Quantification of Iodine Mass Transfer and Height of Emulsion Phase in “Emulsion-flow” Column

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“Emulsion-flow” is a unique regime of counter-current contact between aqueous and organic phases in a column extractor. The operation enables fast mass transfer as well as stable dropwise counter-current of both phases in a simple column-type apparatus. While those advantages have been reported, prediction of the column performance has been difficult because of the lack of correlation with mass transfer coefficient and interfacial area. This study suggests correlation with overall aqueous phase mass transfer capacity coefficient, $K_wa$ and the height of emulsion phase, $H$ for various operating conditions. In iodine extraction, velocity of organic phase had a stronger effect on $H$. Furthermore $K_wa$ was correlated with a root of $H$. This fact suggests that the velocity of the organic phase plays a major role in mass transfer for the case of emulsion-flow. Correlations suggested in the present study are important for rational design and scaling up of emulsion-flow columns.

1. Introduction

Solvent extraction plays an important role in separation techniques. The recovery or recycling of valuable resources attracts keen attention to build a circular economy on a global basis. Solvent extraction is a key method to separate valuable metals from industrial waste and processing solutions. Since extraction was carried out by contacting two immiscible liquids with small density difference, development of efficient apparatus suffers from the tradeoff of enhancing mass transfer, and achieving high throughput. Making fine droplets enlarges the interfacial area and also slows down the rate of phase separation. To cope with the problem, a lot of effort has been given to achieve stable and fast counter-current with the minimum energy input in a simple structure contactor [1-6]. Examples of industrial scale contactors are mixer settler [5-8], centrifugal extractor [9-11], spray column [12-16], packed column [17-18], rotating-disc column [19,20], and pulsed column [21,22]. Conventional mixer-settlers have large volume settlers to complete phase separation and require a large area for installation. Although column type contactors occupy a smaller area than mixer settlers, they have a limitation of droplet size to ensure stable counter-current operation and to avoid dispersed phase flooding. The authors have developed a mixer-settler column equipped with a coalescer inside the
column to enhance phase separation [6]. This enabled fast mass transfer and high throughput at the same time.

To realize a stable counter-current operation and a high extraction ratio in a simple column-type apparatus, centrifugal extractors with Taylor vortices have been developed by Nakase et al. [23]. Applying centrifugal force enhances Taylor-Couette flow that provides effective dispersion of oil and appropriate value of oil holdup. A large number of theoretical stages are realized in comparison to their size. Another suggested idea has been to apply “emulsion-flow” by Yanase et al. [24, 25]. This method is characterized by introducing both liquid phases in the form of droplets whose sizes are uniformly controlled and the resulting emulsion phase formed in the middle of the column. Droplets of both phases in the range of several hundred micrometers accumulated in the column to form the emulsion phase. The height of the emulsion phase reached a constant value depending on the flow rates of each phase. This means that fast phase separation is successfully attained at both ends of the emulsion phase. The method realized highly stable counter-current contact between two phases in the column of simple structure. The apparatus was called “Emulsion-flow column” by the inventor and industrial applications have been increasing. The high performance was first recognized by the separation of Yb(III) and U(VI) from their aqueous HNO₃ solution using D2EHPA as an extractant [24]. A stable emulsion phase was successfully formed in the column even though extractant with slight surface activity is involved in the extraction system. Emulsion-flow operation achieved higher extraction ratio than mixer-setter operation in the system. The method was then applied to nickel recovery from simulated wastewater of the plating industry [26]. In this case, the mixture of LIX-84I and PC88A was used as the extractant and other ionic species were added to prepare the aqueous feed solution. Stable operation was achieved in such a complex system and a high extraction ratio was attained as reported [24-30]. Furthermore, loss of organic phase from the outlet of aqueous phase was significantly suppressed. This fact emphasized the economical advantage of this method. The high operability and advantages of this method were proven; however, quantitative discussion on the mass transfer characteristics should be intensified.

