The Influence of Bicomponent Mixed Surfactants on Drop/Interface Coalescence

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ABSTRACT: *Effects of binary mixtures of ionic/nonionic (sodium dodecyl sulfate/2-heptanol or 1-decanol) and nonionic/nonionic surfactants (2-heptnol/1-decanol) on drop/interface coalescence of water drops in a continuous n-heptane phase were examined. The drop size reduced appreciably and the multi-step coalescence was suppressed finally as the concentration of each of the constituting components of surfactant mixture was increased. The drop became more stable in comparison to single surfactant systems. It was concluded that the mixed surfactants were much more effective on coalescence time and drop lifetime than single surfactant, particularly when one of the components was soluble in the drop phase.*

KEY WORDS: *Drop, Interface, Continuous phase, Coalescence time, Mixed surfactants, Multi-step coalescence.*

INTRODUCTION

Surface active agents as trace impurities or intentionally added to a dispersion are often present in liquid-liquid systems involved in many industrial processes. Adsorbed surfactants affect the hydrodynamic interaction between drops and also between drop and interface of its homophase and modifies the short-range attractive and repulsive forces that act between drop interfaces.

Presence of surfactants can have a significant effect on the drainage and stability of the continuous phase film and thus on the coalescence of drops. In the absence of van der Waals attraction, drops become stable against aggregation because of the large pressure required to expel fluid from the narrow gap between rigid surfaces.

By contrast, surfactant-free spherical drops which are fully mobile coalesce readily upon interaction because the fluid can be more easily squeezed out of the near-contact region. Marangoni stresses (surface tension gradients) arising from gradients of surfactant concentration affect hydrodynamic interactions [1, 2].

The surface active agent helps a symmetrical drainage of intervening film trapped between the drop and its homophase, and hence increases the drop lifetime. On the other hand, if the surfactant is soluble in the drop phase, it will subside internal circulating flows of drop to some extent depending on the concentration of the surfactant to be used [3-7].

The properties of the mixed surfactants are often

better than those attainable in their individual states. This synergism is of considerable interest [8-10]. In addition, mixed surfactants have a great effect on emulsion stability. But single surfactant at its higher concentration causes noticeable instability in an emulsion [11-18]. Also, mixtures of surfactants may improve spreading of liquid on the solid surface and produce better wetting [19,20]. Therefore, it is needed to know how mixed surfactant systems influence the drop/ interface coalescence, which are encountered in many liquid/liquid applications.

It was shown earlier that the relationship between the drop coalescence time and the concentration of single surfactant was in the form of $t \propto c^m$, where $0.45 \le m \le 3.0$ [21].

The proposed correlation for the case when an ionic surfactant is present is [22-24]:

$$t_1 = 0.1736(\frac{\mu_d}{\mu_c})^{0.00765}(\frac{\Delta\rho g L^2}{\sigma})^{-0.1694}C^{0.3300}d^{-1.2761} \quad (1)$$

$$C \ne 0$$

where C is the concentration of surfactant.

For multisteps coalescence, the overall coalescence time was obtained:

$$t = \psi t_1 \quad (2)$$

$$\psi = 529.58\mu_c^{0.668} \quad (3)$$

With some modifications for nonionic surfactant, the coalescence time was proposed as follows [22-24]:

$$t_1 = 529.07(\frac{\mu_d}{\mu_c})^{0.1089}(\frac{\Delta\rho g L^2}{\sigma})^{-1.677}C^{0.3001}d^{-0.5653} \quad (4)$$

$$C \ne 0$$

$$t = \psi t_1 \quad (5)$$

$$\psi = 194.86\mu_c^{0.538} \quad (6)$$

According to these models, the coalescence time is inversely proportional to the drop diameter and increases with concentration of the surfactant. This is in contrast with surfactant- free systems in which the coalescence time increases with drop size [24].

In this research the mixture of surfactants were qualitatively investigated.

EXPERIMENTAL
Apparatus

The experimental apparatus was a coalescence cell that was constructed by authors and described elsewhere [22-24]. Essentially, it contains a receiver cup at the base of the cell, located at the interface of two-phases. Drop nozzle (capillary) is placed just above the cup with an appropriate and adjustable distance from it. Fig. 1 illustrates the coalescence cell, and its details are written in Table 1.

