Drop-Interface Coalescence in liquid-liquid Systems: Effect of Surface Active Agents

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Abstract

Coalescence will usually occur, when a drop approaches a two phase interface, where an interfacial film forms, drains to a certain thickness and then ruptures. Film rupture is very rapid, and so most of the time taken for the coalescence of a drop to occur is the coalescence time. In the present work, time of fall of drop of aqueous phase through an organic pool and its coalescence with its bulk phase has been studied with a typical liquid-liquid extraction system. Effect of surface active agents/ emulsifiers on coalescence has been studied.

Introduction

Coalescence of drops, suspended in a liquid, plays a crucial role in mass transfer contactors. In a mass transfer contactor, efficient dispersification is required to enhance the transport efficiency. On the other side, adequate coalescence of drops is required to reduce emulsification and entrainment losses during phase separation. Emulsification results in poor disengagement of the two phases leading to an inefficient extraction, loss of control on phase ratio and significant entrainment losses. In the most conventional extraction systems, the interface contains interfacially active contaminants. These contaminants modify the interfacial properties, which resist the film drainage and hence retard coalescence. Effects of interfacial properties on coalescence have not been systematically studied for the solvent extraction systems relevant to the department. In liquid membrane based mass transfer contactors, like hollow fiber modules, emulsifiers are often added to stabilize the dispersion during transport. Type and concentration of emulsifier play a crucial role in coalescence of the drops during phase separation in such systems.

A simple technique for studying the rate of coalescence is to measure the “coalescence time”. When a drop of liquid 1 approaches through an immiscible liquid 2 to the interface of phases 1 and 2, it takes rest at the interface before merging with its bulk phase. The time interval, during which the drop rests at the interface, is known as the coalescence time. In the present work, time of approach of a drop of an aqueous phase through an organic phase and its coalescence time with its bulk phase have been studied using high speed camera and illumination system. Emulsifiers play an important role in modulating the coalescence time. Role of emulsifier coupled with the extractant having surface activity has also been seen.

Methodology

The experimental set-up for the present study on drop-drop coalescence under gravitational field consists of a cuvette fixture, in which organic and aqueous phases have been poured to form a liquid-liquid interface. The set-up consists of an auto syringe to release the drop of aqueous phase in organic continuum, illumination system and a high speed camera. Images are taken for drop travelling through the organic pool, sitting on organic-aqueous interface and then merging with its bulk phase. The time of approach of drop of aqueous phase through organic phase as well as the coalescence time of drop with its bulk phase have been observed for different compositions. The organic phase is taken as TBP (0%, 5%, 10%, 20% and 30% v/v) dissolved in dodecane with and without emulsifier SPAN 80 (3 % v/v), while the aqueous phase was distilled water.

Theoretical

A) Deformation of a drop: The deformation of a drop under a compressive force is estimated by considering it to be contained in a fluid between two parallel planes, which are pushed together with a force according to Charles and Mason For deformation, weight of the drop overcomes the interfacial tension force of the drop, as interfacial forces holding the drop together. At equilibrium, resultant of gravitational and buoyant force should be equal to interfacial tension force for a given distortion,

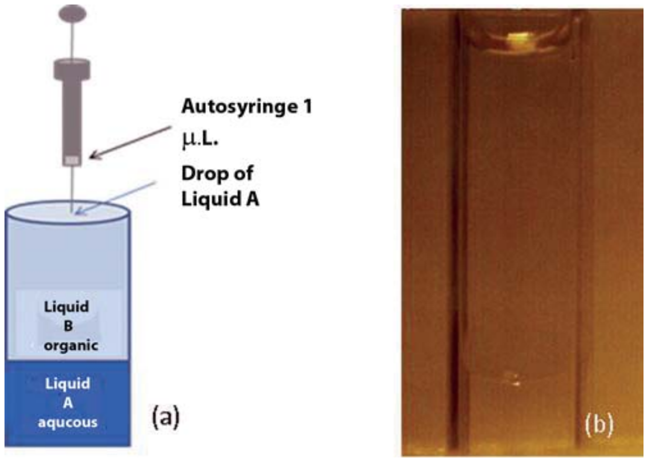

Fig. 1: a) Schematic of the experimental facility, b) video image of the drop resting at the interface

$$\frac{4}{3}\pi b^3 g\Delta\rho = \sigma\pi c^2 \frac{2}{b} \tag{1}$$

$$c = b^2\left[\frac{2\Delta\rho g}{3\sigma}\right]^{1/2} \tag{2}$$

Where, b is the radius of undistorted spherical drop and c is the radius of flat disc formed on the top and bottom, after the drop is deformed. $\Delta\rho$ is the difference in the density of the drop and the surrounding medium. From above equations, force required to produce a given distortion increases with interfacial tension σ and drop curvature $1/b$. Liquid film trapped between the interface is plano-convex in shape and is thinnest along the circumference of a circle of radius c according to Gillespie and Rideal.

