

Drop Formation in Immiscible Liquid Systems under Condition of Mass Transfer

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The drop formation in immiscible liquid-liquid systems under mass transfer conditions was experimentally investigated. To know the exact effect of mass transfer on drop sizes, the decrease of interfacial tensions due to the presence of solutes has to be evaluate. Interfacial tensions of liquid pairs were measured with a Wilhelmy method as a function of the relative amounts at which both the solution and the solvent were mutually saturated. The interfacial tensions between the liquid pairs mutually saturated at an equal amount were found to be appropriate for the prediction of the drop formation accompanying mass transfer.

Keywords: Interfacial tension, Drop size, Extraction, Mass transfer,

1. INTRODUCTION

Drop formation in immiscible liquids through a nozzle at low velocities has been studied by many investigators ^{1,2,3, 4,5}). Almost all the experiments have been carried out under conditions of no mass transfer, although the drop formation in practical equipment is usually accompanied by mass transfer. When a solute diffuses across the interface of a drop forming at a nozzle, complicated phenomena such as eruption and convection cell are observed ⁶). The effect of these interfacial phenomena on mass transfer rates has been discussed by many investigators. However, the effect of mass transfer on the drop size has been little studied, except for the drop formation by the jet breakup ^{7,8,9,10,11}).

The direction of mass transfer was found to affect sizes of drops formed from jets ⁷). Burkholder and Berg⁸) developed the hydrodynamic stability theory of liquid jets in immiscible liquids undergoing mass transfer, and analytically resulted that the mass transfer effect is evaluated by a Marangoni number and depends on the transfer direction. It must be emphasized, however, that the difficulty in estimating the appropriate interfacial tension of non-equilibrium systems prevents from comparing quantitatively the theoretical with the experimental effect of mass transfer on the jet breakup.

Mass transfer across the interface may introduce a twofold effect on the drop formation. One is the Marangoni instability due to the gradient of interfacial tensions or the convection induced by diffusing solutes. The other is the decrease of interfacial tensions due to the presence of solutes. For the determination of any dependence of drop sizes on mass transfer, thus, it is important to make exact distinctions between these two effects.

Little attention has been paid to the interfacial tension of the interface across which a solute was diffusing, although it would play an important role on the prediction of various interfacial phenomena. Hydon¹²) measured interfacial tensions for the system water - acetone - petroleum ether by a drop volume method, maintaining the concentration of acetone in water at a constant. Scheele and Meister ⁵) also applied a drop volume method by keeping the concentration of acetone in both the water and the benzene phase at a same level. Groothuis and Zuideweg ¹³) discussed that interfacial tensions of a benzene - acetic acid - water interface increase to approach the value for a solute-free system when the relatively small amount of drop comes into equilibrium with the large amount of the surrounding solute-free water phase.

Interfacial tensions in all the previous work were measured by a drop volume method. However, mass transfer across the interface may affect the drop size as a result of the Marangoni effect as mentioned above.

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Thus, we must avoid to use the interfacial tension measured by a drop volume method in the study of mass transfer effect on the drop formation.

2. EXPERIMENTAL

Drops were formed by injecting liquids through a nozzle made of a stainless steel hypodermic tube which was settled in the bottom of a test section: a rectangular glass column of 6 x 11 cm in cross section and 50 cm in height. The tip of the nozzle was sharpened to a knife edge as examined under a microscope. Two nozzles were used; the diameter is 0.117 and 0.097 cm.

The flow rate was measured by a calibrated glass globe into which the dispersed liquid overflowed from the top of the test section. The injection velocity was kept below the jetting velocity so drops were formed directly at the nozzle tip throughout the experiment. The drop size was determined by counting its number corresponding to the collected volume. The number of drops was counted by a photo transistor and a digital counter. The maximum frequency of drop formation was 7.5 S^{-1} and the minimum was 0.18 s^{-1} . The drop sizes were measured at $30 \pm 0.5 \text{ }^\circ\text{C}$ ($25 \pm 0.5 \text{ }^\circ\text{C}$ for one system).

The experimental liquid pairs were benzene - distilled water and distilled water - kerosene. As the solutes, acetic acid, acetone and ethanol were used. All the reagents except kerosene were extra pure grade available commercially and used as received. In the experiment of the drop formation under the mass transfer condition, all the liquid pairs were used as unsaturated, while the experiments under no mass transfer condition (the solute free system) were carried out using the saturated liquid pairs.