Materials

The liquid/liquid system of water drops in n-heptane [water (d)/*n*-heptane(c)] was used in this research because of formation of visible and spherical drops [9]. The organic phase was purchased from Merck with a purity of above 99%. It was used as received. All the experiments were conducted at ambient temperature in the range from 20°C to 25°C. As usual, the two phases were completely mixed in a clean beaker before measuring the physical properties. This caused mutual saturation [25]. Density of each phase was measured by
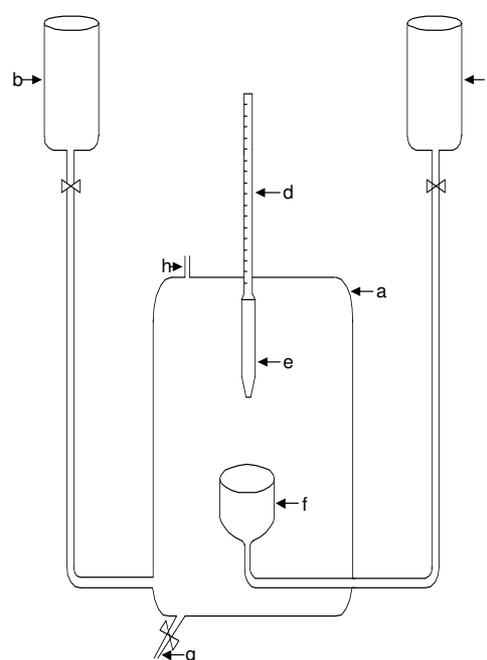
Fig.1: Coalescence cell; a: main body, b,c: continuous and dispersed phase reservoirs, d: microburette, e: capillary, f: drop receiver cup, g: drainage valve, h: outlet way for trapped air or vapor.

Table 1:Details of the coalescence cell

Inside diameter of the main body	8.0 cm
Inside diameter of the receiver cup	4.5 cm
Wall thickness of the main body, and the receiver cup	0.25 cm
Height of the main body	40.0 cm
Height of the receiver cup	4.6 cm
Volume of each of phase reservoirs	240.0 ml
Range of inside diameters of the capillaries	0.4-1.5 mm
Maximum expected and allowable distance between the tip of capillary and the rim of cup	6.0 cm
Inside diameter of connective lines between the phase reservoirs and the main body	0.54 cm

Table 2: Physical properties of the chemical system at ambient temperature

Water (d)/ *n*-heptane (c)	density (kg/m^3)		continuous phase viscosity (mPa.s)	dispersed phase viscosity (mPa.s)	interfacial tension (mN/m)
	(c)	(d)			
	683.7	997.0	0.4509	0.8560	50.1

a picnometer (25.0 milliliters volume) and repeated at least three times and then averaged. Viscositiy of each phase was measured by the Cannon-Fenske viscometer (Petrotest Instrument, GMBH & CO KG) using a stopwatch having 0.01 seconds of precision. Measurements were made at least three times for each phase, and then averaged.

Interfacial tension was measured by a digital tensiometer; the Krüss K10T, Wilhelmy plate (GMBH, Hamburg, Germany). Because of great sensitivity of this method, measurements were made at least l0 times [25] and the appropriate observed quantity was taken as the interfacial tension.

Table 2 shows the measured physical properties of the system.

Three surface active agents were used as follows: sodium dodecyl sulfate (S.D.S), anionic and in the form of fine white powder that was readily dispersed in the aqueous drop phase. The two others were *2*-heptanol and *1*-decanol, nonionic and in the form of liquid with slightly yellow color and soluble in the organic phase. All the surfactants were provided from Merck with a purity above 85%, 99%, and 97%, respectively. Distilled water was used in all the experiments.

Procedure

Before filling the cell, the two phases were allowed to be saturated and reach equilibrium. After that, the cell was filled in such a manner that the interface between the two phases was adjusted precisely at the rim of the receiver cup by controlling volumes of phases through discharge valve. To avoid the entrance of any contaminant, the interface was frequently renewed by discharging some of the dispersed phase from the cup [24].

It was necessary before each run to submerge all parts of the cell inside a freshly made 10% (v/v) chromic acid, then washing with warm distilled water and acetone followed by drying in an oven.

When a drop detached from the nozzle, it descended gently through the continuous phase, and then reached the interface of its homophase that filled the receiver cup [24].

