Suggestion of New Correlations for Drop/Interface Coalescence Phenomena in the Absence and Presence of Single Surfactant

Khadi-Parsi, Parissa * and Moosavian, Mohammad-Ali
Department of Chemical Engineering, Faculty of Engineering, Tehran University, P.O.Box. 11365-4563, Tehran, I.R. IRAN

ABSTRACT: After designing and constructing a coalescence cell, drop/interface coalescence phenomenon was studied in the absence and presence of single surfactant. Two surface active agents of sodium dodecyl sulfate and 1-decanol were used. Distilled water was used as dispersed phase. Toluene, n-heptane and aqueous 60% (v/v) of glycerol were selected as continuous phases, separately. It was found that the coalescence time increased with both drop size and falling height. When the chemical system suffered from multi-step (partial) coalescence, number of coalescence steps decreased with either of these variables. Addition of a single ionic or nonionic surfactant made the drop size smaller, and hence caused the onset of partial coalescence. When the surfactant was soluble in the drop phase, it increased the time more effectively. Also, it was found that the viscosity of the continuous phase played an important role in drop-interface coalescence. Based on the experimental results, new correlations were proposed. Then, the results were compared with the other models by application of the existing condition.

KEY WORDS: Interface, Dispersed phase, Continuous phase, Coalescence time, Surfactant.

INTRODUCTION

Coalescence of a drop at interface of its homophase and another immiscible liquid phase occurs in a number of processes such as liquid/liquid extraction, pharmaceutical and dairy products manufacturing, metallurgical treatments, polymer reactions, and even as a simple phenomenon in the formation of raindrop [1-6].

In general, coalescence happens either between a drop and its interface or between two adjacent drops. Because of difficulties arising from binary drop coalescence, most experiments are conducted in the drop/interface case. It was shown that for a particular chemical system at absolutely fixed physical properties and operating conditions, the measured coalescence time was not usually reproducible. A number of factors were known to be responsible for this inaccuracy of time measurements such as trace contaminants, internal and external motion of drop, and any disturbance or fluctuation at interface related to drop sitting, and etc. [7,8].

*To whom correspondence should be addressed.
+ E-mail: kparsi@ut.ac.ir
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Theoretical and experimental equations (correlations) have been suggested for estimating the drop/interface coalescence time. Among these, the theoretical equation of Stefan-Reynolds is as follows [1]:

\[ t = \frac{\mu_c \Delta \rho g b^5}{4 \sigma^2 h_1^2} \left( \frac{1}{h_2^2} - \frac{1}{h_1^2} \right) \]  

(1)

In this model it is assumed that the interface of two phases is not deformable and is completely rigid while confronting a falling drop.

If \( b_2 \ll h_1 \), then Equation (1) reduces to:

\[ t = \frac{\mu_c \Delta \rho g b^5}{4 \sigma^2 h_2^2} \]  

(2)

With the assumption of multidimensional shape for the two-phase interface, Hartland proposed the theoretical-experimental model as follows [9]:

\[ t = \frac{3}{16 \pi} n^2 \mu_c \left( \frac{a^2}{c^2} \right) \left( \frac{1}{h_2^2} - \frac{1}{h_1^2} \right) \]  

(3)

The Jeffreys-Lawson and the Smith correlations are respectively [10,11]:

\[ \frac{\sigma f}{\mu_c d} = 1.32 \times 10^{-5} \left( \frac{\Delta \rho g d^2}{\sigma} \right)^{0.32} \left( \frac{L}{d} \right)^{0.18} \]  

(4)

\[ \frac{\sigma f}{\mu_c d} = 31.0 \times 10^{-5} \left( \frac{\Delta \rho g d^2}{\sigma} \right)^{-1.24} \left( \frac{\mu_{d-c}}{\mu_c} \right)^{1.03} \]  

(5)

As seen from these models, apart from the physical properties of applied chemical system, the important factors that influence the coalescence time of drop are drop size \( d \) and distance of falling of drop \( L \). On the other hand, drop size in accompany with thickness of the intervening film of the continuous phase trapped between the drop and its homophase \( h \) are significant in the theoretical models. Experiments showed that the theoretical models overestimated the coalescence time [9].

Interfacial properties of a chemical system are altered in presence of surfactant, resulting in an interfacial tension gradient, which in turn give rise to tangential stresses at the interface. These stresses being referred to as Marangoni stresses. Therefore, surfactants can have a significant effect on the drainage and stability of the continuous phase film between drop and its interface [12, 13].