The present study aims to characterize the emulsion phase, which is the main field for extraction in this operation. Change of the thickness of emulsion phase with flow velocities in both phases was expressed with a correlation, and the change provides a significant effect on the rate of extraction of a target. To elucidate mass transfer characteristics in the emulsion phase, extraction of iodine was carried out in a simple system to determine $K_w a$ values. Furthermore, a correlation between $K_w a$ and flow velocities was suggested for the present operation.

2. Experimental

Iodine was selected as the solute for mass transfer experiment and potassium iodide was added into water to increase iodine solubility. As an organic solvent, $n$-heptane was used without further purification. Aqueous feed solution was prepared by dissolving predetermined amount of I₂ with KI into deionized water.
Initial concentration of I$_2$ was set at 1 mmol/dm$^3$ with KI concentration of 50 or 100 mmol/dm$^3$.

Figure 1 shows a schematic diagram of the experiment setup. The emulsion-flow column was similar to the one used in the report by Nagano et al. [29]. The column has an inner diameter of 28 mm and is 300 mm in height. In the bottom part of the column, a sintered glass filter with pore sizes of 40 to 60 µm, was set to disperse organic phase. In the top part, a plastic tube with multiple holes was installed to form aqueous phase droplets. Column operation started by supplying aqueous feed solution from the top distributor. Organic phase was introduced through the bottom distributor. The flow rate of aqueous phase was set in the range of 10 and 50 cm$^3$/min and that of organic phase was changed from 30 to 70 cm$^3$/min. Droplets of each phase were formed when each solution passed through the respective distributors. The flow of droplets of both phases led to the formation of a droplet bed in the middle of the column. With the progress of time, the height of the bed reached a constant value. In the bed, counter-current contact between aqueous and organic phases was attained. Overall flow of organic phase moved upward and aqueous phase flowed downward. Even when the flow regime is still unclear, both W/O and O/W droplets coexist. Thus, the bed can be called the emulsion phase. The temperature for all experiments was set at a constant value in the range of 293 to 298 K.

The height of the emulsion phase is an important characteristic value in the operation of the emulsion-flow column. The previous study [29] set the height near the column height to achieve a high extraction ratio. While in the present study, the height was suppressed to avoid establishing extraction equilibrium in the column. The height of the emulsion phase was measured, and pictures were taken at both the top and bottom parts of the emulsion phase using AQUOS R SHV41, Sharp Co., equipped with a macro lens (12 times Optical glass, Kenko Tokina Co., Ltd.). Iodine concentration was determined by spectrophotometric analysis with an absorbance of 523 nm, as well as iodine titration with sodium thiosulfate as a reducing agent.

![Figure 1. Schematic diagram of experimental apparatus.](image-url)
3. Results and Discussion

The emulsion phase started to grow after introducing both phases, and reached a constant height in approximately thirty minutes. The height changed from 0.01 m to 0.1 m depending on operating conditions. The emulsion phase consists of droplets whose size changes monotonously with vertical position. Figures 2(A) and (B) are images taken at the top and bottom of the emulsion phase, respectively. Millimeter-sized droplets in both pictures stick to the wall and are inert for mass transfer. Sub millimeter-sized droplets work for extraction. In the top of the emulsion phase, most organic phase droplets coalesced to form a clear organic bulk phase. Some large droplets are aqueous phase and may travel downwards to the bottom. Sauter mean diameters of the droplets were approximately 0.6 mm in figure 2(A) and 0.3 mm in figure 2(B), respectively. A similar trend of droplet diameter related to the change of height was reported by Nagano et al. [26]. Droplet size distribution in the bottom part was clearly narrower than that in the top part. Most droplets in the bottom part seem to be organic phase and those droplets traveled upward. During travel, some droplets coalesced to form larger droplets.

