Axial Mixing in Emulsion-flow Column under Iodine Extraction

Mikiro HIRAYAMA, Takashi GOSHIMA, Kei MIZUTA and Susumu NII*
Department of Chemical Engineering, Kagoshima University, 1-21-40, Korimoto, Kagoshima-Shi, Kagoshima 890-0065, Japan
(Received April 24, 2020; Accepted May 9, 2020)

Strength of axial mixing in the emulsion phase during the progress of extraction was evaluated using the Peclet number under various flow conditions. The Peclet numbers were determined with the established tracer technology which applies inert species for iodine extraction. Very little effect of operating velocities of either aqueous and organic phases was found on the Peclet numbers. This fact indicates that an almost constant degree of axial mixing was kept in this column for different flow velocities of both phases. Furthermore, the degree of axial mixing of the emulsion-flow column was compared with conventional spray and packed columns by plotting the droplet Peclet number against the droplet Reynolds number. Points of the Peclet numbers of emulsion-flow column located in the middle of the spray and the packed columns, which suggests that the strength of axial mixing in the present column is in between spray and packed columns.

1. Introduction

A novel operation mode of extraction, “emulsion-flow” allows for both stable counter-current operation and a high extraction ratio [1-5]. The method is characterized by supplying aqueous and organic phases in the form of droplets with uniformly controlled sizes. Extraction proceeds in the stacked layer of droplets called the “emulsion phase” [3,5]. Our previous study quantified the mass-transfer characteristics of iodine extraction in emulsion-flow column operation [6]. Correlations of both the overall mass-transfer capacity coefficient and the height of emulsion phase were developed, being a crucial step for developing a rational design method for the emulsion-flow column. The present study aims to clarify the mixing conditions inside the column. To set a similar droplet condition of the two-phase flow in the reference [6], the composition of two phases was chosen for iodine extraction. Mass-transfer provides less effect on the axial mixing; however, it changes interfacial properties thus alters the droplet condition. Therefore, iodine extraction was conducted during the tracer experiment. Knowing the degree of axial mixing helps to predict the stage efficiency of the operation and effluent concentration of the target in an unsteady state. Furthermore, suppressing axial mixing reduces the height per transfer unit, H.T.U. and thus helps to build a compact column. Therefore, quantifying the axial mixing is crucial in developing a column-type extractor such as an emulsion-flow column. The degree of axial mixing has been determined by applying a simple method of
tracer technology as commonly applied in evaluating various reactors or any types of extraction equipment [7-9]. This method uses the tracer concentration-time profile that was obtained by monitoring the tracer concentration at the outlet of the equipment. The monitoring was started after injecting a small amount of tracer into the feed stream or by stepwise switching the tracer concentration in the feed. A value of Peclet number, $Pe$, which quantifies the degree of axial mixing was found by analyzing the concentration profile.

The present study first reports the Peclet number of the emulsion-flow column under various flow conditions in the process of iodine extraction. Then, the values were compared with conventional column-type extractors (spray and packed columns). The comparison strongly contributes to the characterization of the flow and mixing conditions in an emulsion-flow column.

2. Experimental

A simple extraction system was selected to examine the mixing conditions of the emulsion flow. Iodine was selected as a transferring solute, and no extractant was used.

To prepare the aqueous feed solution, I$_2$ was dissolved in potassium iodide aqueous solution. The concentration of I$_2$ and KI was 1 mmol/dm$^3$ and 100 mmol/dm$^3$, respectively. Normal heptane was used as an organic solvent. To examine the axial dispersion of aqueous phase, sodium chloride was selected as a tracer. Four grams of NaCl was dissolved into 100 cm$^3$ of the aqueous phase feed solution to prepare the tracer solution. All chemicals described above were reagent grade and produced by FUJIFILM Wako Pure Chemical Corporation. At the outlet of the column, electrical conductivity of the effluent was continuously

![Figure 1. Schematic diagram of emulsion-flow column.](image)

