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Effect of Surfactant on Single Drop Mass Transfer in Liquid-Liquid Extraction

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Liquid-liquid mass transfer coefficients for single freely rising drops in the presence of surfactant in an extraction column have been investigated using the system of kerosene-acetic acid-water. The surfactant used in this study was alkyl benzene sulfonate (ABS). The experiments were carried out by bubbling kerosene-acetic acid solution as a series of single drops from the bottom of a column containing water-ABS solution. The column used in this experiment was made from glass of 36 mm inside diameter and constructed of 60, 120, and 180 cm height. The effects of surfactant concentration, column height, and drop diameter on the overall mass transfer coefficient have been studied. The data can all be correlated by $Sh_d = 2.08x10^{-5}\,\mathrm{Re}_d^{4.01}\,We^{-1.97}\left(d_d / H\right)^{0.68}$ with an average deviation of 17.72%. This equation is valid for the ranges of Re_d from 186.68 to 402.19, *We* from 0.80 to 3.33, and d_d/H from 0.0028 to 0.0105.

Keywords: Liquid-liquid extraction, mass transfer coefficient, single drop, *and* surfactant.

INTRODUCTION

Liquid-liquid extraction is an important separation process. It is a widely used separation process in industry. The rate of transfer of solute in any exchange process depends on three factors: the area of contact, the effective driving force, and the transfer coefficient (Handlos and Baron 1957). For an extraction process, mass transfer efficiency is determined by the mass transfer coefficient and the interfacial area (Lee, Maa, and Yang 1998).

Surfactant is a substance that markedly lowers the surface tension of a liquid when added in small quantities. If a small amount of surfactant is added to the extraction system, both mass transfer coefficient and interfacial area may be affected. Many researchers had studied the effect of surfactant on mass transfer coefficient an the extraction system (West et al. 1952, Garner and Hale 1953, Garner and Skelland 1956, Huang and Kintner 1969, Horng and Maa 1986, Lee, Maa, and Yang 1998). It was found that the surfactants usually decrease the mass transfer coefficient, while increasing the interfacial area.

The objective of this study is to investigate the effects of surfactant on the mass transfer coefficient in the extraction of acetic acid from kerosene with water. An apparatus for single drop extraction was used in this study. The parameters studied were surfactant concentration, column height, and drop diameter.

EXPERIMENTAL

In this study, glacial acetic acid produced by Merck was used as solute which is originally contained in kerosene as dispersed phase and extracted by water as the continuous phase. The surfactant used is alkyl benzene sulfonate (ABS), which is a water soluble, anionic surfactant. The ABS was purchased from Brataco Chemika in Kelenteng Street, No. 8, Bandung. The initial concentration of acetic acid in the kerosene was 0.84 mol/L for all of the experiments.

The experimental apparatus used in this study is shown in Figure 1, consisted of glass column, feed or dispersed phase reservoir, raffinate reservoir, valve, and a nozzle. The inside diameter of the glass column was 36 mm and constructed of 60, 120, and 180 cm height. The nozzles were made of stainless steel with three different diameters: 0.3, 1.5, and 3 mm. The feed reservoir was positioned at the appropriate level to enable flowing of the dispersed phase through the continuous phase filled in the glass column.

