan 1989). As a result, not only does the drop offer more resistance to motion, but also the thermocapillary effect is confined to only the free portion of its surface. The consequence is substantial retardation of the droplet. If sufficient surfactant is present, the entire interface can become stagnant, and thermocapillary drift can be completely arrested.

As mentioned above, it seems that theoretical descriptions of insoluble surfactant effect on the motion of a droplet in thermocapillary migration have been established. Unfortunately, experimental data for direct comparisons are not yet available since properly controlled experiments have not been performed to date. Furthermore, for systems containing a soluble surfactant, the effect of insoluble surfactant as mentioned earlier is counter-balanced by exchange of surfactant between the interface and the bulk solution. This exchange involves an adsorption at the front of the drop and a desorption at the rear of the drop, and it may be opposed by slow diffusion into the bulk of the solution or by slow adsorption-desorption kinetics. The droplet motions without and with soluble surfactant in the drop phase under the combined action of gravity and a vertical temperature gradient are schematically shown in figure 1.

To the authors' knowledge, no systematic study of soluble surfactant effect on thermocapillary migration of droplet has ever been performed experimentally or theoretically in the literature. The purpose of this work is to report results from experiments conducted on water drops, in which various amounts of sodium dodecyl sulfate and Triton X-100 were added, migrating in n -butyl benzoate. This is a density matched system wherein an upward temperature gradient is established in a liquid, and drops of a second liquid are inserted at a location where the two densities are matched. The drops migrate upward in the temperature gradient until a new stationary location is reached corresponding to a balance between the thermocapillary force and gravity. In this work, the effects of soluble surfactants in the dispersed phase on the motion of droplets in thermocapillary migration are emphasized.

2. THEORETICAL CONSIDERATIONS

2. I. Without surfactant

The classical theoretical prediction of Young *et al.* (1959) for the terminal velocity, U_x , of a drop under combined action of gravity and a uniform vertical temperature gradient is given as

$$
U_x = -\left[\frac{2R^2g(\hat{\rho} - \rho)(\mu + \hat{\mu})}{3\,\mu(2\,\mu + 3\,\hat{\mu})} + \frac{2Rk}{(2\,\mu + 3\,\hat{\mu})(2k + \hat{k})}\frac{d\sigma}{dT}T'\right]
$$
[1]

where a circumflex denotes a variable associated with the drop phase, ρ , μ and k are density, viscosity, and thermal conductivity, respectively. R is the drop radius, g is the gravitational acceleration, $d\sigma/dT$ is the temperature gradient of interfacial tension, and T' is the upward temperature gradient imposed in the continuous phase fluid at infinity. A positive value of U_{α} in [1] implies upward drop motion. It should be noted that the theory assumes negligible convective transport effects as compared to those of molecular transport. Furthermore, physical properties are assumed constant except for the interfacial tension.

For a density matched system, as described earlier, the drop may reach a stationary position corresponding to a balance between the thermocapiilary and gravitational forces. When the migration velocity vanishes, one obtains from [1]

$$
\rho - \hat{\rho} = \frac{3 \mu k}{g(\mu + \hat{\mu})(2k + \hat{k})} \frac{1}{R} \frac{d\sigma}{dT} T'.
$$
 [2]

Provided that the temperature range is small, the densities of the continuous and drop phases can be assumed to vary linearly with temperature:

$$
\rho = \rho_0 + a_1 (T_{eq} - T_0) \tag{3}
$$

$$
\hat{\rho} = \rho_0 + a_2 (T_{\text{eq}} - T_0) \tag{4}
$$

where T_{eq} is the temperature at which the drop is stationary, a_1 and a_2 are characteristic constants for continuous phase and drop phase fluids, respectively, and ρ_0 is the matched density at temperature T_0 . For water/n-butyl benzoate,

$$
a_1 = -0.855 \text{ kg m}^{-3} \text{ K}^{-1}
$$
, $a_2 = -0.315 \text{ kg m}^{-3} \text{ K}^{-1}$, $\rho_0 = 995.03 \text{ kg m}^{-3}$, $T_0 = 32^{\circ}\text{C}$. [5]

Figure 1. Droplet motions with and without soluble surfactant in the drop phase under the combined action of gravity and vertical temperature gradient.