1: Feed solution (I$_2$-KI sol.)
2: Solvent ($n$-heptane)
3: Loop of aqueous tracer solution
4: Tracer injector for organic phase
5: Diaphragm pump
6: Distributor of aqueous phase
7: Distributor of organic phase
8: I$_2$-containing solvent
9: Raffinate
10: Electrical conductivity meter
a: Organic bulk phase
b: Emulsion phase
c: Aqueous bulk phase
analyzed to monitor the NaCl concentration with an electric conductivity meter (MM-60R, DDK-TOA Co., Japan). For the tracer in the organic phase, a dye, oil-yellow-3G (AIKUMA SENRYO Co., Ltd., Japan) was used. The tracer solution was prepared by dissolving a given amount of the dye into n-heptane. Concentration of the organic tracer was monitored with the maximum absorbance at 355 nm with the UV-vis spectrophotometer (UV-160, Shimadzu Co., Japan). The absorbance was undisturbed by the presence of I2 in n-heptane.

Figure 1 shows a schematic diagram of the experimental setup. The column was the same as the one used in the previous study [6], with an inner diameter of 28 mm and height of 300 mm. The aqueous feed solution was supplied from the top of the column through a distributor, which was a plastic tube with multiple holes with diameters of 1 mm. The flow rate of aqueous feed solution was set at a given value in the range of 10 and 50 cm3/min. The organic solvent was introduced from the bottom of the column through a sintered glass filter with pore sizes of 40 to 50 µm. The flow rate changed from 30 to 50 cm³/min. Droplets of the aqueous phase flowed downwards and those of the organic phase moved upward. Setting an appropriate droplet size led to the formation of a droplet bed in the middle of the column. After reaching a steady state, the height of the bed reached a constant value.

A series of tracer experiments were conducted for both aqueous and organic phases. As noted as No.3 in Figure 1, a loop was set for the aqueous tracer solution. Switching the two 3-way valves brought a predetermined amount of aqueous tracer solution into the column. One milliliter of organic tracer solution was set in a syringe, No. 4 in Figure 1. The solution was shot into the stream in about one second.

3. Theory

A model analysis was conducted to understand mixing strength in the emulsion-flow column. The dispersed plug flow model has been extensively applied to chemical equipment [7-9] to determine the degree of axial mixing. Since the axial mixing in column-type extractors or reactors strongly influences the efficiency of equipment, quantification of axial mixing is important in interpreting experimental results and also in the scaling up. The modeling of our emulsion-flow column started with the basic equation used in the dispersed plug flow model. The primary focus of this study was the axial flow of both phases and the dispersion in this column. Flows of radial direction were ignored. The unsteady state convection-dispersion equation is written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x}$$

where, $D$ and $U$ are the superficial axial dispersion coefficient and the velocity, respectively. The first term in the right-hand side is analogous to the molecular diffusion given by Fick’s law, and the second term describes the effect of transportation by liquid flow. Equation (1) is converted into dimensionless form by taking the dimensionless concentration, $C_\theta$ dimensionless time, $\theta$ and dimensionless length, $z (= (Ut + x)/L)$;
The group of $D/UL$ is termed the dispersion number and is the reciprocal of the $Pe$. There are variations in the way of taking the characteristic length, $L$ and velocity, $U$ in past studies [10,11]. The definitions should be chosen properly for the purpose of research. Since our objective is to quantify the overall column performance, the $L$ value was taken as the column height and the $U$ was superficial velocity of aqueous or organic phase.

Once the change of tracer concentration with time, $C(t)$ was obtained, the residence time distribution function, $E(t)$, the mean residence time, $t_m$, and the $E$’s variance of $\sigma^2$, were determined as follows;

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) dt}$$  \hspace{1cm} (4)

$$t_m = \int_0^\infty tE(t) dt$$  \hspace{1cm} (5)

$$\sigma^2 = \int_0^\infty (t - t_m)^2E(t) dt$$  \hspace{1cm} (6)

To compare the residence time distribution on various flow velocities, these functions were transformed into dimensionless formulas as follows.

$$\theta = \frac{t}{t_m}$$ \hspace{1cm} (7)

$$E(\theta) = t_mE(t)$$ \hspace{1cm} (8)

$$\sigma_{\theta}^2 = \frac{\sigma^2}{t_m^2}$$ \hspace{1cm} (9)

In the case of closed vessels, the dimensionless variance of equation (9) is expressed with $Pe$ as follows [9,12].

$$\sigma_{\theta}^2 = 2 \left( \frac{1}{Pe} \right) - 2 \left( \frac{1}{Pe} \right)^2 \left( 1 - exp\left(-Pe\right) \right)$$ \hspace{1cm} (10)

The $Pe$ was obtained by numerically solving the equation (10).