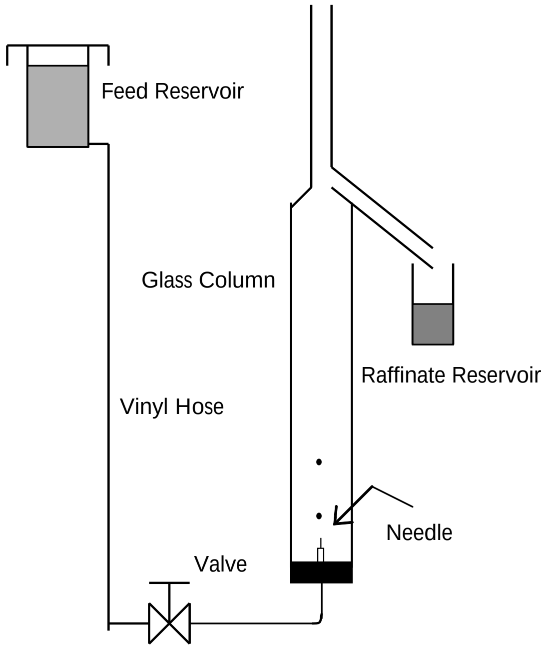

Figure 1. Experimental Apparatus for Single Drop Extraction

Water as continuous phase was filled in the glass column. The dispersed phase from the feed reservoir was supplied to the column as a series of single drops formed at the nozzle in the column base. The flow rate of the drops was controlled by a valve mounted on the vinyl hose between the feed reservoir and the nozzle. The drops upward through the water and then were collected in the raffinate reservoir. The flowing of drops was stopped after about 3 ml of raffinate was collected in the raffinate reservoir. The rise time of the drops was measured in each of the experiments by using a stopwatch. The concentration of acetic acid in the raffinate phase was measured by UV-VIS spectrophotometer in the wave length of 720 nm. Each experiment was carried out in duplicate. The parameters studied in this experiment were surfactant concentration, column height, and drop diameter.

MASS TRANSFER CALCULATION MODEL

In this process, the acetic acid is transferred from drops to the water as continuous phase. From the mass balance of acetic acid in a single drop, the following equation is obtained:

$$K_d a_d \left(C_d - C_d^*\right) = -\frac{d}{dt}\left(V_d C_d\right) \qquad (1)$$

where K_d is the overall mass transfer coefficient for the dispersed phase (kerosene), a_d and V_d are surface area and volume of a drop, C_d is the solute concentration in the dispersed phase, and C_d^* is the solute concentration in the dispersed phase in equilibrium with its concentration in the continuous phase. If the solute concentration in the continuous phase is symbolized by C_c, then C_d^* and C_c can be correlated by the following expression:

$$C_d^* = mC_c \tag{2}$$

where m is the equilibrium distribution coefficient. For the system of acetic acid in "A" oil (mixture of Ondina 17 and kerosene) as a dispersed phase transfers to water as continuous phase, the value of m is 0.0015 (Handlos and Baron 1957). In this system, the value of m is assumed to be 0.0015 and the solute concentration in the continuous phase is very small, so that the value of C_d^* is nearly zero. By neglecting C_d^* and integrating Eq. (1), the following result was obtained (Huang and Kintner 1969, Lee, Maa, and Yang 1998):

$$K_d = \left(\frac{V_d}{a_d t_d}\right) 1\text{n} \left(\frac{C_{d1}}{C_{d2}}\right) \tag{3}$$

With the assumption that the drop is spherical, its surface area and volume are

$$a_d = \pi d_d^{\,2} \tag{4}$$

$$V_d = \frac{\pi}{6} d_d^{\,3} \tag{5}$$

Substituting Eqs. (4) and (5) into Eq. (3) gives:

$$K_d = \frac{d_d}{6t_d} \ln\left(\frac{C_{d1}}{C_{d2}}\right) \tag{6}$$

In this study, the drop diameter (d_d) was calculated from the following equation (McCabe, Smith, and Harriott 1993):

$$d_d = \left[\frac{6 d_o \sigma g_c}{g(\rho_c - \rho_d)}\right]^{1/3} \tag{7}$$

The drop rise time (t_d) in Eq. (6) was experimentally measured by using a stopwatch. C_{d1} and C_{d2} are the measured solute concentrations in the feed and raffinate solutions, respectively. Knowing the values of C_{d1}, C_{d2}, d_d, and t_d, the overall mass transfer coefficient (K_d) can thus be calculated by using Eq. (6).