Substituting [3] and [4] into [2], one can write

$$
T_{\rm eq} = T_0 + \left[\frac{3 \ \mu k}{a g (\mu + \hat{\mu}) (2k + \hat{k})} \right] \left(\frac{1}{R} \frac{d \sigma}{d T} T' \right) \tag{6}
$$

in which $a = a_1 - a_2$.

Therefore, the temperature at which the droplet is stationary is a function of droplet size, R , and the vertical temperature distribution, T' , for a specific density matched system. For constant T' , small droplets would move farther than large ones. In this work, experiments were conducted to measure T_{eq} with R and T' as controlled variables. This has been used for a comparison between theoretical prediction and experimental results.

2.2. With surJactants

As mentioned earlier, no appropriate model is available for describing the effect of soluble surfactant on thermocapillary migration of droplet for the present. Therefore, it is impossible to make any comparison between the predictions of a physically realistic model and the experimental data. Nevertheless, it is possible to pursue merely a model which permits us to interpret the data. The stagnant cap model of Kim and Subramanian (1989a) is chosen for this purpose. The counterpart of [6] for thermocapillary migration of a drop, in the presence of a stagnant cap of an insoluble nondiffusing surfactant, is given as

$$
T_{\rm eq} = T_0 + \frac{3 \ \mu k (2 \pi - \varphi) [\varphi \mu + 2 \pi (2 \ \mu + 3 \ \hat{\mu})]}{2 \pi a \mathbf{g} (\mu + \hat{\mu}) [\varphi \mu + 2 \pi (2 \ \mu + 3 \ \hat{\mu}) (2 k + \hat{k})]} \left(\frac{1}{R} \frac{d \sigma}{d T} T' \right).
$$
 [7]

In [7], φ is a parameter accounting for the effect of surfactant and varies from 0 to 2 π . It is related to the cap angle ϕ , as follows:

$$
\varphi = 2\phi + \sin\phi - \sin 2\phi - \frac{1}{3}\sin 3\phi. \tag{8}
$$

Here, $\phi = 0$ corresponds to a clean interface and $\phi = \pi$ corresponds to an interface covered completely by surfactant. Thus, the drop would mimic a rigid sphere in this limit.

3. EXPERIMENTAL

Examples of experiment performed on density matched systems may be found in papers by Hahnel *et al.* (1989) and Rashidnia and Balasubramaniam (1991). Since thermocapillary forces are in general negligible with respect to buoyancy forces, the only successful possibility to study thermocapillary migration of droplet under gravity exists in the application of the Plateau configuration. Water/ n -butyl benzoate combination, which is the same density matched system studied by Hahnel *et al.* (1989), was used in this work. As shown in figure 2, it can be seen that these two immiscible liquids possess the same density at 32° C and the density of *n*-butyl benzoate (the continuous phase) decreases stronger with temperature than the density of water (the drop phase). In an experiment, a stably stratified temperature field can be realized by heating n-butyl benzoate from above and cooling it from below.

A water drop inserted into *n*-butyl benzoate will then be driven by buoyancy force, F_b , in the direction of equal density point. Consequently, in equilibrium all water drops independent of their size should be localized at the temperature level of equal density. However, as a result of thermocapillary convection, an additional interfacial force acts on water drop. The final position of water drop is thus determined by the balance of thermocapillary and buoyancy forces, both of which depend on the drop radius but in a different manner. Since the interfacial force is proportional to the drop surface area and the gravitational force is proportional to the drop volume, smaller water drops will be displaced farther from the level of equal density than larger ones. The direction of the displacement is determined by the sign of the thermal interfacial tension coefficient $d\sigma/dT$. Because water/n-butyl benzoate system possesses a negative thermal coefficient, as will be described later, the equilibrium level of thermocapillary and gravitational forces will be above the level of equal density.