For conventional extractors like spray and packed columns, modified Peclet numbers, $Pe_p$ were reported in literature [13-24] with a different definition from the equation (3), and were referred to as the Peclet number for droplet or packing, $Pe_p$[9]. The $Pe_p$ was obtained with the diameter of droplet or packing as a characteristic length.

$$Pe_p = \frac{UL}{D_p}, Pe = Pe_p \cdot L \cdot \frac{1}{d_p}$$ \hspace{1cm} (11)
Since the term, $L/d_p$ is regarded as the geometric factor for the column, the $Pe$ given with equation (3) is seen as the product of the intensity of dispersion and the geometric factor [9]. Generally, the $Pe_p$ is plotted against the modified Reynolds number, $Re_p$ to compare different columns [13-24]. The definition of $Re_p$ is

$$Re_p = \frac{\rho Ud_p}{\mu}$$

where $d_p$ is an average droplet diameter or equivalent sphere diameter of packing material, $\rho$ density of the liquid, and $\mu$ viscosity of the liquid. Since our secondary objective is to compare the axial mixing of the present emulsion-flow column with conventional columns, the $Pe_p$ were calculated with equation (10). The results were plotted on the map of $Pe_p$ against $Re_p$ with the reported values for conventional columns.

4. Results and Discussion

4.1 Flows in the emulsion phase

Figure 2 shows a typical example of emulsion phase in the column. The thick layer of accumulated droplets is the emulsion phase, and looks like a packed bed. More appropriately, the bed should be seen as a moving bed because most droplets rise continuously from the bottom of the emulsion phase. Since those droplets coalesced at the top of the phase to dissolve, they were made of organic liquid. The aqueous phase took different paths in the emulsion phase to flow down. Some large aqueous drops rapidly penetrated the emulsion phase. Some portion of aqueous liquid spreads over the surface of organic droplets and flows down film-wise to the bottom. Some small aqueous droplets flow down in between organic droplets. The unique flow pattern of aqueous phase plays an important role in the mass-transfer in the emulsion-flow column.

4.2 Determination of Peclet number

The residence time distribution for the both phases were examined under four different flow conditions. These conditions and results are summarized in Table 1. Where the $U_o$ and $U_w$ are superficial velocities of the organic and the aqueous phase, $H$ is the average height of the emulsion phase, and $d_{p_w}$ and $d_{p_o}$ are average droplet diameters for each phase. Comparison of R-1 and R-2 shows the effect of the organic phase velocity on axial mixing. The range of $U_o$ corresponds to the range for stable operation of the present column. As predicted by the correlation reported in ref. [6], the height of the emulsion phase is proportional to squared $U_o$. The increase of $U_o$ only slightly changed the diameter of organic droplet. It should be noted that the diameter of the aqueous droplet was measured as formed in the organic phase because of the difficulty in isolating aqueous droplets in the emulsion phase. The $Pe$ will be discussed later. Comparison of R-3 and R-4 shows that increasing the velocity of aqueous phase on the emulsion phase. Growth in the height of the emulsion phase was also successfully predicted by the reported correlation. Very little effect was observed.
Table 1. Operating condition and characteristic values of emulsion phase.

| Run No. | Test phase | $U_w$ [mm/s] | $U_o$ [mm/s] | $H$ [mm] | $d_{p,w}$ [mm] | $d_{p,o}$ [mm] | $Pe$ [-] |
|---------|------------|--------------|--------------|---------|----------------|----------------|---------|
| R-1     | Organic    | 0.3          | 0.8          | 10      | 3.6            | 0.6            | 3.1     |
| R-2     | Organic    | 1.4          | 3.1          | 0.5     | 4.0            | 0.6            | 3.2     |
| R-3     | Aqueous    | 0.8          | 0.8          | 28      | 3.6            | 0.6            | 3.9     |
| R-4     | Aqueous    | 1.4          | 4.4          | 3.4     | 3.9            | 0.6            | 3.2     |

Figure 3. Residence time distribution, RTD curves for (A) organic phase and (B) aqueous phase.