The value of K_d in the form of the dimensionless group can then be formulated as a function of the drop Reynolds number, Weber number, and the ratio of drop diameter to the column height as:

$$\left(\frac{K_d d_d}{D_{ad}}\right) = C_1 \left(\frac{\rho_d v_d d_d}{\mu_d}\right)^{C_2} \left(\frac{\rho_d v_d d_d}{\sigma}\right)^{C_3} \left(\frac{d_d}{H}\right)^{C_4} \tag{8}$$

or

$$Sh_d = C_1 \, \text{Re}_d^{\,C_2} \, We^{C_3} \left(\frac{d_d}{H}\right)^{C_4} \tag{9}$$

D_{ad} in Eq. (8), which is the diffusion coefficient of acetic acid in kerosene, was predicted by using the Wilke-Chang correlation (Brodkey and Hershey 1988):

$$D_{ad} = \frac{1.17x10^{-16}(T)(\phi M_d)^{1/2}}{\mu_d V_a^{\,0.6}} \tag{10}$$

The constants C_1, C_2, C_3, and C_4 in Eq. (9) were evaluated using multi dimensions regression.

RESULTS AND DISCUSSIONS

Effect of Surfactant Concentration on Overall Mass Transfer Coefficient

To study the effect of surfactant concentration on the overall mass transfer coefficient, the experiments were carried out at a column height of 60 cm and a nozzle diameter of 0.15 cm using water as continuous phase with various surfactant concentrations. The temperature of fluid in all of the experiments was 28^{o}C. In this condition, the drops rise time was measured to be 5 seconds. In this study, the water interfacial tension as a function of ABS concentration was measured by using the maximum bubble pressure method. The overall mass transfer coefficient was calculated by using Eq. (6).

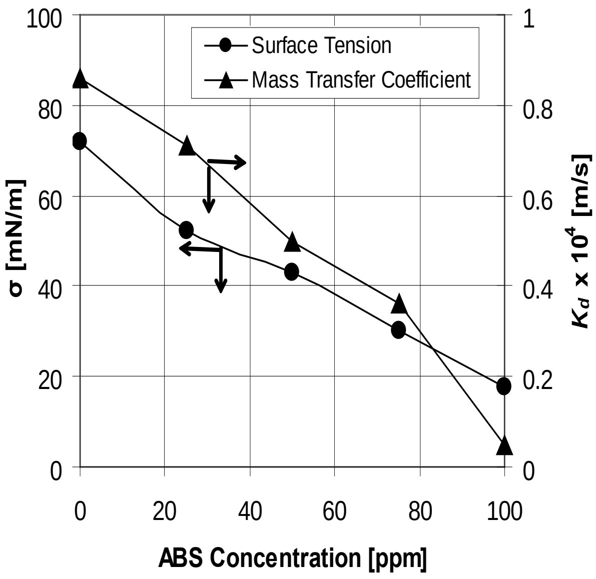

Figure 2. Effect of ABS Concentration on the Surface Tension and Overall Mass Transfer Coefficient

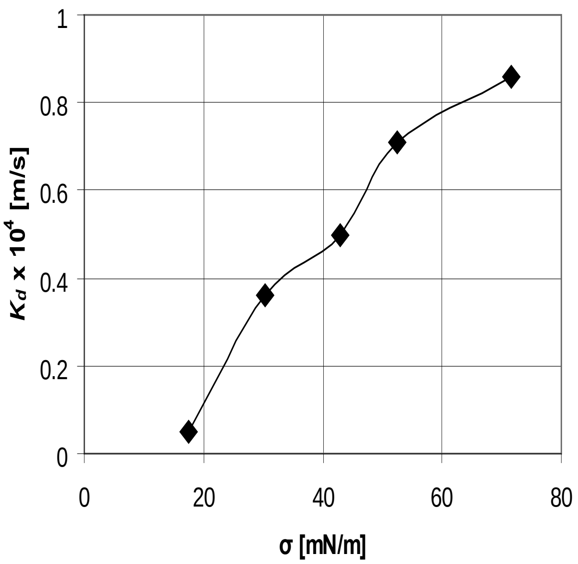

Figure 3. Correlation Between Surface Tension and Overall Mass Transfer Coefficient