In a system of deionized water and Shell sol, effects of droplet size and size distribution on droplet coalescence in emulsion-flow were studied by Shimogouchi et al. [30]. Their column produces organic droplets with an average diameter of 0.2 mm and a narrow size distribution. At droplet generation, the Reynolds number was small enough for laminar condition. In the emulsion phase, the droplet size was in the range of 0.2 to 1 mm. At the end of the emulsion phase, all the droplets coalesced stably to form a clear organic bulk phase. The behavior of the droplets in Shimogouchi’s study is similar to the present study and suppression of fine droplet generation is key for stable counter-current operation.

3.1 Correlation of emulsion phase height

Figure 3 shows the result of the height of emulsion phase, $H$ against the organic phase superficial velocity, $U_o$, at constant aqueous phase superficial velocity, $U_w$ of $0.3 \times 10^{-3}$ m/s. Where $U$ was defined by dividing volumetric flow rate by the cross-sectional area of the column. The height changes with the slope
of 2, which suggests that $H$ is a power function of $U_o^2$. The relation was simply interpreted as an energy balance of accumulated organic phase layer below the coalescing front. Bernoulli’s equation suggests that the height of organic phase is proportional to the square of organic phase velocity.

Figure 5 shows the variation in $H$ by changing both $U_w$ and $U_o$. Slope of $H$ against $U_w$ was approximately 0.5, which was smaller than the slope of $H$ against $U_o$, 2 shown in figure 3. Organic phase velocity, $U_o$ has a stronger effect on $H$ than $U_w$. Furthermore, since the effects of $U_o$ and $U_w$ on $H$ were independent of each other, $H$ is correlated with the power law of $U_o$ and $U_w$ with the following equation.

$$H = \gamma U_w^\alpha U_o^\beta$$  \hspace{1cm} (1)

where, $\gamma$ the constant, and $\alpha$ and $\beta$ are the power law numbers. To determine values of $\alpha$ and $\beta$, slope analysis was carried out and it was found that $\alpha$ and $\beta$ are 0.55 and 2.2, respectively. Figure 4 shows the calculated values of $H$ for $\gamma$ equals to $8.4 \times 10^6 \text{s}^{2.8}/\text{m}^{1.8}$ with a solid line. Dashed lines express $\pm$ 30 % error of $\gamma$. Most observed values fell within the range of 30 % error. Equation (1) was useful to predict the height of emulsion phase for operating conditions in this extraction system.

### 3.2 Overall aqueous phase mass transfer capacity coefficient, $K_{wa}$

Since KI was dissolved in aqueous phase, equilibrium of $I_2$ in aqueous phase is expressed as follows with the equilibrium constant, $K_{eq}$.

$$I_2 + 2I^- \rightleftharpoons I_3^-$$  \hspace{1cm} (2)

$$K_{eq} = \frac{[I_3^-]}{[I_2][I^-]}$$  \hspace{1cm} (3)

Extraction equilibrium of iodine was written as
\[ I_2 \leftrightarrow I_2 \]  
\[ K_p = \frac{[I_2]}{[I_2]} \]  

where overbar refers to species in organic phase. Distribution coefficient of \( I_2 \), \( m \), is defined by the ratio of \( I_2 \) concentration in \( n \)-heptane to all iodine concentration, \([I_2] + [I_3] \), in aqueous phase.

\[ m = \frac{K_p}{1 + K_{eq}[I]} \]  

where \( K_p \) was 36.6 [31], and \( K_{eq} \) was obtained from the correlation with temperature [32]. The system is characterized by adjusting the distribution coefficient with the change of KI concentration. Figure 6 shows the distribution curve at 293 K for the system of \( I_2 \)-KI solution and \( n \)-heptane. In the present study, \( m \) value was set from 0.5 to 1. Figure 7 shows a model of mass transfer in a typical continuous column contactor [33]. By taking mass balance in a differential height of the column, a basic equation was derived as

\[ U_w dC_w = N_A a dz \]  