Figure 4. Dimensionless RTD curves for (A) organic phase and (B) aqueous phase.
on the droplet diameter due to increasing the velocity of aqueous phase.

Figure 3 (A) and (B) show the curves of residence time distribution for the change of organic phase velocity in (A) and the change of aqueous phase velocity in (B). Apparently, there are slight differences in the two curves of the respective figures. However, the difference had little influence on the evaluation of the degree of axial mixing in the emulsion-flow column. Dimensionless form of residence time distribution curve is required to determine the $Pe$ with equation (10). Therefore, data points in Figure 3 (A) and (B) were converted into dimensionless form to draw curves in Figure 4 (A) and (B). The two curves in each (A) and (B) have a similar peak and shape. The $Pe$ for each of the flow conditions was determined from those curves, and the numbers are shown in Table 1. Interestingly, the values for the four conditions were close even if the flow condition changes greatly. This fact indicates that axial mixing in the column was independent on the velocity of aqueous and organic phases. Furthermore, the degree of axial mixing for the aqueous phase was similar to the organic phase. The low $Pe$ suggests that there was a suppression of axial mixing by the droplet layer.

![Figure 5. Comparison of $Pe_p$ of emulsion-flow column with spray and packed columns.](image)

[15] Blackwell et al.
[16] Ebach & White
[17] Strang & Geankoplis
[18] Miller & King
[19] Kubo et al.
[20] Harlebeck & Geankoplis
[21] Henton & Cavers
[22] Geankoplis et al.
[23] Varfolomeev et al.

This work

Jacques & Vermeulen in [19]

Braun in [20]
4.3 Comparison of \(Pe_p\) numbers with spray and packed columns

Figure 5 shows a plot of reported values of \(Pe_p\) against \(Re_p\) for conventional spray [20-24] and packed [14-19] columns as well as the emulsion-flow column. In the range of \(Re_p\) with values lower than 10, packed columns provide larger \(Pe_p\) than other columns, which reflects the well-known plug flow characteristic of a packed bed. Since droplets in spray columns move more freely than those in packed columns, the \(Pe_p\) of spray columns were lower than those in packed columns. Within the range of \(Re_p\) from 1 to 10, the numbers of \(Pe_p\) for the emulsion-flow column were one or two order of magnitude larger than for the spray columns. The \(Pe_p\) values for emulsion-flow column fell between the scattered area for \(Pe_p\) in packed columns and the spray columns. This fact indicates that the axial-mixing strength in the emulsion phase is in the middle of two extreme flow conditions of packed and spray columns. These results provide a view of the coarse and flexible nature of the emulsion phase when compared to the packed bed consisting of solid material. As described in 0, the emulsion phase is seen as a moving rather than a packed bed, and the flow pattern of aqueous phase strongly depends on the bed structure of droplets. Since the liquid droplets can slightly move or deform, flow paths for the aqueous phase in the emulsion phase change the thickness and shape correspondingly. Such a fluctuation moderately enhances the mixing in the emulsion phase. The mixing strength cannot be as strong as it is in the spray columns for the values of \(Re_p\) lower than 10. Knowing the Peclet numbers for the emulsion-flow column provides a clue to obtain the height per transfer unit, H.T.U. of the operation. Discussion of H.T.U. values for various operating conditions and for other columns is an important subject of our future work.