Interfacial tensions were measured by a Wilhelmy plate method (Shimazu surface tensiometer ST-1). Prior to measuring interfacial tensions, the experimental liquid pairs were mutually saturated at a given weight ratio of one to other phase. The preparation of liquid pairs and the measurement of interfacial tensions were carried out at the same temperature as in the drop formation.

3. RESULTS

3.1. Drop Formation

When water drops formed in the benzene phase containing the solute, the drops were observed to undergo

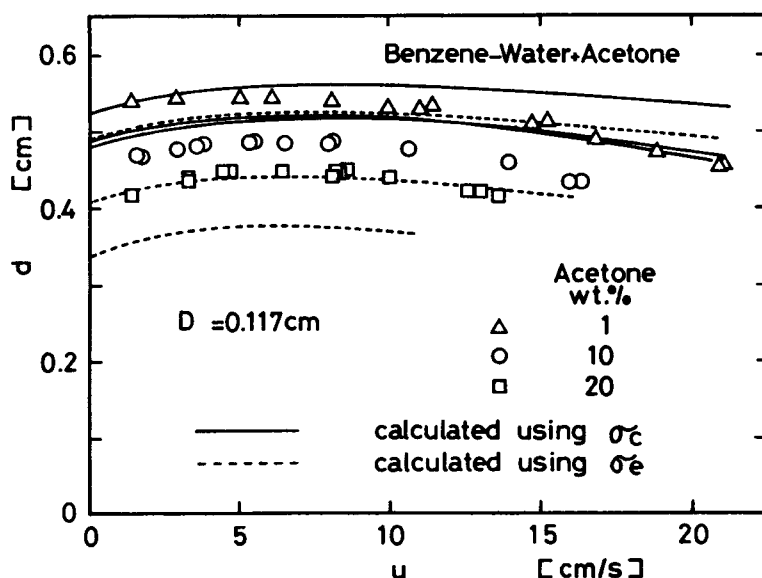


Figure 1 Effect of inward mass transfer on drop diameters for the system where benzene is injected into aqueous acetone solution. Solid curves are prediction from equation (1) using σ_c as interfacial tension. Dotted curves are calculated from equation (1) using σ_e .

erratic pulsation or kicks. In particular, the system (benzene + acetic acid) - water was found to cause violent kicks even at a low concentration level of the solute. On the contrary, no visible kick was observed in the system where the solute is initially in water phase.

Figure 1 shows the effect of inward mass transfer on drop sizes for the system benzene - acetone - water. The effect of outward mass transfer is shown in Figure 2. Figures 3 and 4 show drop diameters for the system benzene - acetic acid - water. In the experiment where acetic acid transfers from benzene to water, violent kicks made the drop size distribution broader and prevented from getting reproducible data of drop sizes at high concentration levels of acetic acid. Figure 5 shows drop sizes for the system aqueous ethanol solution - kerosene. In all experimental systems, the drop sizes decrease with increasing the driving force of either inward or outward mass transfer.

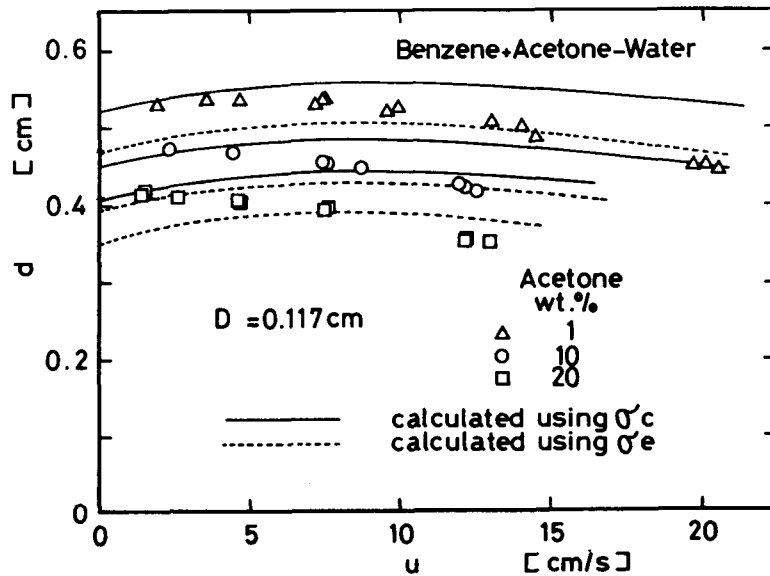


Figure 2 Effect of outward mass transfer on drop diameters for the system (benzene + acetone) - water.

