Korean J. Chem. Eng., **15**(3), 324-329 (1998)

REACTIVE EXTRACTION OF LACTIC ACID IN A PACKED COLUMN

Dong Hoon Han* and Won Hi Hong†

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea
*Hyundai Engineering CO., LTD., 45, Pangi-dong, Songpa-gu, Seoul 138-724, Korea
(Received 5 January 1998 • accepted 29 April 1998)

Abstract – Reactive extraction of lactic acid was performed continuously in a packed column. The 0.6 M trioctylamine (TOA)/1-chlorobutane system was used as an extractant. The initial concentration of lactic acid was 10 wt% based on fermentation results. Raschig rings (5 and 7 mm diameter) were used to measure hydrodynamic data. Disperse phase holdup was nearly constant at $V_d<0.8V_{d,f}$. It can be seen that the flooding data obtained from this study were consistent with the literature. NTU and HTU were calculated. NTU varied from 1 to 2 and HTU from 96 cm to 44 cm with variation of V_d. The overall mass transfer coefficients of the continuous phase were nearly constant to 8.98×10^{-5} mol/cm^{2}s with variation of V_d.

Key words: Reactive Extraction, Lactic Acid, Packed Column, Overall Mass Transfer Coefficient, Disperse Phase Holdup, Flooding

INTRODUCTION

Recovery of lactic acid has recently received increasing attention due to its usage as the monomer of biodegradable polymers. Lactic acid was mainly obtained from the fermentation and hydration of lactonitrile synthesized from hydrogen cyanide and acetaldehyde. The fermentation process has received a great deal of attention as an alternative process to the synthetic process. However, the fermentation process needs an economic separation method to compete with the synthetic process because it contains various impurities of fermentation broth [Kertes and King, 1986].

Reactive extraction using long chain aliphatic amines has been studied as an effective and economic separation process of lactic acid. Various basic factors affecting reactive extraction were studied, and mass action models were applied to evaluate equilibrium data of reactive extraction [Kertes and King, 1986; Tamada et al., 1990; Prochazka et al., 1994; Han and Hong, 1996, 1998].

In addition to these basic studies, continuous processes using reactive extraction have been recently investigated to achieve mass production of lactic acid by fermentation process. Likidis and Schugerl [1987] used a centrifugal reactor to perform continuous separation of lactic acid. Reschke and Schugerl [1984] separated lactic acid by a series of mixer-settler type extractors. However, these processes need long settling time due to difficult phase separation, which also requires additional equipment such as a settler and a centrifuge.

The application of columns was proposed to solve these problems. The application of a packed column for reactive extraction provides an easy operation and short operation time. Differential contacts in columns give an easy phase separation and large interfacial area.

In this study, reactive extraction was performed to investigate the feasibility of continuous operation in a packed column. In packed column operation, basic hydrodynamic data such as flooding velocities and disperse phase hold up were measured.

Based on the hydrodynamic data, the reactive extraction of lactic acid was carried out in the packed column. Volumetric overall mass transfer coefficients were calculated by the NTU-HTU method. Overall mass transfer coefficients were obtained by calculating the interfacial area using Kumar and Hartland [1994]'s correlation.

EXPERIMENTAL

1. Materials

Trioctylamine (TOA), a C_8 straight-chain tertiary amine, was purchased from Acros Co. and was used as an extractant without further purification. 1-Chlorobutane, which was used as an active diluent, was purchased from Acros. The 20 wt% lactic acid, obtained from Acros, was diluted to prepare a continuous phase. All reagents were GR grade. The initial concentration of lactic acid was 10 wt% by considering the concentration of lactic acid obtained from fermentation. The 0.6 M TOA/1-chlorobutane was used to extract lactic acid from aqueous solution based on Han and Hong's [1996] study. The 0.6 M TOA/1-chlorobutane extractant has a lower density than an aqueous solution of lactic acid. In the operation of the packed column, this extractant was used as the disperse phase. The properties of the extractants were measured with various instruments, as listed in Table 1. Packed materials used were Raschig rings with 5 and 7 mm diameters. The Raschig ring specifications are listed in Table 2.