With a time interval of 3.0 minutes between any two successive drops, coalescence time was measured with a stopwatch having 0.01 seconds of precision. Reading the volume of dispersed phase from microburette and counting the number of drops produced at each flow rate gave the drop diameter.

For each drop size, experiments were repeated at least 35 times to assure of the reproducibility of results. The coalescence time including the time interval between detachment of the drop form the tip of the nozzle to its arrival at the interface and entire coalescence at interface was measured. In the case of partial coalescence, a second stopwatch was used to measure subsequent steps of

coalescence time.

RESULTS AND DISCUSSION

As usual any coalescence time less than 0.1 seconds was considered as an instantaneous coalescence process, and hence omitted.

Partial coalescence was rare in the absence of surfactant. Only less than 10 percent of drops experienced this phenomenon. Fig. 2 shows the coalescence time of water drops at *n*-heptane interface as a function of drop diameter and distance of falling.

As seen from this figure, coalescence time increases with either drop size or distance of falling as well as both.

Performance of Single Surfactants

In order to compare the single and mixed surfactant systems with each other, it was necessary to investigate the effect of single surfactant on the coalescence time. Application of each surfactant in water(d)/*n*-heptane(c) system decreased appreciably the drop size between 10 and 40 percent, which is due to abrupt decrease in the interfacial tension. The surfactant enhanced the partial coalescence with a noticeable rate.

Maximum number of steps in multisteps coalescence was five. Lifetime of the secondary drop resulting from partial disappearance of the first drop was always equal to or greater than that of the initial drop. Stability of other steps was very low in comparison with the first step.

Simultaneous increase of drop size (through increasing the nozzle diameter) and the surfactant concentration caused the multisteps coalescence to be suppressed. Complete suppression occurred when the drop size was somewhat larger than 4.0 cm. The overall coalescence time for individual surfactants applied in water (d)/*n*-heptane(c) are shown in Figs. 3 to 5.

As seen from these figures, coalescence time increases with the concentration of surfactant and decreases with drop size, due to rigidity of drops resulting from the presence of surface active agent on their surface. Also, it was found that drop lifetime would be larger if the surfactant were soluble in the drop phase. The reason might be that when the surfactant was particularly ionic in nature or soluble in the drop phase, it spread on the surface of the drop as well as the interface of two phases. It was observed that 2-heptanol had weaker performance in comparison with the other two surfactants. All
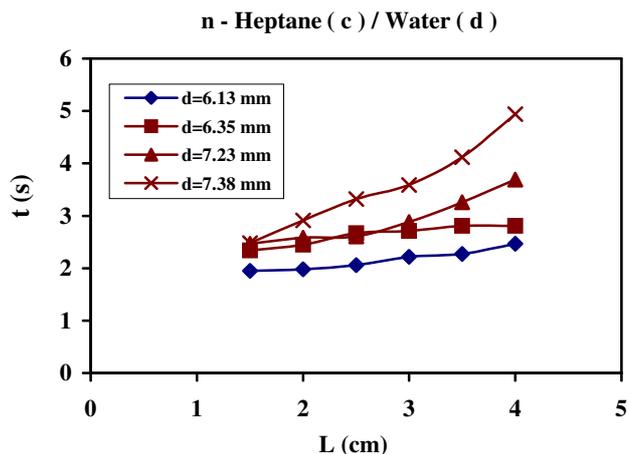
n - Heptane (c) / Water (d)

Fig. 2: Drop coalescence time versus drop size and distance of falling (in the absence of any surfactant) for water (d)/ n-heptane (c).

n - Heptane (c) / S.D.S / Water (d)
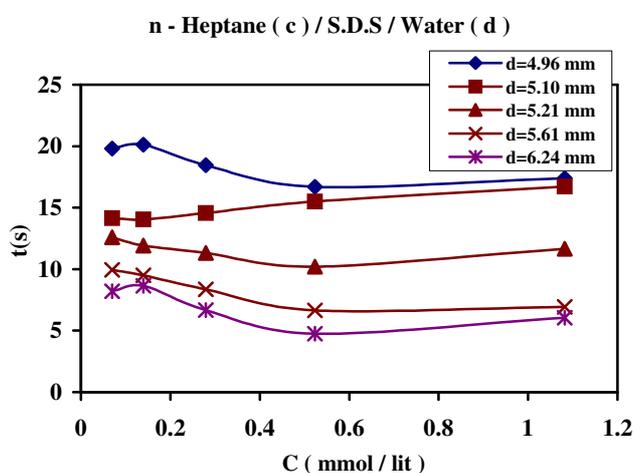
Fig. 3: Overall coalescence time of drop in presence of S.D.S.