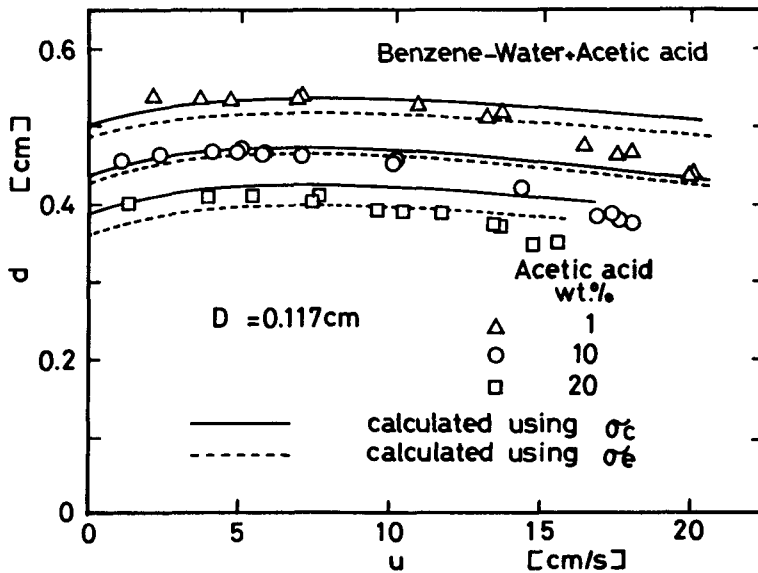


Figure 3 Effect of inward mass transfer on drop diameters for the system benzene - (water + acetic acid).

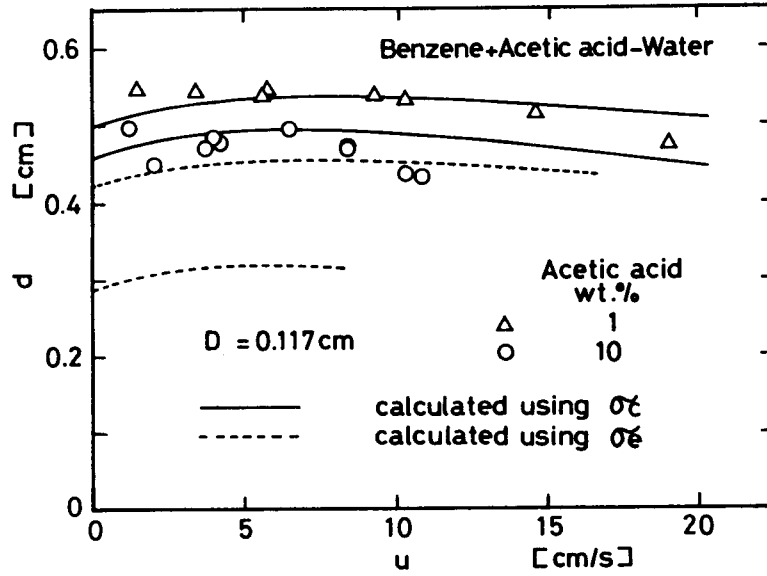


Figure 4 Effect of outward mass transfer on drop diameters for the system (benzene + acetic acid) - water.

3.2 Interfacial Tension

the relative amount at which initial aqueous solutions of acetone are saturated with solute-free benzene.

