MEASUREMENT AND CORRELATION OF THE MASS TRANSFER COEFFICIENT FOR A LIQUID-LIQUID SYSTEM WITH HIGH DENSITY DIFFERENCE

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Abstract - To investigate the mass transfer behavior of a liquid-liquid system with high density difference ($\Delta\rho \approx 500$ kg/m^3), single drop experiments were performed by using the ternary chloroform-ethanol-water system. The mass transfer direction was from the dispersed phase to the continuous phase, while the aqueous phase was dispersed in chloroform to generate drops. The influences of drop diameter, initial solute concentration and temperature on the mass transfer were investigated. The effects of the drop diameter and initial solute concentration on interfacial instability of droplets hanging in the continuous phase were also observed. For the purpose of correlation, a mass transfer enhancement factor F was introduced and then correlated as a function of dimensionless variables. The modified correlation from the mass transfer coefficient model was found to fit well with the experimental values.
Keywords: Single drop; High density difference; Mass transfer coefficient; Enhancement factor (F).

INTRODUCTION

Extraction has been widely used in the chemical industry due to its low-energy consumption. For many decades, researchers have tried to enhance the mass transfer in extraction operations. However, the knowledge concerning the design of liquid-liquid extraction columns is still far from satisfactory because of the complex mass transfer across interfaces in two-phase systems. Nowadays, the scale-up of extraction still depends on large quantities of pilot experiments which are expensive and time-consuming. Measuring mass transfer coefficients by single drop experiments is a promising method to solve the above problem (Rahbar *et al*., 2011). The cause lies mainly in that the behavior of single drops determines the performance of extraction columns with a swarm of drops, regardless of drop breakage and coalescence phenomena, which have to be considered in liquid-liquid extraction operations (Saien *et al*., 2014a).

In an extraction column, a falling or rising drop in the continuous phase may experience three stages: formation and acceleration, free motion, and coalescence (Dehkordi *et al*., 2007). During the whole process, there is an interaction between the mass transfer and the fluid dynamic behavior of droplets (Wegener 2009). On the one hand, the complex motion may enhance the mass transfer by reducing the mass transfer resistance at the movable interface. On the other hand, physical properties of the drops can vary with the development of the mass transfer; the latter in turn influences the evolution of the drop movement.

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Within an ongoing mass transfer, a concentration gradient appears and the interfacial tension varies along the drop surface. Marangoni convection occurs when the interfacial tension gradient is sufficient. In this process, the system tends to minimize its surface energy and expands regions of lower towards regions of higher interfacial tension. This effect causes convection between the surface and the internal region, and promotes radial mixing in droplets (Temos *et al*., 1996). Then the concentration gradient reduces with time and Marangoni convection becomes weaker until it disappears. However, Marangoni convection is different from the toroidal flow in droplets and can cause more complex chaotic flow structures. Thus, strengthening the Marangoni effect decreases the mass transfer resistance and improves the extraction efficiency. In addition, instabilities in larger drops are superposed by internal oscillation and shape deformation (Temos *et al*., 1996). Deformation alters the drag coefficient and the internal circulation pattern development within the droplet. Therefore, drop deformation is another important factor in the calculation of mass transfer coefficients.

The knowledge of the mass transfer in a single drop is the basis for the estimation of the mass transfer coefficients. Although a large number of work with respect to empirical and idealized theoretical equations for predicting the mass transfer coefficient for drops can be found in the open literature, compared with experiments the predictions show both success and failure (Waheed *et al*., 2002). Among these models, a classical one is the Newman equation, which predicts the mass transfer coefficients for rigid spherical drops without internal circulation (Newman, 1931). But when it was applied in circulation or oscillation conditions, the prediction exhibited serious deviations. Kronig and Brink (1951) proposed a model for laminar diffusion with internal circulation. Handlos and Baron (1957) proposed an assumption that internal mixing can be described by random radial convection which superimposes internal circulation. In this model, the Peclet number and the velocity of the drops are required. Later, Henschke and Pfennig (1999) modified the model with an instability constant, C_{IP}, which is defined by incorporating the effect of diffusion and turbulence in droplets. This model can be used to calculate the mass transfer coefficient in oscillation conditions.