Figure 2 shows the interfacial tension of water-surfactant solution and the overall mass transfer coefficient as a function of the surfactant concentration. It appears that interfacial tension decreases linearly as a function of surfactant concentration. It can be seen from Figure 2 that overall mass transfer coefficient decreases as the surfactant concentration increases. The value of K_d for water without surfactant is 0.0086 cm/s and it decreases to 0.0005 cm/s for water with 100 ppm of ABS. So increasing ABS concentration from 0 to 100 ppm decreases the value K_d by 94.2%. Thus, a surfactant will decrease the mass transfer rate an the extraction process.

The correlation between the value of the overall mass transfer coefficient and the interfacial tension is shown in Figure 3. The value of K_d increases with increasing the interfacial tension of the continuous phases. Increasing interfacial tension of the continuous phase causes higher interfacial tension gradient between the continuous phase and the dispersed phase. This difference in surface tension increases interfacial turbulence between the continuous and the dispersed phases, so it increases the value of the overall mass transfer coefficient.

Effect of Column Height

The effect of column height on the overall mass transfer coefficient was studied by carrying out the experiments at three different column heights: 60, 120, and 180 cm with a fixed nozzle diameter and surfactant concentration. The nozzle diameter and surfactant concentration were 0.15 cm and 50 ppm, respectively. For this condition, the diameter of the dispersed phase drop was calculated to be 0.50 cm. The drop rise time for the column height of 60, 120, and 180 cm were measured to be 5, 9, and 15, respectively.

Figure 4 shows the drop rise time and the overall mass transfer coefficient for each column height and Figure 5 reveals the correlation between drop rise time and overall mass transfer coefficient. For a fixed drop diameter and surfactant concentration, the overall mass transfer coefficient decreases with increasing column height since the higher the column height the longer the rise time of the drop. Since column height has a linear correlation with drop rise time, the higher the column height the smaller is the overall mass transfer coefficient. According to Eq. (6), the value of K_d is inversely proportional to the drop rise time, t_d.

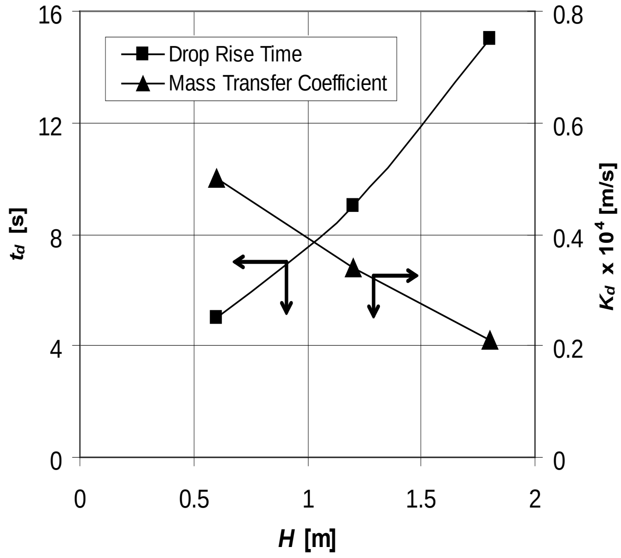

Figure 4. Effect of Column Height on Drop Rise Time and the Overall Mass Transfer Coefficient