5. Conclusion

This study discusses the axial mixing in the emulsion phase of the emulsion-flow column. In the emulsion phase, organic liquid flows dropwise in the form of a moving bed of droplets. Aqueous liquid takes different paths to flow through the emulsion phase. Some amount of aqueous liquid flows film-wise to cover droplets of organic liquid. Some aqueous droplets rapidly penetrate the emulsion phase. The Peclet number, a measure of axial mixing in the emulsion-flow column was determined for various flow velocities under unique flow conditions. No significant change was observed in the Peclet numbers of different velocities of aqueous and organic phases. The result indicates that strength of the axial mixing in the emulsion phase is independent of flow velocity. This is probably due to the suppression of mixing in the layer of stacked droplets in the emulsion phase. The Peclet numbers were compared with reported values measured in conventional spray and packed columns, by plotting the droplet Peclet number against the droplet Reynolds number.

The results for the emulsion-flow column fell between those of spray and packed columns. This result clearly shows that moderate axial mixing conditions are attained in the emulsion phase, and this can be attributed to the coarse packing of droplets and the flexibility of the droplets.
References

1) N. Yanase, H. Naganawa, T. Nagano, A. J. Noro, *Anal. Sci.*, 27, 171-176 (2011).
2) T. Nagano, H. Mitamura, Y. Yamashita, N. Yanase, H. Suzuki, H. Naganawa, *Solvent. Extr. Res. Dev., Jpn.*, 21, 111-117 (2014).
3) H. Naganawa, *Bunseki Kagaku*, 66, 797-808 (2017) in Japanese.
4) T. Nagano, H. Naganawa, H. Suzuki, M. Toshimitsu, H. Mitamura, N. Yanase, B. Grambow, *Anal. Sci.*, 34, 1099-1102 (2018).
5) T. Shimogouchi, H. Naganawa, T. Nagano, B. Grambow, Y. Nagame, *Anal. Sci.*, 35, 955-960 (2019).
6) M. Hirayama, T. Goshima, K. Mizuta, S. Nii, *Solvent. Extr. Res. Dev., Jpn.*, 27, 125-133 (2020).
7) P. V. Danckwerts, *Chem. Eng. Sci.*, 2, 1-13 (1953).
8) O. Levenspiel, W. K. Smith, *Chem. Eng. Sci.*, 6, 227-235 (1957).
9) O. Levenspiel. “Chemical Reaction Engineering”, 2nd ed., John Wiley and Sons Ltd (1974).
10) K. B. Bischoff, O. Levenspiel, *Chem. Eng. Sci.*, 17, 245-255 (1962).
11) T. Miyauchi, T. Kikuchi, *Chem. Eng. Sci.*, 30, 343-348 (1975).
12) E. T. Van Der Laan, *Chem. Eng. Sci.*, 7, 187-191 (1958).
13) B. D. Kulkarni, L. K. Doraiswamy, *Catal. Rev. Sci. Eng.*, 22, 431-483 (1980).
14) J. J. Carberry, R. H. Breton, *AIChE J.*, 4, 367-375 (1958).
15) R. J. Blackwell, J. R. Rayne, W. M. Terry, *SPE-1131-G*, 217, 1-8 (1959).
16) E. A. Ebach, R. R. White, *AIChE J.*, 4, 161-169 (1958).
17) D. A. Strang, C. J. Geankoplis, *Ind. Eng. Chem.*, 50, 1305-1308 (1958).
18) S. F. Miller, C. J. King, *AIChE J.*, 12, 767-773 (1966).
19) K. Kubo, T. Aratani, A. Mishima, *Kagaku Kogaku Ronbunshu*, 7, 304-308 (1981) in Japanese.
20) D. E. Hazlebeck, C. J. Geankoplis, *Ind. Eng. Chem. Fundam.*, 2, 310-315 (1963).
21) J. E. Henton, S. D. Cavers, *Ind. Eng. Chem. Fundam.*, 9, 384-392 (1970).
22) C. J. Geankoplis, F. C. Arnold, J. B. Sapp, G. Marroquin, *Ind. Eng. Chem. Fundam.*, 21, 306-311 (1982).
23) B. G. Varfolomeev, V. L. Pebalk, K. S. Chigogidze, R. S. Fernando, N. N. Lan, *Theor. Found. Chem. Eng.*, 35, 377-382 (2001).
24) M. N. Sovilj, B. G. Nikolovski, M. Đ. Spasojević, *Acta Period. Technol.*, 49, 159-168 (2018).