Up to now, most studies on mass transfer of extraction systems focused on the influences of various experimental conditions, but the properties of systems were seldom considered. Among these, the density difference is an important factor. When the density difference between the continuous and dispersed phases is higher, rising or falling droplets more readily reach higher velocities and thus higher Reynolds numbers, which may affect the mass transfer via more drastic internal mixture or circulation. In this work, therefore, single drop experiments on a system with high density difference (chloroform-ethanol-water, $\Delta\rho \approx 500$ kg/m^3) were conducted. The influences of temperature, initial solute concentration and drop diameter on the overall mass transfer coefficient were studied. Moreover, the interfacial instability of hanging drops was investigated in an optical contact angle measuring instrument. For a high density difference liquid-liquid system, in order to estimate the mass transfer coefficient more accurately, a new empirical model was proposed through introducing a mass transfer enhancement factor F.

EXPERIMENTAL SECTION

Chemical System and Physical Properties

The liquid-liquid extraction system in this study is chloroform-ethanol-water. Chloroform and ethanol were analytical grade with purity > 99%, and the deionized water used had a specific resistance of 18.3MΩ·cm. Chloroform acts as the continuous phase while deionized water acts as the dispersed phase and ethanol as the solute. Unlike the systems recommended by the European Federation of Chemical Engineering, this system exhibits a high density difference. The mass transfer direction is from the dispersed phase to the continuous phase.

The physical properties of the dispersed and continuous phases are summarized in Tables 1 and 2, respectively. Here, densities were measured by the pycnometer method and the apparatus was calibrated with deionized water prior to the measurements. Viscosities were determined by using a Pinkecitch viscometer with the inner diameter of 0.4 mm. Interfacial tensions were determined with a surface/interface tensiometer (JYW-200) with the uncertainty of 0.01 mN/m.

Calculation of the Diffusion Coefficient

In this current paper, the diffusion coefficients were calculated by the Wilke-Chang equation (Wilke and Chang, 1955), given by:

$$D = 7.4 \times 10^{-12} \frac{\left(\varphi\, M\right)^{1/2} T}{\mu\, V_{A}^{0.6}} \tag{1}$$

where D is the diffusion coefficient, m^2/s, φ is the association constant, M is the molecular weight of solvent, g/mol, μ is the viscosity of the solvent, mPa·s, and V_A represents the molar volumes at the normal boiling point, cm^3/mol. Here V_A was estimated by a group contribution method (Ma, 2008).

Table 1: Physical properties of the dispersed phase used in the experiments.

$C_{Ethanol}$ (g/mL)	ρ (kg/m^3)	μ (mPa·s)
Temperature=303.15 K		
0.05	987.3	0.93
0.10	979.5	1.10
0.15	974.4	1.30
0.20	965.7	1.49
0.25	959.0	1.66
Temperature=308.15 K		
0.05	985.5	0.83
0.10	977.5	0.97
0.15	972.2	1.13
0.20	963.2	1.28
0.25	953.8	1.39
Temperature=313.15 K		
0.05	983.5	0.74
0.10	975.5	0.86
0.15	969.7	0.99
0.20	960.7	1.11
0.25	950.7	1.20
Temperature=318.15 K		
0.05	980.8	0.64
0.10	972.6	0.71
0.15	967.2	0.78
0.20	957.4	0.85
0.25	947.2	0.94

Table 2: Physical properties of the continuous phase used in the experiments.

T (K)	ρ (kg/m^3)	μ (mPa·s)
303.15	1467.3	0.52
308.15	1460.9	0.50
313.15	1451.3	0.47
318.15	1441.9	0.45

Setup and Procedure

The single drop experiments were carried out in two glass columns (38 mm × 200 mm and 38 mm × 500 mm). The inner diameter is large enough to avoid wall effects in the experiments. The column is equipped with a jacket. As shown in Figure 1, the temperature of the system was adjusted by circulating water. A precision thermostat was used for temperature control with an uncertainty of ± 0.1 K. The column was filled with chloroform as the continuous phase. The dispersed phase was held in a syringe connected to a precise syringe pump (HX-901A), and drops were formed at the top of stainless steel nozzles when the pump ran at a suitable rate. By using nozzles with different inner diameters, variety sizes of drops were generated in the column.