Interfacial tensions of partially soluble liquid pairs that contain a solute depend on the concentration of the solute. A mathematical model for this situation leads an interfacial concentration that is a function of the diffusivity, the distribution coefficient and the initial concentration¹⁴⁾. For the case of finite mass of two phases, however, the interfacial concentration depends on the contacting time⁶⁾. For many liquid - liquid systems, furthermore, the phase equilibrium is not linear and not always available. Thus, it is impractical to obtain the

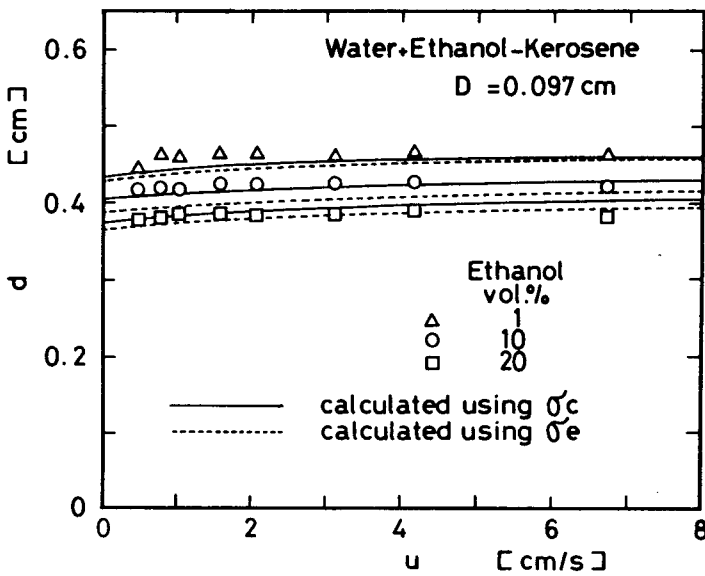


Figure 5 Effect of outward mass transfer on drop diameters for the system (water + ethanol) - kerosene.

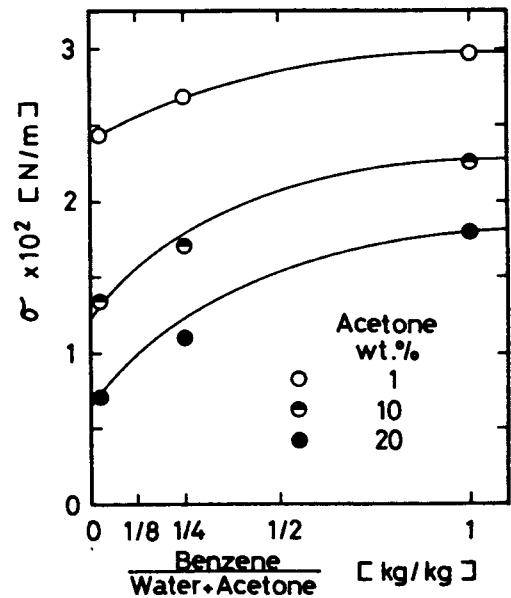


Figure 6 Interfacial tensions between benzene and (water + acetone) as a function of

interfacial tension from knowledge of the interfacial concentration.

To determine the interfacial tension for non-equilibrium conditions, the interfacial tensions of the saturated liquid pairs were measured as a function of the relative amount at which both the solution and the solvent were mutually saturated; the concentration of the distributed solute in both phases depends not only on the phase equilibrium but on the relative amount.

In Figure 6, interfacial tensions for the system (water + acetone) - benzene are shown against the weight ratio of acetone in both phases is almost equivalent,

Figures 7 and 8 show interfacial tensions for the system water - acetic acid - benzene. Since acetic acid is selectively soluble in water phase, the interfacial tensions for the system (benzene + acetic acid) - water strongly depend on the relative amount. When acetic acid is initially in the water phase, on the contrary, the interfacial tensions are less sensitive to the relative amount.

The interfacial tension between the initial solution and the liquid equilibrated to it, written as σ_e , can be determined by extrapolating the relative amount to zero. This is a characteristic value for the non-equilibrium liquid-liquid interface. As mentioned before, the interfacial concentration of solutes depends on several factors. In the limiting case where the diffusivities in both phases are the same magnitude and the distribution coefficient is unity, the interfacial concentration after infinite contacting time corresponds to the bulk concentration of the solution saturated with the same amount of the solvent. Thus, the liquid pair whose relative amount is unity will produce an informative value. The interfacial tensions approach a pseudo constant when the relative amount increases beyond a critical value as shown in Figures 6, 7 and 8. This critical amount is less than unity in most of the experimental systems.

Thus, the interfacial tension at the relative amount of unity is employed as another characteristic value and written as σ_c . All experimental values for the both interfacial tensions are listed in Table 1. Which is more effective as the interfacial tension for non-equilibrium conditions should be discussed.