**EXPERIMENTAL**

**Apparatus**

Based upon the initial design of coalescence cell, the apparatus shown in Fig.1 was designed and constructed with substituting a microburette in place of a micrometer for a better drop formation [14–17]. The cell was improved for last experimental condition after several preliminary runs with selected chemical systems. To prevent possible corrosive effects of chemicals, all parts of the cell were made of Pyrex glass. Ratio of effective height to the inside diameter of the cell was large enough, and hence any undesirable wall effect was eliminated.

**Materials**

Selection of chemicals based primarily on the recommended systems [18] as stated in Table 1. They were selected in such a way that covered approximately a wide range of interfacial tension, and also formed spherical and visible drops. Chemicals were purchased...
Table 1: Physical properties of chemicals at ambient temperature

<table>
<thead>
<tr>
<th>Continuous(c)/Dispersed (d) phases</th>
<th>( \rho_c ) (kg/m(^3))</th>
<th>( \rho_d ) (kg/m(^3))</th>
<th>( \mu_c ) (mPa.s)</th>
<th>( \mu_d ) (mPa.s)</th>
<th>( \sigma ) (mN/m)</th>
<th>( \mu_d / \mu_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene(c)/Water(d)</td>
<td>862.10</td>
<td>996.84</td>
<td>0.6689</td>
<td>0.8140</td>
<td>36.1</td>
<td>1.217</td>
</tr>
<tr>
<td>n-Heptane(c)/Water(d)</td>
<td>683.70</td>
<td>997.00</td>
<td>0.4509</td>
<td>0.8560</td>
<td>50.1</td>
<td>1.901</td>
</tr>
<tr>
<td>Toluene(c)/60% (v/v) aq. Glycerol(d)</td>
<td>860.00</td>
<td>1139.10</td>
<td>0.5805</td>
<td>7.4140</td>
<td>53.4</td>
<td>12.772</td>
</tr>
</tbody>
</table>

from Merck and were used as received. The purity of all organic phases that were used for the continuous phase was above 99%. Distilled water was used as dispersed phase. All the experiments were conducted at ambient temperature in the range from 20°C to 25°C. 

Appropriate amounts of two immiscible liquid phases were mixed in a clean beaker (washed completely with chromic acid, acetone and water) for 15 minutes and left undisturbed for becoming saturated mutually, and then separated from each other [19].

For each phase, density was measured by a picnometer (25.0 milliliters volume) and repeated at least three times, and then averaged. Viscosity of each phase was measured by the Cannon-Fenske viscometer (Petrotest Instrument, GMBH & CO KG) using a chronometer with 0.01 seconds of precision. Measurements were made at least three times for each phase, and then averaged. Interfacial tensions were measured by digital tensiometer; the Krüss K10T, Wilhelmy plate (GMBH, Hamburg, Germany). Because of great sensitivity of this method, measurements were made at least 10 times and appropriate observed quantity was taken as the correct value [19].

Two surface active agents were used. Sodium dodecyl sulfate (S.D.S) that was ionic in nature and soluble in the aqueous phase. The second one was 1-decanol, nonionic and soluble in the organic phase. The purities of these two surfactants were above 85% and 97%, respectively.

Procedure

Before each run, it was necessary to saturate the two immiscible phases by one another in a separate beaker, and then transfer them to their respective reservoirs. To eliminate any contingency of naturally occurred contaminants, all parts of the cell were submerged in a freshly made 10% (v/v) chromic acid then washing with warm distilled water and acetone followed by drying in oven.

Care being taken in handling and assembling all parts of the cell together. No lubricant was used for valves or joints. To examine possible leakage, the cell was filled and discharged with distilled water. To renew the liquid/liquid interface after each experiment, the dispersed phase was allowed to flow from its reservoir to the receiver cup for a moment, and then the content was led to the bottom of the cell and discharging line.

The tip of each nozzle was immersed completely inside the dispersed phase in a separate beaker. It caused the drop to form correctly and symmetrically all around the outside periphery of the nozzle tip and this prevented any undesirable prematurity of formed drop. Time interval between every two successive detached drops from the nozzle tip was adjusted from 2.0 to 3.0 minutes to suppress any disturbance or corrugation, which was inevitably produced due to the former drop/interface coalescence.