After the detachment from the nozzle, drops rose in the column and were collected by an inverted glass funnel which was installed at the top of the column. The interfacial area within the funnel just above the neck was minimized by occasionally pulling drops into the pipe connected to the funnel. Additional mass transfer at this point could be minimized since there was only minimal contact between drops which coalesced in the channel and the continuous phase in the column. The distance apart between two consecutive droplets was large enough (> 60 mm) so that fluid motion was dampened before the next droplet arrives. Thus, interactions between drops should be negligible (Skelland and Vasti, 1985). Three samples were taken in each run and then analyzed by gas chromatography (GC7900).
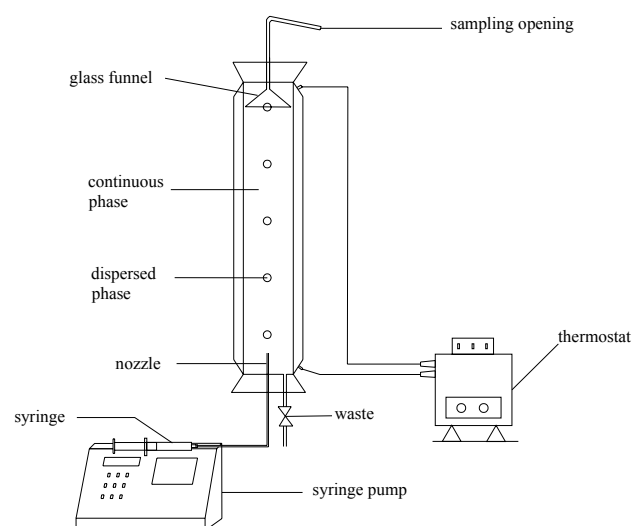

Figure 1: Sketch of experimental setup.

The average drop volume was calculated from the number of formed drops and the input volume of the dispersed phase. Considering the drop to be a rigid sphere, the drop diameter was then determined. As observed in the experiments, drop motion tended to reach a steady value after 50 mm of traveling in the continuous phase. Coincidentally, Saien *et al*. (2012) reported a distance of about 40 mm in the system of toluene-acetic acid-water as adequate to have steady movement. Slater *et al*. (1988) observed a distance of about 30 mm for the chemical system of cumene-acetic acid-water. The terminal velocity of the drops was measured with a stopwatch between two points spaced 400 mm apart, at a minimum of 50 mm from the tip of the nozzle. Five measurements were

repeated in each condition and the results were averaged.

To avoid the effect of unsteady mass transfer during drop formation and coalescence, named the "end effect", two columns were used with different heights of 200 mm and 500 mm. To eliminate additional mass transfer of solvents, the continuous phase and the dispersed phase were mutually saturated with each other in a vessel before all experiments conducted. In order to keep the system free of contaminants, a specific cleaning procedure was performed. Thus, all materials in contact either with the continuous phase or the dispersed phase sample were cleaned several times mechanically, then rinsed with deionized water and dried inside a vacuum drying oven.

In addition, an optical contact angle measuring instrument (OCA 20) was used to study the interfacial instability of hanging drops within this system. The instrument consists of three major components: (1) illumination section, (2) sample section, and (3) camera section. The camera can take 25 pictures per second.

RESULTS AND DISCUSSION

Hydrodynamic Investigation

Since the hydrodynamic behavior of the droplets significantly affects the mass transfer, verifying the condition of droplets tends to be vitally necessary. In this work, some empirical criteria were adopted to determine the conditions of the generated droplets, including the range of Reynolds number ($Re = du_t\rho_c / \mu_c$), the range of Weber number ($We = du_t^2\rho_c / \gamma$) defined by Hu (1955), the dimensionless group H ($H = 4/3 E\ddot{o}M^{-0.149}(\mu_d/\mu_c)^{-0.14}$, $E\ddot{o} = g\Delta\rho d^2 / \gamma$, $M = g\mu_c^4\Delta\rho / (\rho_c^2\gamma^3)$) defined by Grace et al. (1976), and the range of $Re/N_{PG}^{0.15}$ (Skelland, 1992). As presented in Table 3, the lower limits given for each criterion indicate the onset of oscillation in drops. Comparison of calculated results with criterion values, showed that most drops were under the oscillation condition. Klee and Treybal (1956) proposed an expression for the critical diameter d_{cr}, $d_{cr} = 0.33\rho_c^{-0.14}\Delta\rho^{-0.43}\mu_c^{0.30}\gamma^{0.24}$, at which drop oscillation occurs. So all the critical drop sizes were calculated and are presented in Figure 2. Note that the diameters of droplets ranged from 1.66 to 3.49 mm and were larger than the calculated d_{cr}. Based on all the discussions above, the oscillation condition of the droplets in this work was confirmed.

Table 3: Different criteria for determining conditions of drops.