†To whom all correspondence should be addressed.
E-mail : whhong@hanbit.kaist.ac.kr

Table 1. Properties of 0.6 M TOA/1-chlorobutane/10 wt% lactic acid

Properties of system	0.6 M TOA/ 1-chlorobutane	10 wt% Lactic acid
γ (dyne/cm)	13.79	13.99
ρ (g/cm^3)	0.859	1.05
μ (cP)	1.301	1.24

Table 2. Specifications of packing used

Specification	5 mm	7 mm
Voidage	0.64	0.68
Packing surface area per unit volume of column (cm^2/cm^3)	5.63	3.04

2. Equipment

A schematic diagram of a reactive extraction apparatus used in this study is presented in Fig. 1. The column part consisted mainly of a glass tube with 50 mm i.d. and 1,000 mm of length, an expanded endpiece with 100 mm i.d., and a tapered section. The height of the packed bed was 950 mm. The packing was supported on a glass bar and larger packings. The distributor was placed at the bottom of the column, consisting of an inverted cone with nine holes of 1 mm diameter. The separator with expanded endpiece and tapered section was 200 mm long. Along the packed bed, four sample ports were made for measuring the concentration profile of lactic acid developed in the bed. All parts of the column were made of glass.

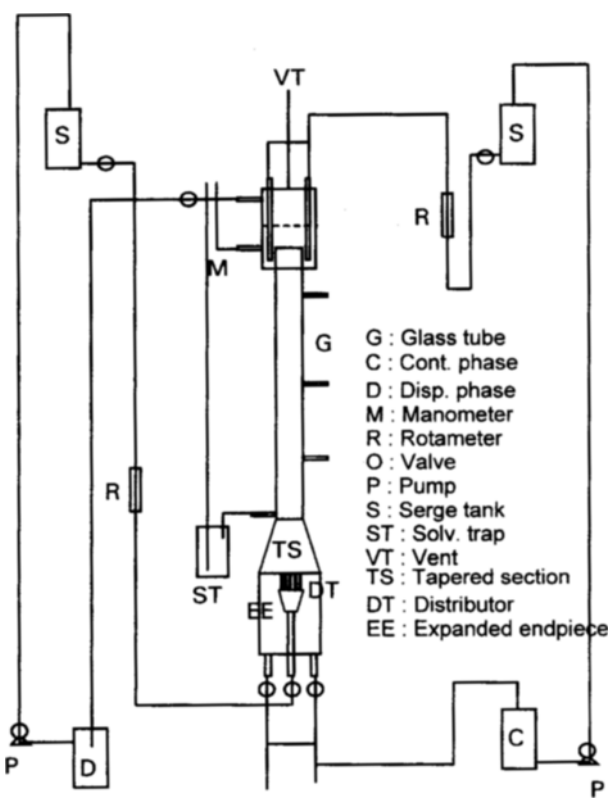

Fig. 1. Schematic diagram of reactive extraction in a packed column.

3. Measurements of Hydrodynamic Data in a Packed Column

The operation of the system was based on a counter-current continuous process. The superficial velocity of the disperse phase was varied from 0.0 cm/s to 0.8 cm/s. For the continuous phase, the superficial velocity was controlled between 0.0 cm/s and 0.41 cm/s. The 10 wt% lactic acid solution was charged into the packed column until the solution reached to the top of it. After the continuous phase in the packed column was charged, both phases were supplied into the packed column at given flow rates. The disperse phase was supplied by the distributor, and the continuous phase was also introduced from the top of the column.

To measure hydrodynamic data, the interface of two phases was controlled so as to be positioned at the joint of a packed bed and a separator while steady state was maintained. Disperse phase holdup was measured by a mass cylinder after steady state was attained. The flooding point was defined as the state that the disperse phase was accumulated in the bottom of the packed bed or that the interface of the two phases in the top of the packed bed was raised abruptly due to the accumulation of the disperse phase. The raffinate concentration of lactic acid was measured in the exit of aqueous phase with time. After steady state, the concentration of lactic acid was measured with packing height.

4. Analysis

The concentration of lactic acid was titrated by 0.1 N NaOH using phenolphthalein as an indicator. The water concentration in the organic phase was analyzed by a Coulometric Karl-Fisher Titrimeter (Coulometric K-F Titrimeter, Model 447, Pittsburgh, PA).

Density was determined by a pycnometer at an operation temperature. A tensiomat, purchased from Fisher scientific, was used to measure the interfacial tension between two phases. The viscosities of materials used were measured by ARES (Advanced rheometric extended system; Rheometric Scientific).