A stopwatch having a precision of 0.01 seconds measured the coalescence time. For each chemical system, the drop diameter was determined by counting a definite number of successive detached drops from the nozzle tip, followed by measuring the total volume of dispersed phase. This procedure was repeated for various rates of drop formation and each size of capillary by adjusting the valve of microburette.

Falling heights of each drop ranged from about 1.5 to 4.0 centimeters depending on the drop size. For each drop size, the experiments were repeated at least 35 times to assure of the reproducibility of the results.

Coalescence time including the time interval between detachment of the drop form the tip of the nozzle to its arrival at interface and entire coalescence at interface was measured. For partial coalescence, as soon as one step of multisteps process was completed, the time for the second and subsequent steps was measured, and the coalescence...
time measurement continued until the drop disappeared completely at the interface.

RESULTS AND DISCUSSION

Observations and results

Systems without any surfactant

When a drop released from the tip of capillary, it just encountered the continuous phase that filled the upper part of the main body of cell surrounding the capillary. The drop descended gently towards the interface of two phases at the rim of receiver cup. As soon as the drop reached the interface bounced vertically and horizontally depending mainly on the drop diameter, the falling distance, and the ratio of drop to continuous phase viscosity. After resting on the interface the whole process of coalescence began. Because of the high ratio of dispersed to continuous phase viscosity, interfacial fluctuations of glycerol drops were not observed. It is worthy to note that any coalescence time less than 0.1 seconds was omitted from the observed data and considered as an instantaneous coalescence process.

The phenomenon of multisteps or partial coalescence [20-22] of drop was observed severely in water(d)/toluene(c) system. Approximately 65 percent of drops in each run indicated partial coalescence, with maximum steps of five for each drop. The lifetime of the secondary drop issued from partial disappearing of the first drop was always equal to or greater than that of the initial drop. The lifetimes of drops in the subsequent steps were very small in comparison with the second and the first steps. This matter was weaker in water(d)/n-heptane(c) because of its higher interfacial tension. Only less than 10% of drops underwent this phenomenon. Therefore, it was ignored. This fact did not occur in the system of 60% (v/v) aqueous glycerol(d)/toluene(c) at all due to the high interfacial tension, and also the large viscosity ratio of the dispersed to continuous phase.

In Fig. 2, the results of the first step coalescence time of drops in water(d)/toluene(c) system and in Figs. 3 and 4, the coalescence time of drops for the two other systems are depicted versus drop diameter and distance of falling of drops. Fig. 5 shows the overall steps of coalescence time for the system of water(d)/toluene(c).
With regard to these figures, coalescence time increased with drop size or falling distance as well as both. By increasing the drop size, the effect of falling height was more obvious. On the other hand, increasing the interfacial tension and the viscosity ratio of dispersed to continuous phase caused a decrease in influence of falling height. The effect of drop size was more obvious for moderate value of interfacial tension. To reduce the steps of partial coalescence, it was necessary to increase both the drop size and the falling distance.

Furthermore, it was observed that vertical or horizontal fluctuations of a base drop at interface and probable collisions with other drops, and also the external gentle shakings of apparatus caused the drop stability.

**Systems with single surfactants**

Application of each of S.D.S and 1-decanol in each chemical system caused an appreciable drop size reduction of about 10 to 40 percent compared to surfactant–free systems. Probably, this was due to reduction of interfacial tensions [20]. In this case, the partial coalescence appeared in water (d) / n-heptane (c). As before, the 60% (v/v) aqueous glycerol(d)/toluene (c) had no sign of this phenomenon and resisted severely against it.

The overall coalescence time of each drop undergoing partial coalescence in water(d)/toluene(c) was always greater than that of a drop in water(d)/n-heptane(c). The simultaneous increase of surfactant concentration and drop size led to a fewer steps in multisteps coalescence.

To suppress this phenomenon entirely, it was found that the drop size must be approximately over 4.0 millimeters. In spite of this fact, 1-decanol could not completely inhibit the water(d)/toluene(c) system from partial coalescence. This was likely because of the high and strong tendency of this system to partial coalescence. The trend of behavior of the coalescence time for all liquid/liquid systems containing either of these two surfactants are shown in Figs. 6 to 11.

As seen from these figures, the coalescence time increased with a decrease in drop size or an increase in surfactant concentration. This can be due to ensuing rigidity of drop in presence of surface active agent.

Adsorbed surfactant affects hydrodynamic interaction between drops and also between drop and interface and modifies the short-range attractive and repulsive forces that act between drop interfaces. Also, it was found that the drop lifetime would be more, if the surfactant were soluble in it (for the case of S.D.S).