Criteria	$H > 59.3$	$We > 3.58$	$Re > 500$	$Re/N_{PG}^{0.15} > 20$
Value in this work	56.15-151.46	2.83-7.68	479-1370	20.32-39.65

One datum with $Re<500$, thirteen data with $We<3.58$ and two data with $H<59.3$
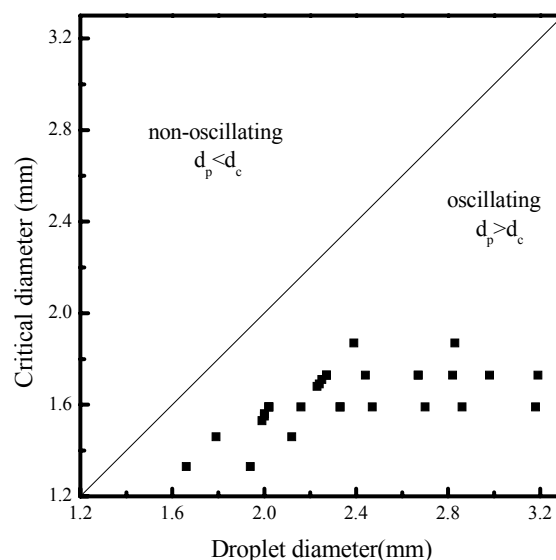
Figure 2: Experimental droplet diameter and critical droplet diameter.

Mass Transfer Investigation

Overall Mass Transfer Coefficient

When taking the component concentration difference as the driving force, the mass transfer rate R expressed in terms of the dispersed phase concentration can be given by the following equation (Sun et al., 2014).

$$R = \frac{V_d dC_d(t)}{A dt} = K_{od}[C_d(t) - C_d^*] \qquad (2)$$

Then, the time-average overall mass transfer coefficient can be expressed with the following equation,

$$d\ln[C_{d(t)} - C_d^*] = \frac{AK_{od}}{V_d}dt = \frac{6K_{od}}{d}dt \qquad (3)$$

After the integration of the above equation, the overall mass transfer coefficient K_{od} can be obtained experimentally using this expression,

$$K_{od} = -\frac{d}{6t}\ln(1-E) \tag{4}$$

where t is the contact time and E is the extraction fraction, defined by

$$E = \frac{C_{df} - C_{di}}{C_d * - C_{di}} \tag{5}$$

Here, C_{df}, C_{di}, and C_d* are the final, initial and equilibrium solute concentrations in the dispersed phase, respectively. Because the solute concentration in the continuous phase is zero and the direction of the mass transfer is from the dispersed phase to the continuous phase, C_d* can be assumed to be zero.

Effect of Drop Size on Mass Transfer

To investigate the effect of drop size on mass transfer, single drop experiments were carried out with initial solute concentrations of 0.10 g/mL and 0.15 g/mL at 303.15 K. As shown in Figure 3, the overall mass transfer coefficient increased significantly with drop size. When the drop diameter varied from 2.02 to 3.49 mm, the overall mass transfer coefficient increased from 0.0263 to 0.1180 mm/s. The same results were obtained by Sun *et al.* (2014) in the system of MIBK-water-phenol.

When drops are small enough, the Reynolds number tends to be very low and drops can be seen as rigid spheres. No circulation or complex mixture occurs inside the drops and mass transfer mainly depends on molecular diffusion, resulting in a low mass transfer coefficient. But with the increase of the drop size, the shape of the drops deforms to a symmetry-axis oblate ellipsoid, and more complicated internal circulation may facilitate the mass transfer in interphases and thus a higher mass transfer coefficient can be obtained. Moreover, the change of droplet trajectories from a vertical rise path to a zigzag trajectory can be obviously observed during the experiments. Deviations from a straight rise path are closely connected with an asymmetric deformation of the droplet, which has been confirmed by Engberg (2014) and Wegener (2007). Otherwise, the drag coefficient closely depends on the droplet shape, the bigger the drop diameter, the higher the drag coefficient. The increasing tangential shear stress deforms the drop, and then internal circulation patterns may vary and more vigorous internal circulation patterns may occur.

For a more intuitive understanding of the impact of the drop size on mass transfer, visual observation of hanging drops in the continuous phase were carried out with an initial solute concentration of 0.15 g/mL under ambient temperature. The drop diameters were set to be 2.12, 2.37 and 2.67 mm, which were the same as that in single drop experiments. As shown in Figure 4, the results clearly indicated that larger drops experienced more severe deformation and shaking in the mass transfer process. The bigger the drop size, the earlier and the more violent the interfacial phenomena that occur. Hence, it can be deduced that the interfacial instability will facilitate mass transfer and enhance the mass transfer coefficient.
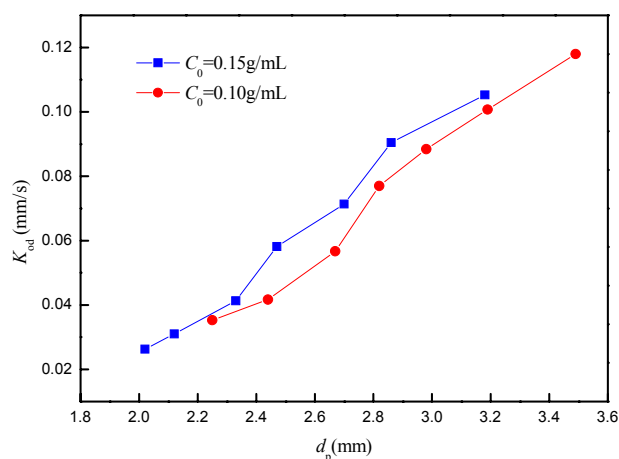