4. DISCUSSION

Prior to discussing which value of interfacial tensions is appropriate to estimate the drop formation undergoing mass transfer, the effect of interfacial tensions on drop sizes must be known. Scheele and Meister⁵⁾ proposed the following equation for a drop formed under condition of no mass transfer.

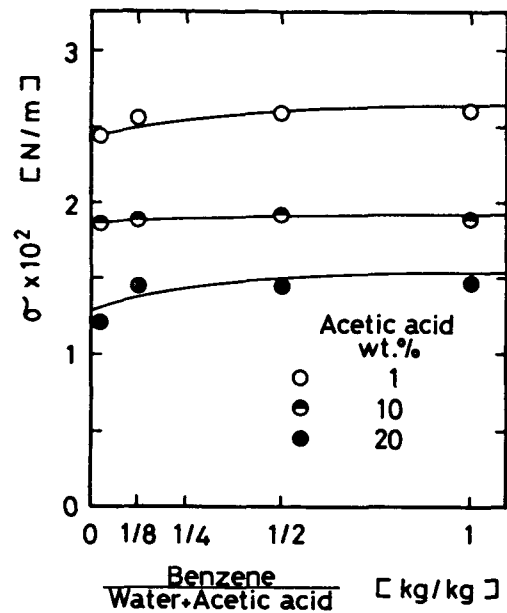


Figure 7 Interfacial tensions for the system benzene - (water + acetic acid).

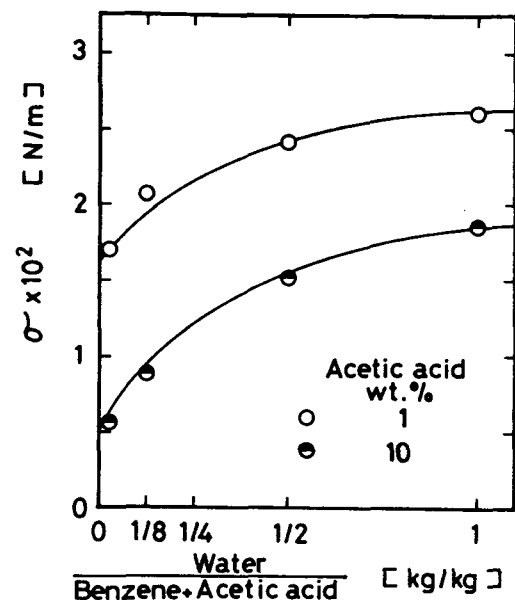


Figure 8 Interfacial tensions for the system water - (benzene + acetic acid).

$$d^3 = \frac{6F}{\pi} \left[\frac{\pi \sigma D}{g \Delta \rho} + \frac{20 \mu_c \bar{V} D}{d^2 g \Delta \rho} - \frac{4 \rho_D V u}{3 g \Delta \rho} + 4.5 \left\{ \frac{V^2 D^2 \rho_D \sigma}{(g \Delta \rho)^2} \right\}^{1/3} \right] \quad (1)$$

Hozawa et al³⁾ proposed a simple nomograph to predict the drop size, which is applicable to a wide range of liquid-liquid systems.

Figure 9 shows the comparison of the experimental drop sizes under no mass transfer condition with the two predictions. The difference between the two predictions is less than 7 % except at higher injection velocities; the experimental jetting velocity in this system is about 23 cm/s. The prediction from equation (1) is in good agreement with the experimental drop sizes at low injection velocities (less than 10 cm/s). Thus equation (1) is used to evaluate the effect of interfacial tension on drop sizes.

Experimental drop sizes at low liquid velocities under mass transfer condition are compared with the predictions from equation (1); both σ_c and σ_e are used to examine which is effective. The predictions for the experimental systems are shown in Figures 1 ~ 6 by the solid curves (using σ_c) and the dotted curves (σ_e). All predictions are based on the physical properties of the initial and unsaturated state except for the interfacial tensions. Table 2 shows these physical properties; they were experimentally measured.

For the system of low mass flux (Figures 3 and 5), the predictions using σ_c are in good agreement with the experimental drop sizes, especially in low injection velocities. On the contrary, the use of σ_e as the interfacial tension predicts smaller drop sizes.