RESULTS AND DISCUSSION

1. Disperse Phase Holdup in a Packed Column

Disperse phase holdup means the fraction of organic phase in the packed column. These values depend mainly on the properties of the applied system, the voidage of the packed bed, and the velocities of the two phases.

In this study, the disperse phase holdup was measured with the superficial velocities of each phase in the packed column of 50.8 mm. The voidage of packing was adjusted by changing packing size (5 and 7 mm). Fig. 2 and 3 show the disperse phase holdup data of the 5 and 7 mm Raschig rings, respectively. As can be seen from Fig. 2 and 3, the disperse phase holdup increased with an increase in the superficial velocity of the disperse phase for both the 5 and 7 mm packings. However, the superficial velocity of the continuous phase had little influence on the disperse phase holdup data. At $V_d<0.8V_{d,f}$, disperse phase holdup was nearly constant. These were similar to the results of work done by Billet and Macowiak [1980] who found that the velocity of the continuous phase has no effect on disperse phase holdup data in the range of $V_d<0.65V_{d,f}$.

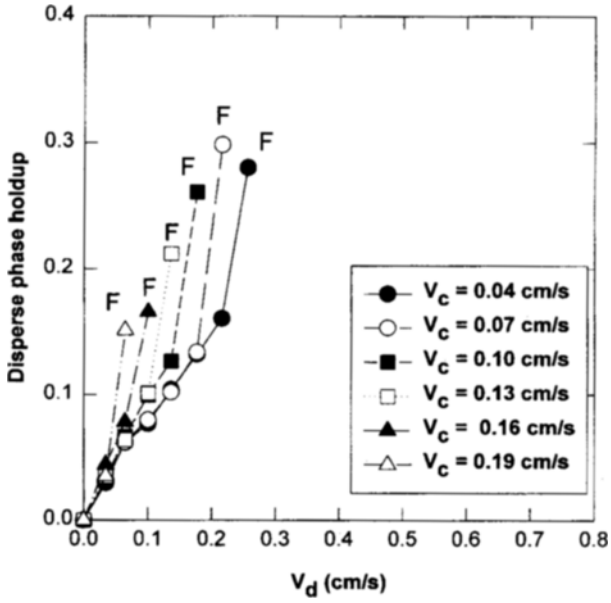

Fig. 2. Disperse phase holdup in a packed column (0.6 M TOA/ 1-chlorobutane, 5 mm Raschig rings).

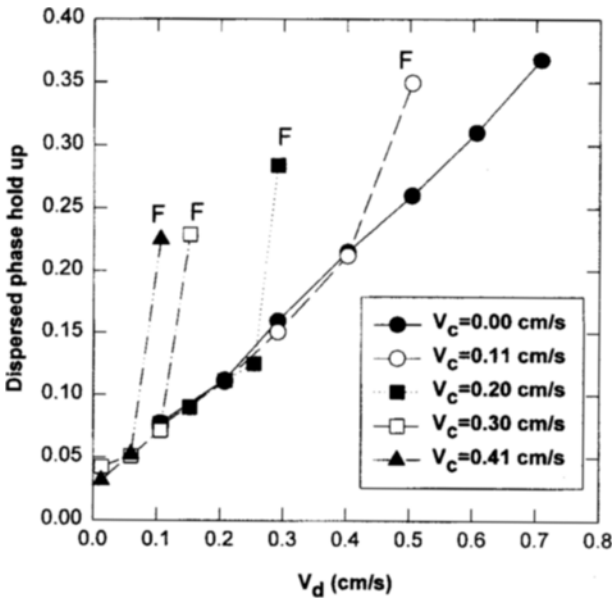

Fig. 3. Disperse phase holdup in a packed column (0.6 M TOA/ 1-chlorobutane, 7 mm Raschig rings).

From Fig. 2 and 3, it was inferred that disperse phase holdup depends largely on the voidage. However, the increase of voidage has a little influence on V_C dependence on disperse phase holdup.

Based on these data, we can calculate the interfacial area between two phases. In the design of a packed column, the diameter of a column can be determined by disperse phase holdup at an operating condition.