B) Thinning of the film: Following Assumptions are involved for the thinning of the film of continuous phase according to Reynolds; a) Space between the drop and the two phase interface is so small that the motion of fluid is assumed to be free from eddies i.e. laminar flow. b) Forces arising from weight and inertia are altogether small compared with the stresses arising from viscosity. c) Flow is radial i.e. z-component of fluid velocity is zero.

The close approach of surfaces immersed in a viscous fluid in response to a constant force F has been considered. Separation at any time t is given by $z = h$ at $r = 0$. At a distance r from the origin, separation is ξ, which is function of r. Velocity of approaching surface at time t is $V = -dh/dt$. During approach, incompressible fluid of viscosity η is expelled radially from between the two surfaces at a velocity $u\ (z,r)$. Radial velocity $u(z,r)$ is given by Eq 3. It implies a parabolic profile without slip at the adjacent surfaces, i.e. $u(z,r) = 0$ at $z = 0$ and ξ. $u(z,r)$ will be greatest half-way between the surfaces. Fluid will be pulled towards the middle by the viscosity. The volumetric flow rate across a cylindrical surface at r is represented by Eq. 4,

$$u(z,r) = z\ (\xi - z)\ \phi(r) \tag{3}$$

$$Q = \int_0^{\xi} u(z,r)\ 2\pi r dz \tag{4}$$

Further, by equating the change in volumetric flow rate to the volume of liquid displaced by the approaching surface in unit time,

$$dQ = 2\pi r\, dr\, V \tag{5}$$

$$\phi\ (r) = 3rV/\ \xi^3 \tag{6}$$

Now, equating mechanical work to the energy dissipated due to viscosity,

$$FV = \int \tau(\partial u/\partial z)\ 2\pi r\, dr\, dz \tag{7}$$

$$FV = \int_0^r \int_0^{\xi} \tau \frac{\partial u}{\partial z}\ 2\pi r\ dr\ dz \tag{8}$$

Substituting for $\partial u/\partial z$ and integrating with respect to z yields the relation

$$V = \frac{-dh}{dt} = \frac{F}{6\pi\mu \int_0^r \frac{r^3}{\xi^3} dr} \tag{9}$$

When approaching surface is flat disc of radius c, i.e. ξ = constant = h

Time required for the thinning of the film from thickness h_1 to h_2 is,

$$t_{1,2} = \frac{\mu\Delta\rho g b^5}{4\sigma^2}\left[\frac{1}{h_2^2} - \frac{1}{h_1^2}\right] \tag{10}$$

Assumptions involved in obtaining Eq 10 are as following, a) Liquid drop of radius b approaches a flat interface under its own weight. b) Drop undergoes a small deformation. Film does not drain regularly and it may rupture before drainage is complete, resulting in a distribution of coalescence times.

Observations and Predictions

Time of fall of drop of distill water through organic phase towards the two phase interface has been observed and presented in Figure 2. With increase in the concentration of TBP, time of fall of drop towards the phase interface increases. This is because of increased density and the viscosity of the organic surrounding the drop. In presence of emulsifier SPAN 80 (3 % v/v), time of fall has larger values as shown in