Figure 2. Principle of the Plateau configuration for water-n-butyl benzoate system. Buoyancy force F_b acting on a water droplet due to density difference $(\rho - \hat{\rho})$ at various heights z in the test cell subject to a vertical upward temperature gradient.

3.1. Physical properties of water and n-butyl benzoate

Distilled water with specific conductance of about 7.0 \pm 0.5 $\mu\Omega^{-1}$ cm⁻¹ was used as the drop phase, n-Butyl benzoate supplied by TCI Ltd, with purity higher than 99.0% was used as received.

The most important property for thermocapillary migration is the thermal coefficient of interfacial tension $d\sigma/dT$. The interfacial tension/temperature function can be determined by measuring the interfacial tension of mutually saturated liquids at different temperatures. The data may then be suitably fitted, and $d\sigma/dT$ for the best fit line over the measured temperature range can be determined. However, many traditional interfacial tension measurement techniques such as the capillary height method, ring method, and drop weight method, contain a density difference term and, therefore, zero as for the cases of equal density liquids. In this work, the new method proposed by Karri and Mathur (1988) was duplicated for measuring interfacial tension of water and *n*-butyl benzoate over a temperature range of $20-50^{\circ}$ C. The device that is suitable for both equal and unequal density liquid consists of two cups, connected by a U-shaped tube, one leg of which is a capillary tube. The interfacial tension is related to the heights of the liquids in the cups of the U-tube above the interface in the capillary. The readers are referred to Chen (1995) for further details.

Table 1 summarizes the other pertinent physical properties of the fluid system from the literature. It is worthy of note that 32° C is the equal density temperature for this system.

3.2. Surfactants

Sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4N_a$) and polyoxyethylated t-octylphenol (Triton X-100, $CH_3C(CH_3)_2CH_2C(H_3)_2C_6H_4(OCH_2CH_2)_nOH$, $n = 10$) supplied by Sigma Chemical Company and Aldrich Chemical Company, respectively, were used as additives to the drop (water) phase. SDS is a water soluble anionic surfactant and Triton X-100 is also a water soluble but nonionic surfactant. Aqueous surfactant solutions with various concentrations, parts per million (ppm) by

Figure 3. (a) Schematic diagram of the apparatus. (b) Thermocapillary migration assembly.

weight, were prepared by dissolving known amounts of each surfactant in known amounts of distilled water. The concentrations of SDS and Triton X-100 were up to 700 and 1600 ppm, respectively.

3.3. Apparatus and procedure

Figure 3(a) shows the apparatus used in this work. It comprises a thermocapillary migration assembly, two thermostats, an optical table, a travelling optical microscope, a light source, and a data acquisition system. The thermocapillary migration assembly is shown schematically in figure 3(b). It consists of a rectangular cell $(60 \times 30 \times 20 \text{ mm})$ filled with the continuous phase liquid (n-butyl benzoate). The cell is made from two rectangular copper channels and four thickwall Pyrex windows which help to minimize heat loss and the possible perturbation of the temperature field. A compartment is therefore created between the upper and bottom copper plates, which are the lower and upper surfaces of the upper and lower channels, respectively. It is within this cell that the experiments occur. In all of the experiments the upper plate of the cell was maintained at a higher temperature than the bottom plate by connecting the upper and lower channels to higher and lower constant temperature baths, respectively. This results in a stably stratified liquid layer without unwanted flows due to buoyancy in the liquid filling the cell. Sealing by use of epoxy resin

Figure 4. Temperature dependence of interfacial tension for water/n-butyl benzoate.

Figure 5. Comparison between theoretical and experimental results. Without surfactant.

was done to prevent any possible leakage. The experiments were viewed and recorded through the glass windows.