where \( C_w, N_A \) and \( a \) are iodine concentration in aqueous phase, mass transfer flux of the iodine and specific interfacial area, respectively. The mass transfer flux is expressed as

\[ N_A = K_w (C_w - C_{w}^*) \]  

where \( K_w \) and \( C_{w}^* \) are mass transfer coefficient based on aqueous phase and iodine equilibrium concentration in aqueous phase. Substituting equation (8) into equation (7) and integrating from \( z = 0 \) to \( Z \) and from \( C = C_{w, top} \) to \( C = C_{w, bot} \) yields

\[ K_w a = \frac{U_w}{Z} \int_{C_{w, top}}^{C_{w, bot}} \frac{dC_w}{C_w - C_{w}^*} \]  

Figure 6. Distribution curve of \( I_2 \) in system of \( I_2 \)-KI solution and \( n \)-heptane.

Figure 7. Mass transfer model in continuous contact column.
Figures 8. Change of $K_{wa}$ against (A) $U_o$ and (B) $U_w$. Overall aqueous phase mass transfer capacity coefficient, $K_{wa}$ is obtained by equation (9).

Figures 8 (A) and (B) show the results of $K_{wa}$ against the change of $U_w$ and $U_o$. As shown in figure 8 (A), $K_{wa}$ increases with increasing $U_o$ with the slope of unity. Most observed $K_{wa}$ was located along the line. It should be noted that the slope of unity corresponds to the power number of the root of $U_o^2$ as was found in the correlation for $H$. While in figure 8 (B), $K_{wa}$ was found to increase with $U_o$ with the slope of 0.25 in the range of higher $U_w$. Values of $K_{wa}$ in the lower $U_w$ range slightly deviate from the slope of 0.25 due to relatively small thickness of emulsion phase. Aqueous phase is likely to flow unevenly in such a shallow bed of droplets. Interestingly, the slope value is also similar to the power number of root of $U_w^{0.55}$ which was appeared in the correlation of $H$ and $U_w$. Therefore, an equation to predict $K_{wa}$, was proposed in the following equation.

$$K_{wa} = 0.23 \times 10^{-2} U_w^{0.27} U_o^{1.1} = 8.0 \times 10^{-3} \sqrt{H} \quad (10)$$

Values of $K_{wa}$ were smaller than a mixer settler [6] and comparable to a spray column [15]. The former
has $K_{wA}$ values from 0.01 to 0.5 s$^{-1}$ and the latter gives from $5 \times 10^{-4}$ to $3 \times 10^{-3}$ s$^{-1}$. In terms of mass transfer coefficient and interfacial area, the column is not necessarily large because the column was operated with millimeter or sub-millimeter droplets. The advantage of the emulsion-flow column is to obtain stable drop coalescence or counter-current operation in a simple device. Furthermore, according to Naganawa [28], the throughput of emulsion-flow column for nickel extraction was more than 10 times of that of a mixer settler.

Figure 9 shows the comparison of predicted and observed values. Most observed values were in the range of plus minus 30% error, which shows good agreement. The fact clearly indicates a linear relation between $K_{wA}$ and the height of emulsion phase, $H$. The knowledge provides us a clue to control the emulsion-flow column as necessary.

4. Conclusion

To enhance characterization of mass transfer in an emulsion-flow column, change in the height of emulsion phase, $H$ was examined depending on $U_o$ and $U_w$. Organic phase velocity had a stronger effect on $H$ than $U_w$, and a correlation of $H$ was suggested. Supply of organic phase plays a major role in the growth of emulsion phase. Furthermore, mass transfer in the emulsion phase was characterized by iodine extraction in a simple extraction system. Overall aqueous phase mass transfer capacity coefficient, $K_{wA}$ was observed for various flow conditions. $K_{wA}$ was found to be closely related with $H$, and a correlation of $K_{wA}$ and flow velocities was obtained for the present operation.

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