n - Heptane (c) / 2 - Heptanol / Water (d)
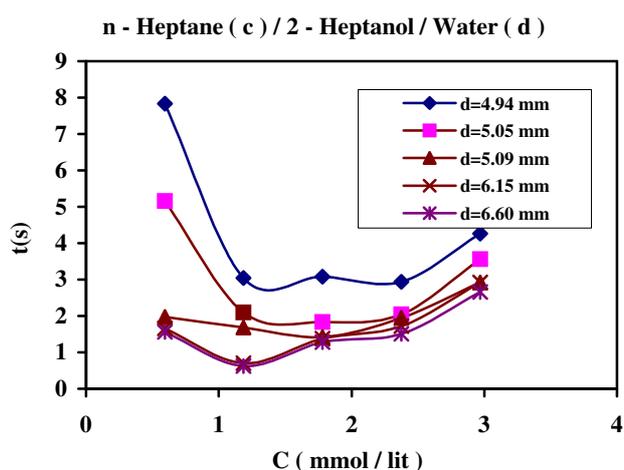
Fig. 4: Overall coalescence time of drop in presence of 2-heptanol.

nonionic surfactants, yielded approximately similar ranges of drop size, and similar distributions of drop coalescence time. Sodium dodecyl sulfate (anionic) formed a higher and wider distribution of drop coalescence time for the same drop size range compared to nonionic surfactants, probably because of its solubility in drop phase.

Performance of Bicomponent Surfactants

Mixture of Ionic and Nonionic Surfactants

Experiments were conducted by keeping the concentration of one surfactant constant while the other was increased gradually, vice versa.

Gradual increase in S.D.S concentration at fixed amount of *2*-heptanol to water(d)/*n*-heptane(c) system caused a reduction of drop size down to 52%. At higher mole fractions of S.D.S, partial coalescence was suppressed and then subsided. On the other hand, increasing the concentration of 2-heptanol caused the drop size to be reduced down to 43%.

In both cases, the coalescence time increased as drop size reduced. Contrary to the single surfactant condition, increasing the mole fraction of any surfactant reduced simultaneously the drop size and the steps of partial coalescence. Variations of the first and subsequent steps of coalescence time, as well as the drop size versus mole fraction of *2*-heptanol (x) are depicted in Figs. 6 to 9.

Larson's model is typical of the many lattice models available and uses a fully occupied lattice [26,27]. Each lattice point represents either a water-like molecule, an oil-like molecule or a surfactant segment (head and tail). This model is designed for water-amphiphile-oil systems and characterized by energy parameter, the difference in energy between the favorable contacts (water-water or oil-oil) and the unfavorable contacts (oil-water). Surfactants are constructed by linking together a number of oil-like and water-like lattice points.

The synergistic effect can be explained by this model. A decrease in the value of interaction energy parameter causes a reduction in the total amount of energy of the system. On the other hand, the reduction of the mole fraction of less hydrophobic surfactant causes an increase in the hydrophobic effect. Consequently, these two factors increase the synergistic effects.