For the system (benzene + acetone) - water, the prediction using σ_c agrees with the experimental data at low liquid velocities. However, the calculations using σ_c for the system benzene - (water + acetone) are larger than the experimental drop sizes except for the system for 1 wt % acetone. This disagreement is due to the increase in density difference. Transfer of acetone into benzene reduces the density of benzene phase and increases the density of water phase, as can be seen in Table 2. The higher concentration of acetone increases the divergence in density difference from the initial state during the drop formation, so the drop size becomes smaller than the prediction based on the physical properties for the initial and unsaturated condition. Furthermore, the large density difference between the transferring solute and the bulk phase introduces the convection flow that sifts the force balance to reduce the drop volume.

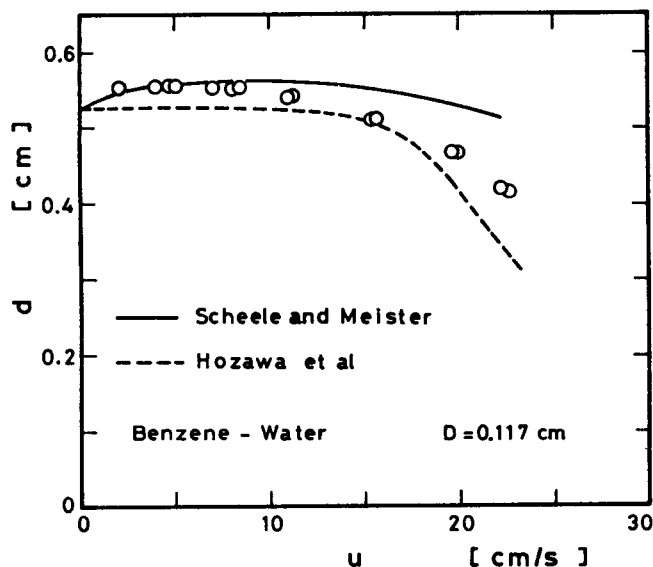


Figure 9 Comparison of prediction from previous work with experimental drop sizes under no mass transfer condition (the system benzene - water). A solid curve shows equation (1)⁵⁾ and a dotted curve is prediction from Hozawa's nomograph³⁾.

Table 1 Interfacial tensions of experimental liquid pairs

Liquid pairs	$\sigma_e/10^{-3} \text{ Nm}^{-1}$	$\sigma_c/10^{-3} \text{ Nm}^{-1}$	Interfacial tension calculated from drop size at $u=0/10^{-3} \text{ Nm}^{-1}$
Benzene - Acetone/Water(1/99)	24.1	29.7	31.7
Benzene - Acetone/Water(10/90)	12.6	22.8	18.3
Benzene - Acetone/Water(20/80)	6.6	18.1	11.1
Acetone/Benzene(1/99) - Water	22.3	30.2	31.2
Acetone/Benzene(10/90) - Water	14.4	21.1	23.8
Acetone/Benzene(20/80) - Water	11.4	17.1	18.8
Benzene - Acetic acid/Water(1/99)	24.3	26.4	32.1
Benzene - Acetic acid/Water(10/90)	18.6	19.2	22.2
Benzene - Acetic acid/Water(20/80)	12.8	15.3	16.8
Acetic acid/Benzene(1/99) - Water	16.3	26.2	35.0
Acetic acid/Benzene(10/90) - Water	5.0	18.6	14.2
Ethanol/Water(1/99)* - Kerosene	33.4	34.0	34.0
Ethanol/Water(10/90)* - Kerosene	23.6	26.1	28.6
Ethanol/Water(20/80)* - Kerosene	18.7	20.1	19.9

*Ratios in parentheses are on weight basis while those with an asterisk (ethanol/water) are on volume basis. Systems ethanol/water - kerosene were measured at 25 °C, while all other systems were at 30 °C.