2. Flooding in a Packed Column

In flooding conditions, the disperse phase could not pass through the packed bed due to the flow of the continuous phase. In this condition, the disperse phase accumulated at the bottom of the packed section and the interface above the packed section went up abruptly due to the accumulation of the disperse phase. As the result of these phenomena, the flooding makes it impossible to perform a normal operation with the packed column. Flooding conditions depend mainly on the properties of the applied system, the voidage of the packed column and the velocities of two phases. Thus, in countercurrent operation, flooding can be a criterion for setting up operating conditions.

As can be seen in Figs. 2 and 3, the decrease of voidage in the packed column brought about early flooding. Experimental work for determining flooding velocity is shown in Fig. 4, where flooding data were plotted as the following equations [Dell and Pratt, 1951].

$$1+0.835\left(\frac{\rho_d}{\rho_c}\right)^{\frac{1}{4}}\left(\frac{V_d}{V_c}\right)^{\frac{1}{2}}=C\left[\left(\frac{V_c^2 a}{g\varepsilon^3}\right)\left(\frac{\rho_c}{\Delta\rho}\right)\gamma^{\frac{1}{4}}\right]^{-\frac{1}{4}} \tag{1}$$

In this study, C has the values of 0.46 and 0.55 for 5 and 7 mm Raschig rings, respectively. Dell and Pratt [1951] found that the C value increased with increasing packing size, having a value of 0.68 for 12.7 mm Raschig rings. Therefore, it can be seen that the results of this study are consistent with their work.

3. Drop Size and Interfacial Area in a Packed Column

The interfacial area is an important factor for evaluating mass transfer in a packed column. Interfacial area was calculated from disperse phase hold up and the drop size of the disperse phase. However, it is difficult to measure the real drop size of the disperse phase. In the packing section, the drop size is not constant due to the breakage and the coalescence of drops. Thus, the average drop size was introduced as follows [Kumar and Hartland, 1994].

$$d_{32}=C'\left(\frac{\gamma}{\Delta\rho g}\right)^{0.5} \tag{2}$$

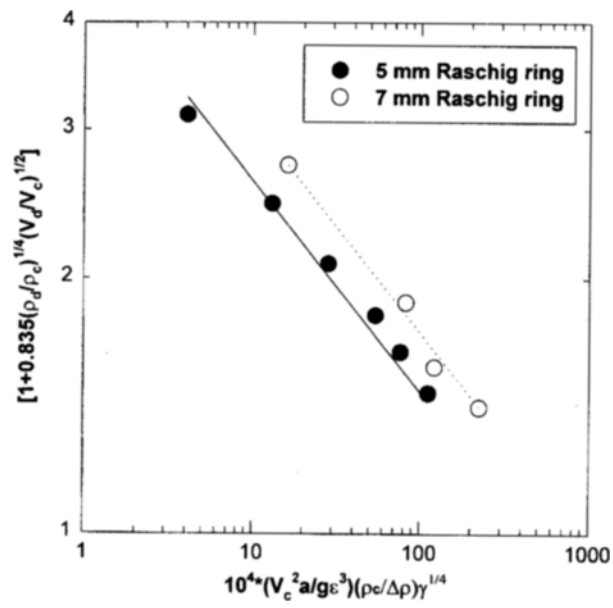

Fig. 4. Flooding velocities using 5 and 7 mm Raschig rings in a packed column (0.6 M TOA/1-chlorobutane/water).

In this equation, the value of C' was characterized by various constant values or dimensionless groups. In this study, Kumar and Hartland [1994]'s correlation was used. The value of C' was defined as follows.

$$C' = C_1 \left[\frac{\mu_w g^{1/4} \rho_w}{\Delta\rho^{1/4} \gamma^{3/4} \rho_d} \right]^{0.19} \tag{3}$$

The values of parameter, C_1, are 2.54, 2.24 and 3.13 for no mass transfer, the mass transfer from the continuous phase to the disperse phase, and the mass transfer from the disperse phase to the continuous phase, respectively.

Based on above equations, the interfacial area was defined as follows [Billet et al., 1985].

$$a = \frac{6\varepsilon\phi}{d_{32}} \tag{4}$$

By Eqs. (2), (3) and (4), interfacial areas were calculated with V_d and summarized in Table 3.

4. Mass Transfer Operation in a Packed Column

In this study, the initial mole fraction of lactic acid was 0.022 (10 wt%) and the exit mole fraction of lactic acid was assumed as 0.002 to obtain 90% extraction efficiency. Operating conditions were determined based on hydrodynamic data and specification of product. Operating conditions are summarized in Table 4. Mass transfer operation was performed in a packed column with 7 mm Raschig rings.