Mixture of Two Nonionic Surfactants

Experiments were carried out similar to the previous
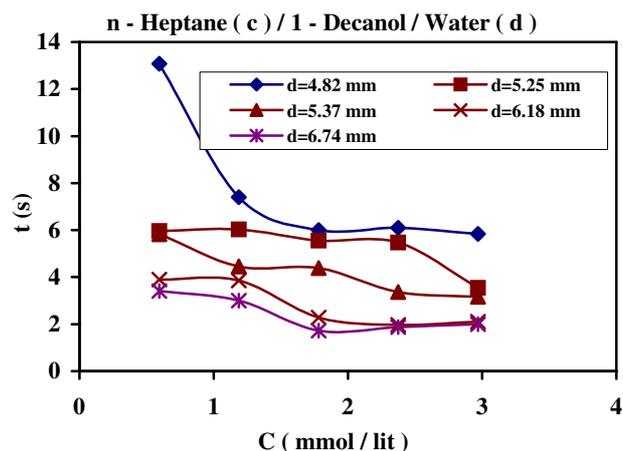
Fig. 5: Overall coalescence time of drop in presence of 1-decanol
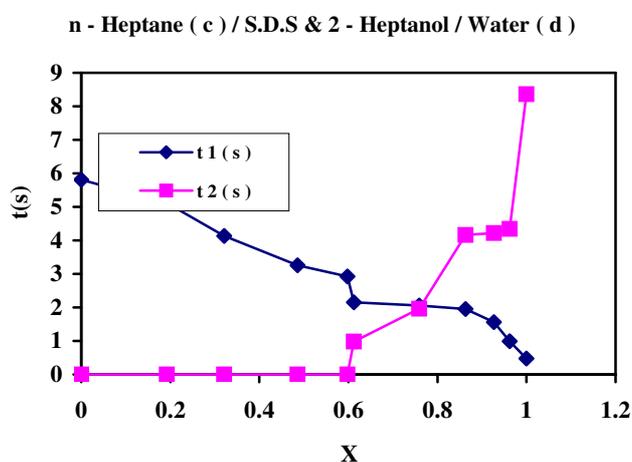
Fig. 6: The first and subsequent steps of drop coalescence time versus mole fraction of S.D.S (1-x).
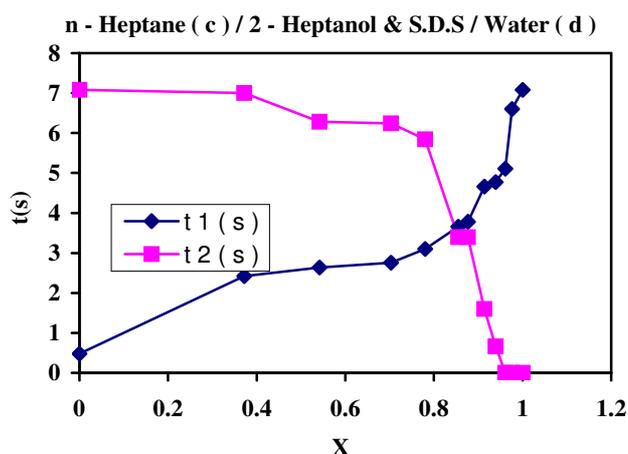
Fig. 7: The first and subsequent steps of drop coalescence time versus mole fraction Of 2-heptanol (x).
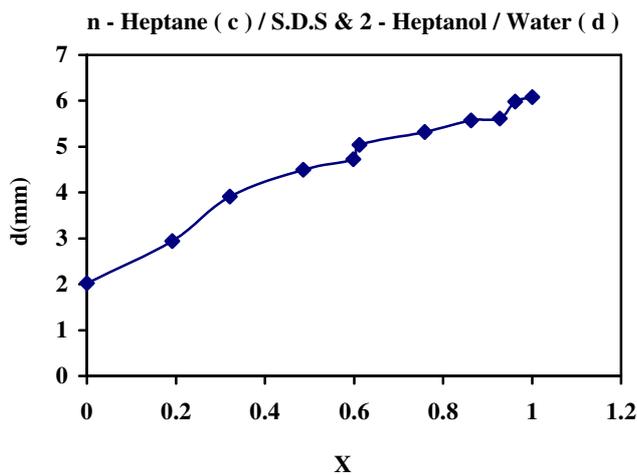
Fig. 8: Drop size versus mole fraction of S.D.S (1-x).
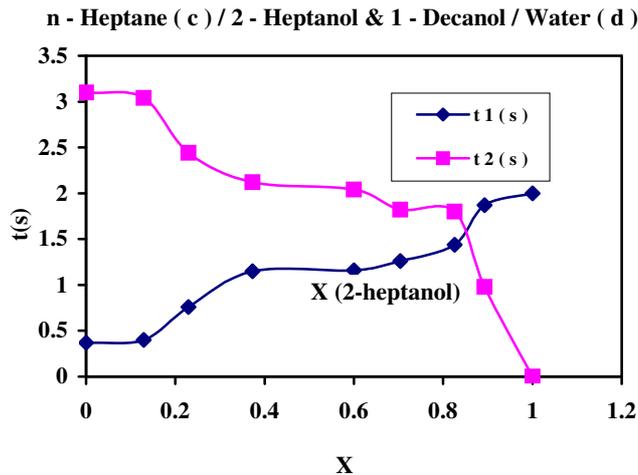
Fig. 9: Drop size versus mole fraction of 2-heptanol (x).