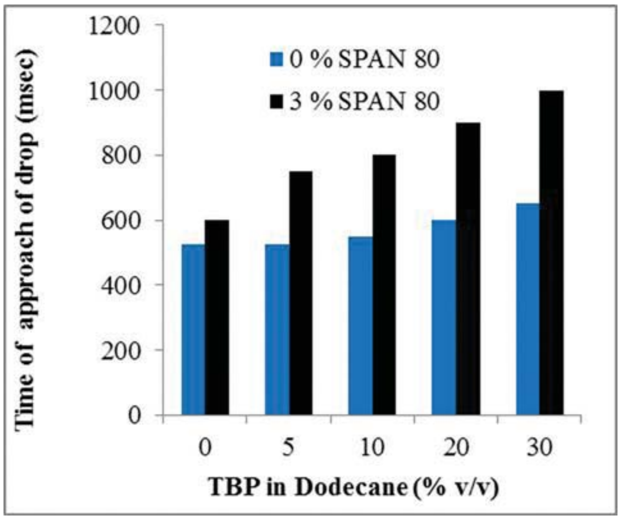

Fig. 2: Time of approach of drop to interface

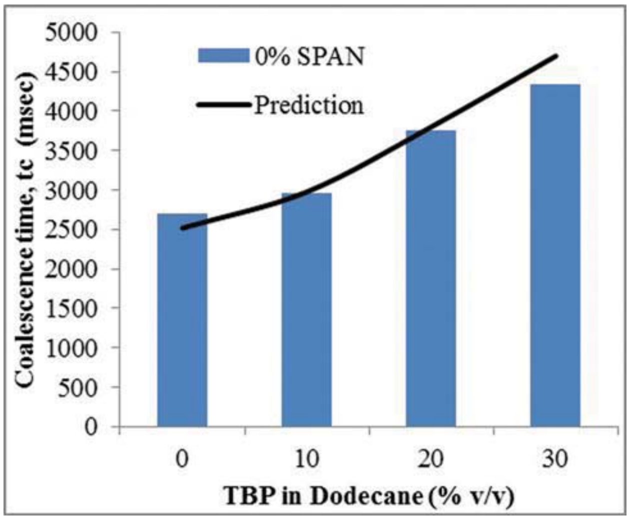

Fig. 3: Coalescence time of drop

Figure 2. This is because of further rise in the density and viscosity of the continuous phase with the emulsifier. Approach velocity of drop, u_t, towards the two phase interface has been found to be in between Stokes and Newton's law regime through *K* values $(K = D_P\{g\text{ñ}\,(\text{ñ}_P-\text{ñ})/\text{ì}^2\}^{1/3})$ Density and viscosity have been estimated through densitymeter and viscometer for varying composition of solutions. Emulsification carried out in laboratory at a speed of 3000 RPM, leads to drop diameter of dispersed phase of the order of 1 mm. Accordingly, spherical drop of 1 microlitre volume has been taken for D_P as 0.124e-02 m. u_t has been calculated through Equation 11 using a value of C_D found by trial, shown in Table 1.

Table 1: Theoretical values of approach velocity of drop towards the Interface

TBP in dodecane v/v	C_D	u_t m/s	$Re_{P\ cal}$	$Re_{P\ theoretical}$
0%	1.85	0.04955	34.775	34.8
5%	1.85	0.04817	34.217	34.8
10%	2	0.04497	30.772	30
20%	2.32	0.03924	25.231	25.4
30%	2.5	0.03533	22.26	22.5

$$u_t = \{((4\,D_P g\,(\text{ñ}_P-\text{ñ}))/3\,C_D\,\text{ñ}\}^{1/2.} \qquad (11)$$

Through u_t, time of approach of drop to interface has been evaluated and shown in Table 2 with the experimental data. Distance of travel for the drop is taken as 3.75e-02 m. Time for coalescence of drop of distilled water to its bulk phase has been observed and presented in Figure 3. With gradual increase in concentration of TBP, coalescence time also increases. This is because of the increase in viscosity of organic and decrease in its interfacial tension with the increase in TBP concentration. Theoretical values for the coalescence time (shown in Figure 3 along with the data) have been estimated through Equation 10 using physical properties of solutions and film thicknesses according to Ghosh and Juvekar. Interfacial tension of solutions has been measured using spinning drop tensiometer.

Table 2: Time of approach of drop to interface

TBP % v/v	u_t m/s	Time (Data)	Time (Eq 11)
0%	0.04955	600 ms	756.81 ms
5%	0.04817	750 ms	778.49 ms
10%	0.04497	800 ms	833.89 ms
20%	0.03924	900 ms	955.66 ms
30%	0.03533	1000 ms	1061.42 ms

It has been observed that with presence of emulsifier in organic phase (3 % SPAN v/v), coalescence time are two orders of magnitude higher than the coalescence time when no emulsifier present. This is because of one order of magnitude reduction of interfacial tension when emulsifier is present in the organic phase. Further, it has been observed that presence of emulsifier leads to decrease in coalescence time with increase in concentration of TBP. This is due to the increase in interfacial tension with increasing TBP in presence of emulsifier. Theoretical values are found to be in agreement with the data. The small deviations between predicted and observed values are expected to reduce further if the effect of the approach velocity of drop is accounted in the mathematical model.

Conclusions

Coalescence time has been found virtually one order of magnitude greater than the time of approach of drop towards the interface for the present organic pool length. Presence of emulsifier leads to higher approach and coalescence time due to increase in the viscosity of continuous phase and reduction in interfacial tension. Time of approach of drop towards the interface also rises with the increase in the concentration of the TBP, which is more prominent in presence of emulsifier. Increasing TBP concentration in presence of emulsifier, leads to decrease in coalescence time. The study will be helpful in online characterization of dispersion stability and coalescence during a liquid liquid extraction process.

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