Figure 3: Variations of K_{od} with different d_p at different initial concentrations.
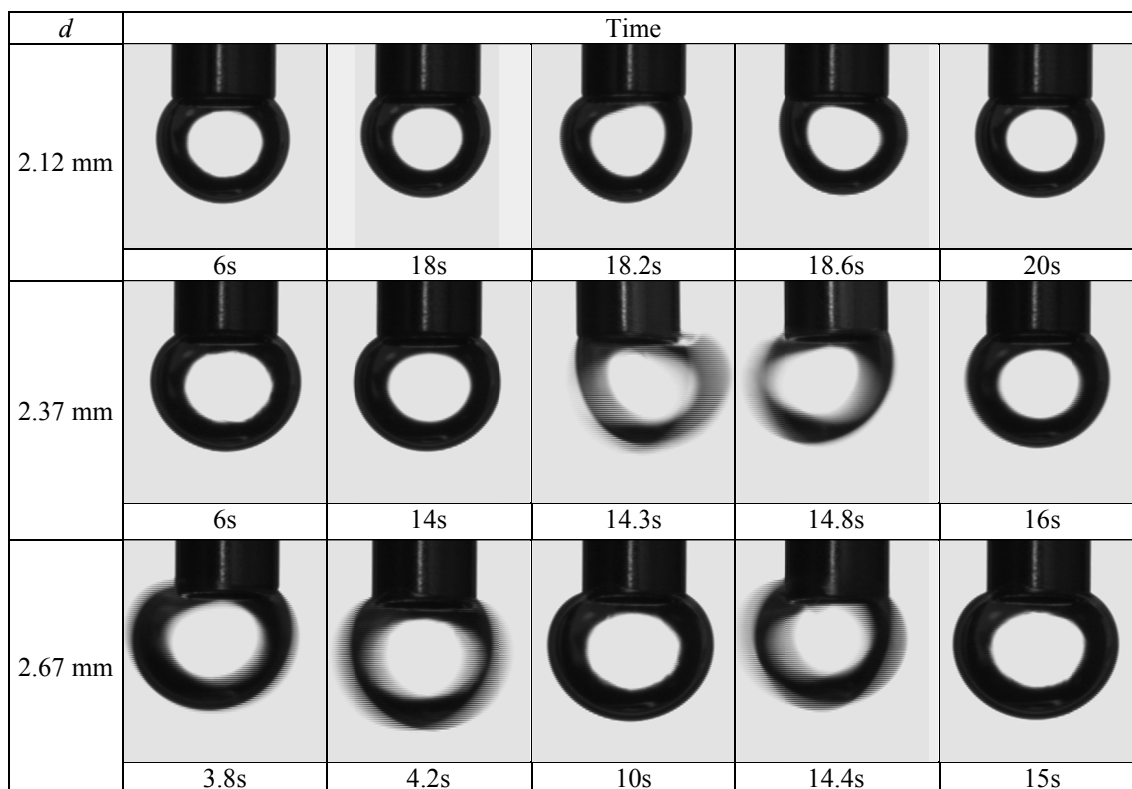
Figure 4: Interfacial phenomena of a drop hanging in the continuous phase.

Effect of Initial Concentration of the Dispersed Phase on Mass Transfer

The influence of the initial solute concentration on the mass transfer coefficient is shown in Figure 5. When the solute concentration increases, the mass transfer coefficient presents a tendency to decrease. The obtained mass transfer coefficient ranged from 0.0228 to 0.0757 mm/s. The interfacial tension changes distinctly with the initial solute concentration in the chloroform-ethanol-water system (as shown in Figure 6), so the drop size deceases with the increase of the initial solute concentration under the same conditions (as shown in Figure 7), further resulting in the decrease of the mass transfer coefficient.