The experimental results were correlated by appropriate models [12, 14].

**Coalescence time correlation (without any surfactant)**

The simultaneous functionality of the coalescence time versus drop size and falling distance were found to be in the forms of $t \propto d^{3.373}$ and $t \propto \frac{L}{\mu_c}$, respectively [14], and found that the continuous phase viscosity had a major role in drop coalescence compared to that of drop phase [23]:

$$\frac{\sigma_t}{\mu_c d} = 4.846 \times 10^3 \left( \frac{N_{p,s}}{\sigma} \right)^{1.512} \frac{L}{d}^{0.651} \left( \frac{\mu}{\mu_c} \right)^{0.203} \left( \frac{\Delta \rho}{\rho_c} \right)^{0.406}$$

(6)

where $t_1$ is the overall coalescence time of drop for systems without any partial coalescence, and is also the first step coalescence time of drop for systems with partial coalescence.

For system with partial coalescence, it was found that the overall coalescence time was a function of continuous phase viscosity [24]:

$$t = \psi t_1$$

(7)

where the coefficient of $\psi$ is given as [14, 24]:

$$\psi = \mu_c^n$$

$(-0.27 \leq n \leq -0.10)$

(8)
Fig. 6: First step coalescence time of drop in presence of S.D.S (water(d)/toluene(c)).

Fig. 7: First step coalescence time of drop in presence of S.D.S (water(d)/n-heptane(c)).

Fig. 8: Drop coalescence time in presence of S.D.S (60% v/v aq. glycerol(d)/toluene(c)).

Fig. 9: First step coalescence time of drop in presence of 1-decanol (water(d)/toluene(c)).

Fig. 10: First step coalescence time of drop in presence of 1-decanol (water(d)/n-heptane(c)).

Fig. 11: Drop coalescence time in presence of 1-decanol (60% v/v aq. glycerol(d)/toluene(c)).
hence:

\[ t = \mu_c^2 t_1 \]  

(9)

**Coalescence time correlations (with surfactant)**

Separate models were derived for the two surfactants:

**I) Sodium Dodecyl Sulfate (S.D.S)**

The first step coalescence time:

\[ t_1 = 0.1736 \left( \frac{\mu_d}{\mu_c} \right)^{0.00765} \]

\[ \left( \frac{\Delta \rho g L^2}{\sigma} \right)^{-0.1694} C^{0.3300} d^{-1.2761} \quad C \neq 0 \]  

(10)

where \( C \) is the concentration of surfactant.

Overall coalescence time:

\[ t = 529.58 \mu_c^{0.668} t_1 \]  

(11)

where

\[ \psi = 529.58 \mu_c^{0.668} \]  

(12)

**II) 1-Decanol**

The first step coalescence time:

\[ t_1 = 529.07 \left( \frac{\mu_d}{\mu_c} \right)^{0.1089} \]

\[ \left( \frac{\Delta \rho g L^2}{\sigma} \right)^{-1.677} C^{0.3001} d^{-0.5653} \quad C \neq 0 \]  

(13)

Overall coalescence time:

\[ t = 194.86 \mu_c^{0.538} t_1 \]  

(14)

where

\[ \psi = 194.86 \mu_c^{0.538} \]  

(15)

As corroborated by these models, coalescence time was conversely proportional to the drop diameter and increased with the concentration of surfactant. Tables 2 to 4 show appropriate consistencies between experimental data and calculated values by these correlations based on

\[
\text{%AAD (\% AAD = \frac{100}{N} \sum_{i=1}^{N} \frac{|\exp_i - cal_i|}{\exp_i})}
\]

**Comparison with other models**

The proposed model, Equation (6) was compared to the models of Smith and Jeffreys-Lawson [10,11]. Figs. 12 to 14 show these comparisons for each liquid-liquid system in the absence of surfactant.

As seen from these figures, the model of Jeffreys-Lawson overestimates the drop/interface coalescence time up to 15 folds. But the model of Smith is appropriate for medium and high values of interfacial tension, and also medium values of the viscosity ratio of dispersed to continuous phase. On the other hand, the former model is better for the glycerol system. Also, considering the experimental data that led to a new correlation, it can be concluded that the continuous phase viscosity had a major role in drop/interface coalescence compared to the drop phase viscosity.

It is necessary to note that the theoretical equations were not included in these comparisons because of their great overestimations even up to 200 folds for the presented data.