As can be seen from Fig. 5, the exit concentration of lactic acid in the continuous phase was nearly constant after 20 min of extraction. Effective extraction was performed by the increase of V_d. We found that reactive extraction came to steady state after 25 min. Steady state was obtained quickly due to the reactivity between the amine and the lactic acid.

Fig. 6 shows the profile of the concentration of lactic acid in the continuous phase with a variation of packing height. In Fig. 5 and 6, the initial concentrations of lactic acid were nearly constant for given flow rates of the disperse phase. However, the exit concentrations of lactic acid were reduced for an increase of V_d.

Based on these data, operating lines were drawn in Fig. 7. The equilibrium line can be expressed by a modified mass action model [Han and Hong, 1996].

Table 3. Interfacial areas with variation of V_d (d_{32}=0.28 cm)

V_d (cm/s)	Disperse phase holdup	Interfacial area (cm^2/cm^3)
0.11	0.046	0.66
0.15	0.067	0.96
0.20	0.088	1.27
0.24	0.109	1.58

Table 4. Operation conditions in 7 mm Raschig ring packed column

Experiment	V_d (cm/s)	V_c (cm/s)
1	0.11	0.11
2	0.15	0.11
3	0.20	0.11
4	0.24	0.11

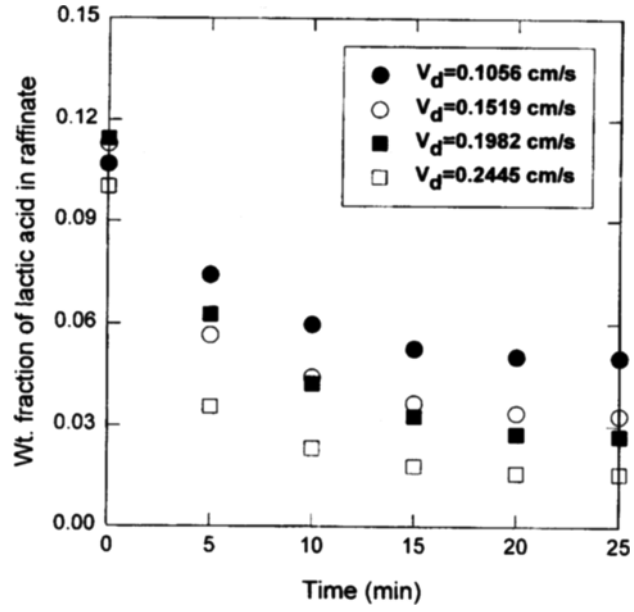

Fig. 5. Variation of raffinate concentration of lactic acid at column exit with variation of extraction time.

In this figure, it was assumed that molar flow rates of both phases were nearly constant. The operating line was expressed by a mass balance as follows:

$$y = \frac{L}{D} x + y_b - \frac{L}{D} x_b \tag{5}$$

The slopes of the operating lines decreased with an increase of velocity of the disperse phase based on the above equation.

We calculated the volumetric overall mass transfer coefficient of the continuous phase. An equilibrium curve and operating line were integrated as a form of $1/(y-y^*)$ over the range

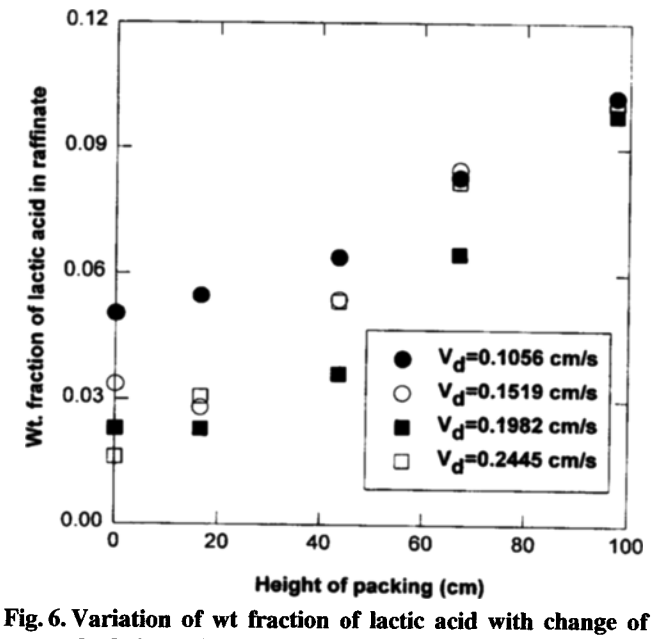

Fig. 6. Variation of wt fraction of lactic acid with change of the height of packing.