Fig. 10: The first and subsequent steps of drop coalescence time versus mole fraction of 1-decanol (1-x)

Fig. 11: The first and subsequent steps of drop coalescence time versus mole fraction of 2-heptanol (x).

Fig. 12: Drop size versus mole fraction of 1-decanol (1-x)
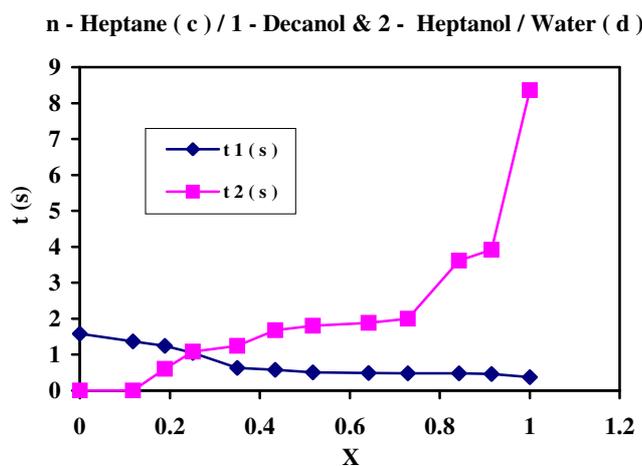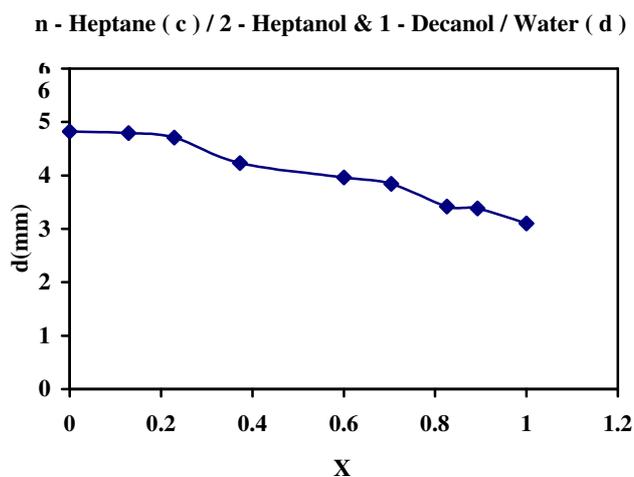
Fig. 13: Drop size versus mole fraction of 2- heptanol(x).

section. The maximum observed reduction of drop size was about *45%*. Increasing the *2*-heptanol could not completely suppress the partial coalescence, which was probably due to its weaker nature compared to *1*-decanol. Generally, because of the similar nature of these two surfactants, there was no significant difference between them. The behavior of the first and subsequent steps of coalescence time, and also drop size versus mole fraction of *2*-heptanol are depicted in Figs. 10 to 13.

From the regular solution point of view, these behaviors are explained primarily on the basis of comparison between the cohesive energies of hydrophilic and hydrophobic groups of a surfactant molecule [28]. Thus, it is clear that the solubility of two phases will be more if their cohesive energy densities are almost equal, which is true for the two nonionic surfactants used i.e. 2-heptanol and 1-decanol.

CONCLUSION

The presence of a single ionic or nonionic surfactant in a liquid/liquid system made the drop size smaller and hence caused the partial coalescence phenomenon. In general, it increased the coalescence time due to the reduction of drop size along with the occurrence of multi-step coalescence. If the surfactant was soluble in drop phase, it would increase the time even more.

Compared to single surfactant system, the mixture of ionic/nonionic surfactants had pronounced effect on the drop size reduction. On the other hand, it caused a complete reduction in steps of partial coalescence of drop by increasing the concentration of one of the constituents. This was in contrary to single surfactant system.

It was concluded that a binary mixture of surfactants, especially when one of them was soluble in drop phase was more effective than single surfactant in increasing the drop coalescence time and its stability.

Nomenclature

C concentration of surfactant (*mol/L*)
d drop diameter (*m*)
g acceleration gravity (*m/s^2*)
L distance of falling (*m*)
t time (*s*)
x mole fraction of surfactant of *2*-heptanol

Greek Letters

μ viscosity (*Pa.s*)

ρ density (*kg/m^3*)
σ interfacial tension (*N/m*)

Subscripts

1,2 first and subsequent steps of coalescence time, respectively
c, d continuous and dispersed (drop) phases, respectively

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