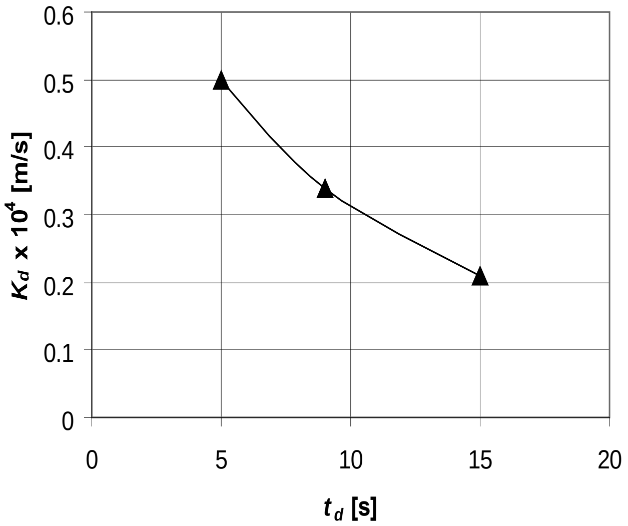

Figure 5. Correlation between Drop Rise Time and Overall Mass Transfer Coefficient

Effect of Drop Diameter

The effect of dispersed phase drop diameter on the overall mass transfer coefficient was studied at the column height of 60 cm with the surfactant concentration of 50 ppm. The nozzle diameter was varied to 0.03, 0.15 and 0.3 cm. For these nozzle diameters, the calculated drop diameters were 0.29, 0.50, and 0.63 cm, respectively. The rise time for the drops diameter of 0.29, 0.50, and 0.63 cm were measured at 6, 5, and 4.8 seconds, respectively.

Figure 6 shows the drop rise time for its diameter and reveals the effect of drop diameter on the overall mass transfer coefficient. It is clear that overall mass transfer coefficient increases with increasing drop diameter. Increasing drop diameter from 0.29 to 0.63 cm (117.2%) increased the overall mass transfer coefficient from 0.0022 to 0.0096 cm/s (336.4%). This phenomenon can be explained by the fact that interface turbulence between the continuous phase and the dispersed phase increased by increasing the drop diameter. As shown in Eq. (6), the value of the overall mass transfer coefficient is proportional to the drop diameter.

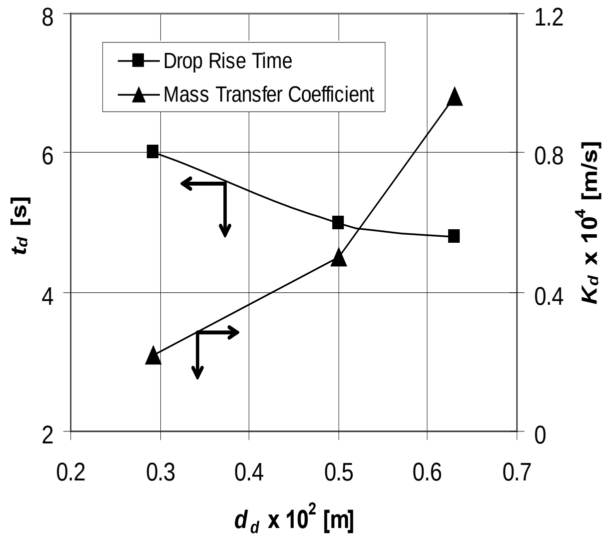

Figure 6. Effect of Drop Diameter on the Drop Rise Time and Overall Mass Transfer Coefficient

Correlation Equation

The effects of the investigated parameters on the overall mass transfer coefficient can all be correlated in the form of dimensionless groups and is expressed as

$$Sh_d = 2.08x10^{-5}\,\mathrm{Re}_d^{\,4.01}\,We^{-1.97}\left(\frac{d_d}{H}\right)^{0.68} \qquad (11)$$

The average deviation of Eq. (11) to the experimental data is 17.72%. Eq. (11) is valid for the ranges of Re_d from 186.68 to 402.19, *We* from 0.80 to 3.33, and d_d/H from 0.0028 to 0.0105. The comparison between the value of Sh_d calculated from Eq. (11) and the value of Sh_d from the experimental data is shown in Figure 7.