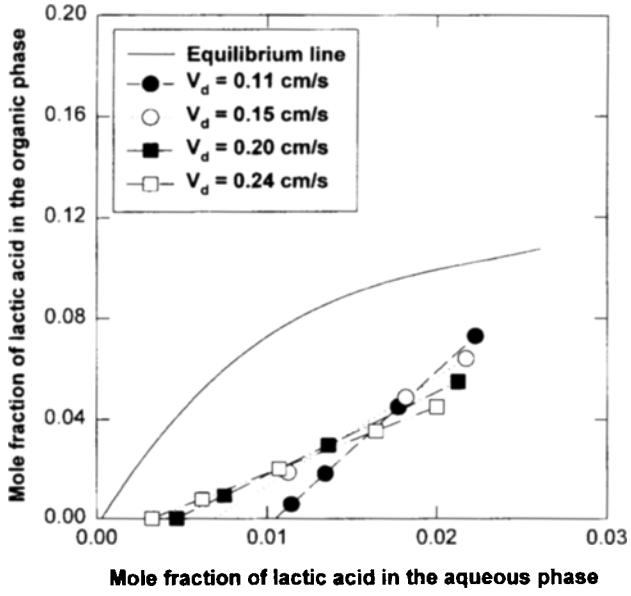

Fig. 7. Change of operating lines with variation of V_d.

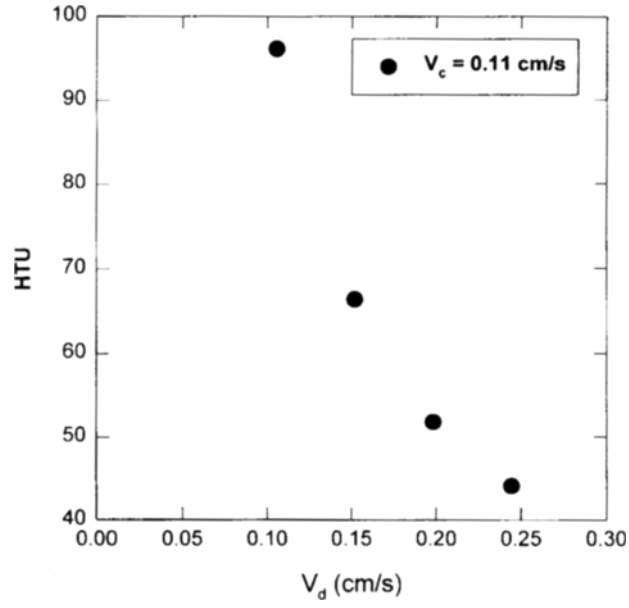

Fig. 9. Effect of velocity of disperse phase on HTU.

of operating composition, and NTU was calculated with a variation of V_d. Using Z=NTU×HTU, HTU was evaluated with the change of V_d.

As can be seen from Fig. 8, NTU increased from 1 to 2 due to the increase of V_d. Fig. 9 shows that HTU decreased from 96 cm to 44 cm with increasing V_d. These results can be explained as follows. As shown in Table 3, the disperse phase holdup was increased with increasing V_d. With the increase of disperse phase holdup, the interfacial area also increased based on Eq. (4). Therefore, the efficiency of mass transfer and NTU was increased due to the increase of interfacial area per unit packed section. On the other hand, HTU decreased with the increase of V_d.