Due to the effects of Marangoni convection and Rayleigh convection, the drops even with the same diameter might have different mass transfer rates. As shown in Figures 5 and 7, the diameters of drop A and B were very close, but K_{od} of drop A was 1.2 times larger than that of drop B. Sternling (1959) revealed that when the interfacial tension is sensitive enough to the solute concentration, which varies over the droplet surface, Marangoni convection will occur. Figure 6 shows that the interfacial tension changes distinctly with the initial solute concentration in the chloroform-ethanol-water system. Thus, Marangoni convection is likely to appear under this condition and finally affects the mass transfer rate. It should be noted that the density of the dispersed phase decreases with the increase of the solute concentration (as shown in Table 1). Researchers have figured out that, in an interfacial mass transfer process, if the density gradient generated by a concentration gradient opposes gravity, Rayleigh instability may be triggered by an infinitesimal perturbation. Thus, Rayleigh convection can affect definitely the concentration distribution pattern and hence interfacial mass transfer (Grahn, 2006).
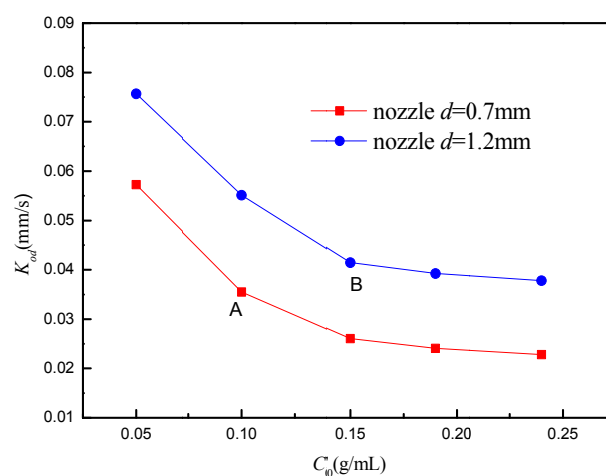

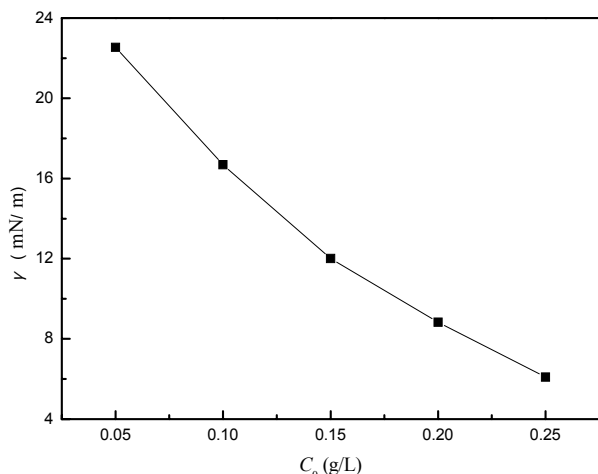**Figure 5:** Variations of K_{od} with initial solute concentration.

Figure 6: Variations of interfacial tension with different initial solute concentration.
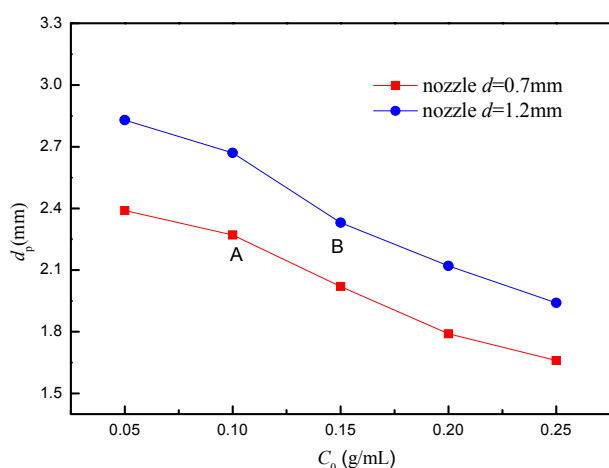

Figure 7: Variations of drop diameter with initial concentration for different nozzles.

Effect of Temperature on Mass Transfer

Temperature is also an important parameter that not only can alter significantly the physical properties of the system, but also can be easily controlled to improve the performance of the extraction column. Therefore, the influence of temperature on the mass transfer of the single drop was carried out in the temperature range of 303.15~318.15 K with the initial solute concentrations of 0.10 and 0.15 g/mL.