CONCLUSIONS

Based on the results of this study, the following conclusions are made.

1. Surfactant addition in continuous phase decreases the overall mass transfer coefficient, K_d. Increasing ABS concentration from 0 to 100 ppm decreases the value of K_d from 0.0086 to 0.0005 cm/s or by 94.2%.

2. The value of K_d decreases by increasing the column height. Increasing the column height from 60 to 180 cm decreases the value of K_d from 0.0050 to 0.0021 cm/s or by 58%.

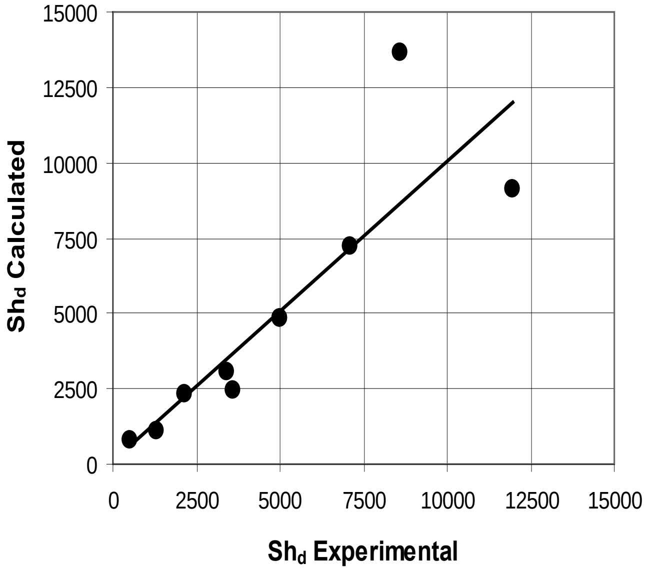

Figure 7. Comparison between the Experimental Dispersed Phase Sherwood Number and the Calculated One

3. The value of K_d increases in proportion to the drop size. Increasing drop diameter from 0.29 to 0.63 cm increases the value of K_d from 0.0022 to 0.0096 cm/s or by 336.36%.

4. The correlation between the value of K_d and the investigated parameters can be expressed as Eq, (11), with an average deviation of 17.72%. This equation is valid for the ranges of Re_d from 186.68 to 402.19, *We* from 0.80 to 3.33, and d_d/H from 0.0028 to 0.0105.

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NOTATION

Roman Letters

a_d = interfacial area of a drop [m^2]
$C_{1\text{-}4}$ = constants in Eqs. (8) and (9)
C_c = solute concentration in continuous phase [mol/m^3]
C_d = solute concentration in dispersed phase [mol/m^3]
C_d^* = solute concentration in dispersed phase in equilibrium with its concentration in the continuous phase [mol/m^3]
D_{ad} = diffusion coefficient of acetic acid in kerosene [m^2/s]
d_d = drop diameter [m]
d_o = nozzle diameter [m]
g = gravitational acceleration [m/s^2]
g_c = gravitational conversion constant [32.1740 $1b_m/1b_f \cdot$ft/s^2]
H = column height [m]
K_d = overall mass transfer coefficient for dispersed phase [m/s]
M_d = molecular weight of kerosene [kg/kgmol]
m = equilibrium distribution coefficient [-]
Re_d = dispersed phase Reynolds number [-]
Sh_d = dispersed phase Sherwood number [-]
T = temperature [K]

t_d = drop rise time [s]
V_a = molal volume of acetic acid at its normal boiling point [m^3/kmol]
V_d = drop volume [m^3]
v_d = drop velocity [m/s]
We = Weber number [-]

Greek letters

μ = viscosity [kg/m/s]
ρ = density [kg/m^3]
σ = surface tension [mN/m]
ϕ = Wilke-Chang "association parameter," assumed to be 1 for kerosene

Subscripts

c = continuous phase
d = dispersed phase
1 = feed stream
2 = output stream

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