Based on values of HTU, overall mass transfer coefficients

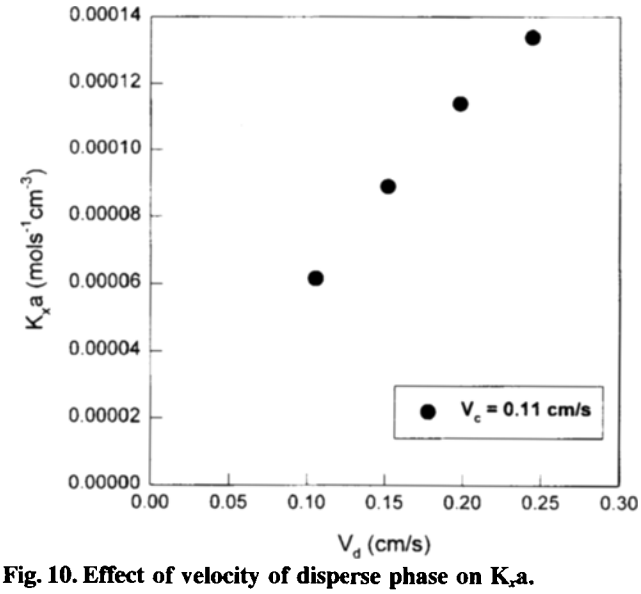

Fig. 10. Effect of velocity of disperse phase on K_xa.

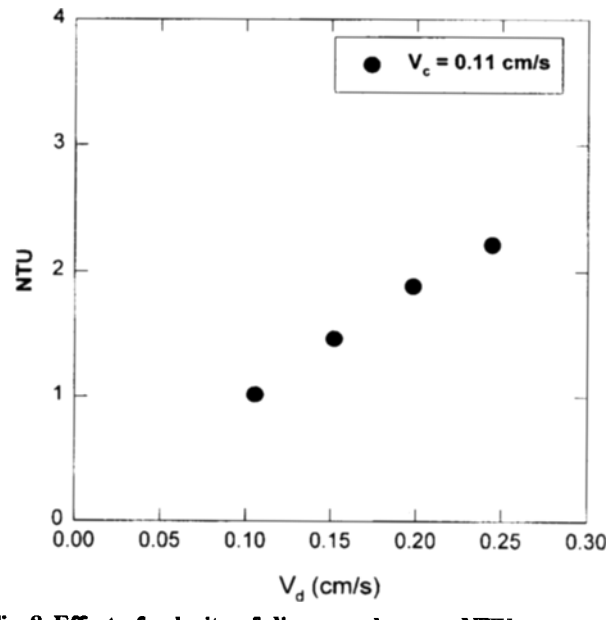

Fig. 8. Effect of velocity of disperse phase on NTU.

of the continuous phase (K_xa) were obtained. Fig. 10 shows that the volumetric overall mass transfer coefficients of the continuous phase increased with an increase of V_d. The K_xa is not constant for the applied system due to the variation of interfacial area as described above.

Using the interfacial area in Table 3, overall mass transfer coefficients of the continuous phase (K_x) were shown in Fig. 11. As can be seen from Fig. 11, overall mass transfer coefficients of the continuous phase are nearly constant to 8.98×10^{-5} mol/cm^{2}s with variation of V_d.

CONCLUSION

Reactive extraction was performed in a packed column. The 5 and 7 mm Raschig rings were used to measure the hydrodynamic data. The holdup of the disperse phase increased with

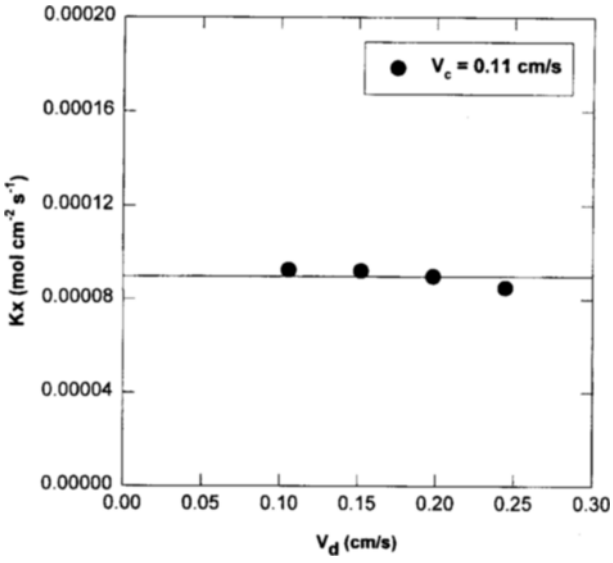

Fig. 11. Overall mass transfer coefficients (K_x) with variation of V_d.

an increase of superficial velocity of the disperse phase for the 5 and 7 mm packings. However, the superficial velocity of the continuous phase had little influence on the holdup data of the disperse phase. At V_d<0.8 $V_{d,f}$, the holdup of the disperse phase was nearly constant.