As shown in Figure 8, the mass transfer coefficient K_{od} increases with temperature. On the one hand, the molecular diffusivity depends directly on the absolute temperature of the liquid media and inversely on the viscosity of the solvent (Saien *et al.*, 2014b). The viscosity of the continuous phase decreases as the temperature increases. On the other hand, the Reynolds number varies from 654 to 920, and higher temperature causes higher Reynolds num-

ber. The droplets at higher temperature tended to have more complex internal turbulence and thus a higher mass transfer rate was achieved. The disturbance can also provide intensification of the Marangoni phenomenon (Saien *et al.*, 2012). Higher mass transfer coefficients can be obtained at higher temperature, but the mutual solubility of phases more or less increases with temperature, which provides a negative impact on subsequent separations. Hence, an optimum temperature is determined by balancing mass transfer and separation efficiencies.
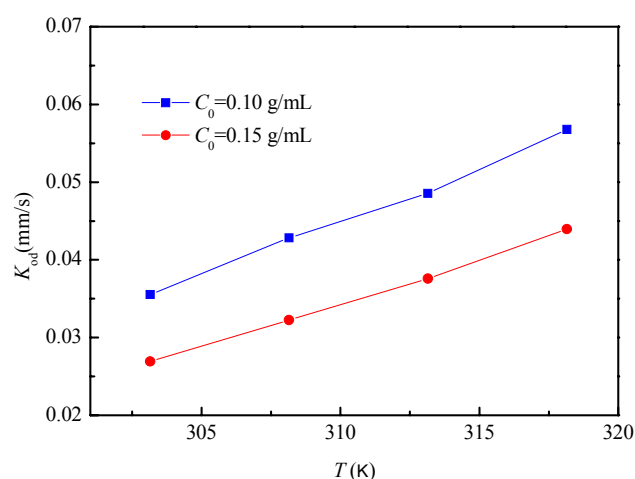

Figure 8: Variations of K_{od} with temperature for different initial solute concentration.

Modeling the Overall Mass-Transfer Coefficient

According to the Whitman two-film theory, K_{od} can be expressed based on mass transfer resistances existing in both dispersed and continuous phases, as expressed by the following equation:

$$\frac{1}{K_{od}} = \frac{1}{k_d} + \frac{m}{k_c} \tag{6}$$

in which m indicates the solute distribution coefficient and k_d and k_c are local mass transfer coefficients in the dispersed and continuous phase, respectively. The distribution coefficients m in this study varied from 2.64 to 2.82. The mass transfer resistance can be judged by the following equation (Brauer, 1978 and Zheng *et al.*, 2014).

$$J = m\left(\frac{D_d}{D_c}\right)^{0.5} \tag{7}$$

Here the calculated J values vary from 1.79 to 3.01, indicating that the mass transfer resistance

exists in both phases.

Though various mathematical models have been developed to estimate the dispersed phase mass transfer coefficient for single drops, they are usually available for special systems or conditions. Therefore, many researchers have tried to make modifications that expand the applicable scope of the established models. Among these, the Newman equation, which is applicable to describe rigid spheres, was often modified to predict various systems.

$$k_d = -\frac{d}{6t}\ln\left[\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\frac{-4\pi^2 n^2 D_d t}{d^2}\right] \qquad (8)$$

Sherwood (1939) used an overall effective D_{oe}, $D_{oe}=RD_d$, to replace the molecular diffusivity in the Newman equation. Thus, the modified model can be applied in circulation conditions or even oscillation conditions. Steiner (1986 and 1990) tested this method with numerous data and further correlated the empirical factor against the physical properties. Both Saien *et al*. (2012) and Sun *et al*. (2014) used this correlation to predict the mass transfer process in their works. However, the mass transfer resistance on both sides could not be neglected in the system of chloroform-ethanol-water. Therefore, such a modification of the Newman equation may be not suitable in this case.

For the continuous phase mass transfer coefficient, there also exist many empirical correlations. According to Kumar *et al*. (1991), when a drop is internally stagnant and the continuous phase velocity is zero, the expression for the continuous phase coefficient is:

$$k_c = \frac{2D_c}{d} \qquad (9)$$

Using Equations (6), (8) and (9), the overall mass transfer coefficient for a rigid drop, $K_{od,rig}$, can be obtained. As mentioned above, drops in the oscillation regime have distinct deformations and complex internal circulation. Marangoni convection may also occur inside the drops. All these factors could influence the mass transfer. If these contributions are included in an enhancement factor F, it can be defined as the ratio of the overall mass transfer coefficient for an ordinary drop to that for a rigid drop.

$$F = \frac{K_{od}}{K_{od,rig}} \qquad (10)$$

The values of F were found to be in the range

from 12.39 to 219.26. The result exactly indicates that mass transfer coefficients in oscillating drops are much bigger than in rigid drops.