Table 2 Physical properties of experimental systems

Dispersed phase	$\rho_D/\text{kg m}^{-3}$	Continuous phase	$\rho_C/\text{kg m}^{-3}$	$\mu_C/10^{-4}\text{Pa s}$	$\Delta\rho/\text{kg m}^{-3}$
Benzene	872.2	Acetone/Water(1/99)	995.2	8.20	123.0
		Acetone/Water(10/90)	980.3	9.76	108.1
		Acetone/Water(20/80)	963.9	11.3	91.7
Acetone/Benzene(1/99)	871.5	Water	997.0	8.04	125.5
Acetone/Benzene(10/90)	863.4				133.6
Acetone/Benzene(20/80)	854.7				142.3
Benzene	872.2	Acetic acid/Water(1/99)	998.7	8.15	126.5
		Acetic acid/Water(10/90)	1009	9.55	136.8
		Acetic acid/Water(20/80)	1021	11.1	148.8
Acetic acid/Benzene(1/99)	873.2	Water	997.0	8.04	123.8
Acetic acid/Benzene(10/90)	882.8				114.2
Ethanol/Water(1/99)*	996.2	Kerosene	788.2	14.0	208.0
Ethanol/Water(10/90)*	985.3				197.1
Ethanol/Water(20/80)*	973.1				184.9
Benzene	872.2	Water $\sigma = 0.031 \text{ N/m}$	997.0	8.04	124.8

* Systems ethanol/water - kerosene are on volume ratio basis and at 25 °C, while all other systems are on weight ratio basis and at 30 °C.

In the system (benzene + acetone) -water, transfer of acetone reduces the density difference; this reduction could increase the drop volume. On the contrary, the convection induced by the transferring solute neutralizes the effect of the decrease in density difference. Thus the drop size in this system is probably insensitive to the change in density difference.

As acetic acid is selectively distributed to the water phase, the mass flux in the system (benzene + acetic acid) - water is much higher than the other systems. Furthermore, the violent kick during the drop formation makes the distribution of drop sizes significantly broad. In spite of the above fact that plays a negative role, the predictions using σ_c are in good agreement with the experimental data, as shown in Figure 4.

The drop sizes in almost all the experimental systems can be successfully predicted by the application of σ_c . The reason why σ_c is effective in the drop formation is as follows. The penetration distance of the solute from the interface is equivalent in both liquids because the diffusivity of the solute either in water or in organic phase is almost same magnitude. Thus, the interfacial tension during the drop formation is kept equivalent to that between the phases saturated at an equal amount, provided the convection induced by the density difference is not so significant.

The comparison of σ_c with the interfacial tension obtained from the experimental drop volume at $u=0$ (drop volume method) are shown in Table 1. The drop volume at $u=0$ was obtained by extrapolating the drop size data. The interfacial tensions by the drop volume method agree essentially with σ_c measured by a Wilhelmy method except for the system where the effect of the convection is significant and the mass flux is rather high. It is emphasized that a drop volume method may include the Marangoni or the convection effect so the interfacial tension must be determined by other method such as a Wilhelmy method for the purpose to investigate the effect of mass transfer on the drop formation.

5. CONCLUSIONS

The effect of mass transfer on the size of drops forming from a single nozzle has been experimentally investigated. It is necessary to distinguish the influence due to the decrease of interfacial tensions from the effect induced by the Marangoni instability because the drop formation under mass transfer conditions include the both effects. Thus, the interfacial tensions of liquid pairs mutually saturated were measured with a Wilhelmy plate method as a function of the relative amounts of the pairs. Then, the interfacial tension at an equal amount is found to be effective to predict the size of drops formed under mass transfer conditions. In the system benzene - water + acetone, however, the experimental drop sizes are smaller than the prediction; this difference is due to the convection induced by diffusing solutes. Furthermore, the experimental drop sizes beyond moderate injection velocities under higher flux conditions are apparently smaller than the prediction; the effect of mass transfer in this region is a future problem to investigate.

NOMENCLATURE

D	= diameter of nozzle	[m]
d	= diameter of drops	[m]
F	= Harkins-Brown correction factor	[-]
g	= gravitational acceleration	[m/s ²]
u	= injection velocity of dispersed liquid	[m/s]
V	= flow rate of dispersed liquid	[m ³ /m]

Greek letters

μ_c	= viscosity of continuous phase	[Pa s]
ρ	= density	[kg/m ³]
$\Delta\rho$	= density difference	[kg/m ³]
σ	= interfacial tension	[N/m]
σ_c	= interfacial tension between liquid pairs mutually saturated at an equal amount	[N/m]

σ_e = interfacial tension between solution and solvent under equilibrated condition [N/m]

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