Flooding data were plotted by Dell and Pratt's [1951] equation of dimensionless groups. In this experiment, C has the values 0.46 and 0.55 for 5 and 7 mm Raschig rings, respectively. It can be seen that the flooding data obtained from this study are consistent with the literature.

We calculated the volumetric overall mass transfer coefficients of the continuous phase. The volumetric overall mass transfer coefficient of the continuous phase increased with an increase of V_d. The NTU varied from 1 to 2 and the HTU varied from 96 cm to 44 cm with a variation of V_d.

Considering the interfacial area that was calculated by the correlation, the overall mass transfer coefficients of the continuous phase were calculated. The overall mass transfer coefficients of the continuous phase were nearly constant to 8.98 $\times 10^{-5}$ mol/cm^{2}s with a variation of V_d.

ACKNOWLEDGEMENT

This work was supported by Korea Advanced Institute of Science and Technology and Korean Science and Engineering Foundation, under contract No. KOSEF 951-1104-050-2.

NOMENCLATURE

μ_w : viscosity of water [cP]
$\Delta\rho$: density difference between continuous phase and disperse phase
ρ_d : density of disperse phase [g/cm^3]
ρ_c : density of continuous phase [g/cm^3]
γ : interfacial tension [dyne/cm]
g : gravity force [cm/s^2]
V_c : superficial velocity of continuous phase [cm/s]
V_d : superficial velocity of disperse phase [cm/s]
ρ_w : density of water [g/cm^3]
ε : voidage
a : interfacial area [cm^2/cm^3]
d_{32} : sauter diameter [cm]
ϕ : disperse phase holdup
D : molar flow rate of disperse phase [mol/s]
L : molar flow rate of continuous phase [mol/s]
x : mole fraction of continuous phase
y : mole fraction of disperse phase
x_b : mole fraction of disperse phase in bottom of column
y_b : mole fraction of continuous phase in bottom of column

REFERENCES

Billet, R. and Mackowiak, J., "Hydraulic Behavior and Mass Transfer in an Extraction Column with Stacked Packings", *Ger. Chem. Eng.*, **3**, 234 (1980).

Billet, R., Mackowiak, J. and Pajak, M., "Hydraulics and Mass Transfer in Filled Tube Columns", *Chem. Eng. Process*, **19**, 39 (1985).

Dell, F. R. and Pratt, H. R. C., "Part I : Flooding Rates for Packed Columns", *Trans. Instn. Chem. Engrs.*, **29**, 89 (1951).

Han, D. H. and Hong, W. H., "Reactive Extraction of Lactic Acid with Trioctylamine/Methylene Chloride/n-Hexane", *Sep. Sci. Technol.*, **31**(8), 1123 (1996).

Han, D. H. and Hong, W. H., "Water Enhanced Solubilities of Lactic Acid in Reactive Extraction Using Trioctylamine/Various Active Diluents Systems", *Sep. Sci. Technol.*, **33** (2), 1123 (1998).

Likidis, Z. and Schugerl, K., "Recovery of Penicillin by Reactive Extraction in Centrifugal Extractors", *Biotech. Bioeng.*, **30**, 1032 (1987).

Kertes, A. S. and King, C. J., "Extraction Chemistry of Fermentation Product Carboxylic Acids", *Biotech. Bioeng.*, **28**, 269 (1986).

Kumar, A. and Hartland, S., "Prediction of Drop Size, Dispersed-Phase Holdup, Slip Velocity and Limiting Throughputs in Packed Extraction Columns", *Trans I Chem E, part A*, **72**, 89 (1994).

Prochazka, J., Heyberger, A., Bizek, V., Kousova, M. and Bolaufova, E., "Amine Extraction of Hydroxycarboxylic Acids. 2. Comparison of Equilibria for Lactic, Malic, and Citric Acids", *Ind. Eng. Res. Chem.*, **33**, 1565 (1994).

Reschke, M. and Schugerl, K., "Reactive Extraction of Penicillin III: Kinetics", *Chem. Eng. J.*, **28**, B21 (1984).

Tamada, J. A., Kertes, A. S. and King, C. J., "Extraction of Carboxylic Acids with Amine Extractants. 1. Equilibrium and Law of Mass Action Modeling", *Ind. Eng. Res. Chem.*, **29**, 1319 (1990).