**CONCLUSION**

With regard to the experimental results, it was concluded that when the drop size and the falling distance increased simultaneously or individually, an increase in drop/interface coalescence time was obtained. On the other hand, for the case of high interfacial tension or high viscosity ratio of dispersed to continuous phase, the falling distance of drop had a less effect on the coalescence time.

The most severe case of partial coalescence was observed in the system having medium interfacial tension, and almost equal phase viscosities. Any increase in drop diameter and distance of falling caused a decrease in the steps of coalescence. It was observed that vertical or horizontal fluctuations of a base drop at interface and probable collisions with other drops, and also the external gentle shakings of apparatus could cause the drop stability.

Addition of single ionic or nonionic surfactant depending on its type, made the drop size smaller, and hence caused an onset of partial coalescence for the system having equal values of phase viscosities and on the whole, it caused a decrease in the coalescence time. If the surfactant was soluble in drop phase, it would increase the time more effectively.

Comparison between the proposed correlations and the experimental data, and also for the case of surfactant-free systems with other models, corroborated their accuracy within defined ranges of physical properties and operating parameters.
Table 2: Comparison between experimental data and calculated values resulted from proposed model, Equations 6 and 9 (absence of surfactant)

<table>
<thead>
<tr>
<th>Chemical System(c)/(d)</th>
<th>First Coalescence Time: %AAD</th>
<th>Overall Coalescence Time: %AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene/ Water</td>
<td>2.171</td>
<td>9.026</td>
</tr>
<tr>
<td>n-Heptane/ Water</td>
<td>7.523</td>
<td>---</td>
</tr>
<tr>
<td>Toluene/ 60%(v/v) Glycerol</td>
<td>11.915</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 3: Comparison between experimental data and calculated values resulted from proposed model, Equations 10 and 11 (with surfactant S.D.S)

<table>
<thead>
<tr>
<th>Chemical System(c)/surfactant/(d)</th>
<th>First Coalescence Time: %AAD</th>
<th>Overall Coalescence Time: %AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene/S.D.S/ Water</td>
<td>5.141</td>
<td>12.833</td>
</tr>
<tr>
<td>n-Heptane/S.D.S/ Water</td>
<td>6.040</td>
<td>9.194</td>
</tr>
<tr>
<td>Toluene/S.D.S/ 60%(v/v) Glycerol</td>
<td>9.608</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 4: Comparison between experimental data and calculated values resulted from proposed model, Equations 13 and 14 (with surfactant 1-decanol)

<table>
<thead>
<tr>
<th>Chemical System (c)/surfactant/(d)</th>
<th>First Coalescence Time: %AAD</th>
<th>Overall Coalescence Time: %AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene/1-decanol/ Water</td>
<td>2.629</td>
<td>11.464</td>
</tr>
<tr>
<td>n-Heptane/1-decanol/ Water</td>
<td>14.420</td>
<td>20.235</td>
</tr>
<tr>
<td>Toluene/1-decanol/ 60%(v/v) Glycerol</td>
<td>2.459</td>
<td>---</td>
</tr>
</tbody>
</table>

Comparison of Equations for : Toluene (c) / Water (d)

Comparison of Equations for : n - Heptane (c) / Water (d)

Fig. 12: Comparison between predicted values of drop coalescence times by model (6) and the other models (water(d)/toluene(c)).

Fig. 13: Comparison between predicted values of drop coalescence times by model (6) and the other models (water(d)/n-heptane(c)).
Fig. 14: Comparison between predicted values of drop coalescence times by model (6) and the other models (60% v/v aq. glycerol(d)/toluene(c)).

Nomenclature

- $a$: surface occupied by a sitting drop (m$^2$)
- $b$: drop radius (m)
- $C$: concentration (kg/m$^3$)
- $d$: drop diameter (m)
- $F$: force (N)
- $g$: gravity acceleration (m/s$^2$)
- $h$: thickness of intervening film (m)
- $L$: distance of falling of drop (m)
- $n$: number of quiescent surfaces at intervening film
- $N$: number of experimental data
- $t$: time (s)

Greek letters

- $\mu$: viscosity (Pa.s)
- $\rho$: density (kg/m$^3$)
- $\sigma$: interfacial tension (mN/m)

subscripts

- $c$: continuous phase
- $d$: dispersed (drop) phase
- $l$: first coalescence time
- $1, 2$: initial and final conditions

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