The condition of the drops can be determined from the Reynolds number and Weber number, the Schmidt number indicates the diffusion behavior, and the density ratio ρ_d / ρ_c can reveal the influence of the density difference on the mass transfer. Therefore, after calculating the experimental values of the enhancement factor, the following model is derived in terms of several dimensionless numbers, including the Reynolds number, Schmidt number, Weber number, and density ratio, by using the least squares method.

$$F = 18.95 + 0.76\times \text{Re}^{2.93} Sc_d^{0.94}(\rho_d / \rho_c)^{57.04} We^{0.66} \quad (11)$$

The calculated values of the enhancement factor were used to estimate overall mass transfer coefficients. The experimental K_{od} and predicted K_{od} calculated by the different models are presented in Figure 9. Note that the present model gives a satisfactory agreement between the experimental and calculated values with a maximum relative deviation of 25.3% and the average relative deviation of 9.92%.
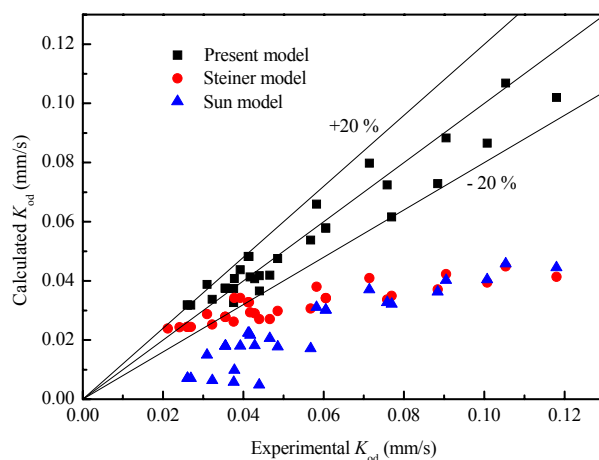

Figure 9: Comparison of experimental K_{od} and calculated K_{od}.

CONCLUSIONS

Single drop experiments with the system chloroform-ethanol-water, which characterizes a high density difference, have been carried out to investigate the mass transfer behavior. The overall mass transfer coefficient increased with the drop size and temperature and decreased with the initial solute concentration. The observation of hanging drops in the continuous phase showed that more violent interfacial

instability appeared in drops with larger diameter or higher solute concentration. The mass transfer enhancement factor F was introduced and then correlated with a function of several dimensionless numbers, including the Reynolds number, the Schmidt number, the ratio of density in both phases, and the Weber number. The correlation obtained was used to predict the mass transfer coefficients under different experimental conditions. The prediction was acceptable with a maximum deviation of 25.3% and an average deviation of 9.92%.

ACKNOWLEDGMENTS

NOMENCLATURE

A	drop surface area (m^2)
C	solute concentration (g/mL)
C_{IP}	instability constant
d	drop diameter (mm)
D	diffusion coefficient (m^2/s)
E	extraction fraction, dimensionless
$E\ddot{o}$	Bond number ($g\Delta\rho d^2 / \gamma$)
F	mass transfer enhancement factor
H	dimensionless group $(4/3 E\ddot{o} M^{-0.149}(\mu_d / \mu_c)^{-0.14})$
J	judgment of the mass transfer resistance
k	mass transfer coefficient (mm/s)
K	overall mass transfer coefficient (mm/s)
M	Morton dimensionless number $(g\mu_c^4\Delta\rho / (\rho_c^2\gamma^3))$
M_B	molecular weight of the solvent (g/mol)
m	solute distribution coefficient, dimensionless
N_{PG}	inverse of Morton dimensionless number
Pe	Peclect number ($d_p u_t/D_d$)
R	mass transfer rate (g/mm^2·s)
Re	drop Reynolds number ($du_t\rho_c/\mu_c$)
Sc	Schmidt number ($\mu/\rho D$)
T	temperature (K)
t	contact time (s)
u	velocity (m/s)
V	drop volume (m^3)
V_A	molar volume (cm^3/mol)
We	drop Weber number ($\rho_c u_t^2 d/\gamma$)

Greek Symbols

g	acceleration of gravity (m/s^2)
γ	interfacial tension (mN/ m)
μ	viscosity (mPa·s)
ρ	density (kg/m^3)
Δ	difference
φ	association parameter

Subscripts and Superscripts

c	continuous phase
cr	critical
d	dispersed phase
f	final value
i	initial value
oe	overall effective
od	overall dispersed value
rig	rigid drop
*	equilibrium

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