The upper copper plate has one 3 mm diameter hole near the edge. This hole is used to fill the cell with the continuous phase liquid. The lower copper plate has two holes, one 1 mm diameter hole at the center is used for droplet injection, another 3 mm diameter hole near the edge is used for drainage of the continuous phase liquid.

An injector was designed to produce droplets from 0.l to 2 mm. The injector is a 0.5 mm diameter and 33 mm long hypodermic needle and is connected via a 3.18 mm diameter teflon tube to a micro pump, which can be actuated to produce single droplets of volumes up to $50 \mu l$.

For temperature measurement, two calibrated T-type thermocouples extended into the cell through a small slit in the side wall were used. The positions of thermocouple junctions can be determined accurately by the travelling microscope. In a preliminary experiment, the vertical temperature distribution monitored by a moveable thermocouple showed that no significant deviation from a linear temperature profile was noticed under the typical operating conditions of this work. This therefore enables the temperature gradient and the temperature at which the droplet is stationary to be determined by the temperature measurements of two thermocouples at two known positions.

The experimental procedure is as follows. At the beginning of each experiment, the old liquid inside the cell is drained, and the cell is cleaned and rinsed with fresh n-butyl benzoate. The cell is then assembled and filled carefully. The circulating baths are turned on to bring the upper and lower plates of the cell to the desired temperatures. When the vertical temperature field is

System: water/n-butyl benzoate without surfactant. Vertical temperature gradient: 1306 K/m.

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Figure 6. Depression of thermocapillary efficiency by 350 ppm SDS.

Figure 7. Depression of thermocapillary efficiency by 800 ppm Triton X-100.

established the droplet is injected into the cell and its size and equilibrium position are monitored and measured. At the same time, the positions of the two thermocouples are also recorded. After the droplet has reached its final position, a new droplet can then be injected. The procedure is repeated for other runs of different temperature gradient and surfactant concentration.

4. RESULTS AND DISCUSSION

4.1. Thermal coefficient of interfacial tension for water/n-butyl benzoate

Interfacial tension of water/n-butyl benzoate was measured over a temperature range of $20-50^{\circ}$ C. Four measurements were made for each temperature. As shown in figure 4, the symbol and the bar represent the average value and the interval of four measurement values, respectively, for a particular temperature. The thermal coefficient of interfacial tension, $d\sigma/dT$, was determined to be -3.03×10^{-2} mN/m^oC. It is noted that this value of thermal coefficient is somewhat lower than that determined from thermocapillary migration experiments (-4.4×10^{-2} mN/m^oC) for the same density matched system by Hahnel *et al.* (1989).

Figure 8. Concentration effects of surfactants on thermocapillary efficiency.

4.2. Thermocapillary migration

From $[6]$, one found that a drop of radius R under an imposed vertical temperature gradient T' will migrate in another fluid to a stationary position with temperature T_{eq} . This theoretical prediction for water/n-butyl benzoate is shown in figure 5. It is nearly a straight line. The experimental results under four imposed vertical temperature gradients for water/n-butyl benzoate without surfactant are also shown in the same figure. A 'thermocapillary efficiency', $E\%$, is defined as the ratio of the actual to the predicted values of $(T_{eq} - T_0)$ for the given droplet size under the given vertical temperature gradient:

$$
E\% = \frac{T_{eq}(\text{actual}) - T_0}{T_{eq}(\text{predicted}) - T_0} \times 100\%.
$$
 [9]

The data in figure 5 show that experimental results for the clean interface are 19-30% less efficient than the theoretical predictions. One typical set of data are shown in table 2, for example. It is noteworthy that the Marangoni numbers corresponding to the data were also calculated and shown in table 2. The Marangoni number, which can be regarded as the product of Prandtl number and Reynolds number, is defined by

$$
\mathbf{M}\mathbf{a} = \mathbf{R}\mathbf{e} \quad \mathbf{Pr} = \frac{R^2}{\mu \alpha} \left| \frac{\mathrm{d}\sigma}{\mathrm{d}T} \right| |T'| \tag{10}
$$

where α is the thermal diffusivity. Strictly speaking the classical theory of Young *et al.* (1959) is only valid for creeping flow and negligible thermal convection ($Re \rightarrow 0$, $Ma \rightarrow 0$).

Obviously, the 'high' values of Ma may be one of the reasons which cause the deviation from theoretical predictions. As mentioned above, however, Nallani and Subramanian (1993) found that even though convective heat transport effects were quite negligible in their experiments and virtually all of the assumptions made in the model of Young *et al.* (1959) were fulfilled, their data were not either consistent with the theoretical predictions. From the foregoing analysis, it then comes to a tentative conclusion that the lower efficiency of the clean interface may be attributed to the thermal convection effect and/or the trace surface active impurities effect which are neglected in the theory.

Samples of surfactant effect on thermocapillary migration of water droplet are shown in figures 6 and 7 for 350 ppm SDS and 800 ppm Triton X-100, respectively. And average thermocapillary efficiencies were found to be depressed to 52 and 14%, correspondingly. As also shown in figures 6 and 7, the corresponding cap angles, ϕ , of the stagnant cap model of Kim and Subramaniam (1989a) for 350 ppm SDS and 800 ppm Triton X-100 are evaluated to be about 70 and 110 $^{\circ}$,

respectively. It should be noted that this is not an accurate interpretation of the data because SDS and Triton X-100 are soluble rather than insoluble surfactants. This quantification is just for convenience.

Table 3 shows results of thermocapillary migration experiments for surfactant SDS. Depression of thermocapillary efficiency was observed. The experimental results for surfactant Triton X-100 are shown in table 4. Seven hundred parts per million SDS and 1600 ppm Triton X-100 were both found to inhibit the thermocapillary effect completely. Under such conditions, water droplet descended from the injection point onto the cool plate, which was always controlled somewhat higher than 32° C, rather than ascending to a stationary point above that of equal density.

Concentration effects of SDS and Triton X-100 on thermocapillary efficiency are shown in figure 8. Significant depression was found for both surfactants but with a different trend. To the authors' knowledge, this is the first systematic study and evidence of soluble surfactant effect on the motion of droplet in thermocapillary migration.

5. CONCLUSIONS

Systematic study of soluble surfactant effect on thermocapillary migration was performed experimentally in this work. Water/n-butyl benzoate was selected as a density matched system to study the effects of sodium dodecyl sulfate and Triton X-100 on the motion of water droplet in thermocapillary migration under earth gravity. Some conclusions can be drawn from the experimental results.

(1) The thermal coefficient of interfacial tension, *da/dT,* was determined to be -3.03×10^{-2} mN/m^oC for water/n-butyl benzoate. Temperature dependence of interfacial tension over a temperature range of $20-50^{\circ}$ C can be satisfactorily described by a linear correlation

$$
\sigma = 23.67 - 3.03 \times 10^{-2} T.
$$

(2) In the absence of intentionally introduced surfactant, experimental results of thermocapillary migration were found to be 19-30% less efficient than the classical theoretical predictions of Young *et al.* This is attributed to the thermal convection effect and/or the trace surface active impurities effect, which were neglected in the theory.

(3) Thermocapillary migration is significantly depressed by the deliberately introduced water soluble surfactants. Seven hundred parts per million SDS and 1600 ppm Triton X-100 were both shown to inhibit the thermocapillary effect completely. The relationship between thermocapillary efficiency $(E, \%)$ and surfactant concentration (C, ppm) was correlated by

$$
E = 75.03 - 1.19 \times 10^{-2}C - 1.74 \times 10^{-4}C^2
$$

for SDS, and

$$
E = 79.08 \exp(-2.54 \times 10^{-3} C)
$$

for Triton X-100. No theoretical model, however, is available in literature for describing this effect of soluble surfactants.

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