SOLVENT EXTRACTION OF HYDROCHLORIC ACID BY LONG-CHAIN ALKYLAMINE IN A STIRRED TRANSFER CELL

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Authors indicated previously that the interfacial rate process was significant in low concentration range of long-chain alkylamine for the extraction of hydrochloric acid in a horizontal rectangular channel contactor. This paper is concerned with the effects of interfacial rate process for the same extraction system in a stirred transfer cell.

It was found from the analysis of the initial rate of extraction that the interfacial rate process was significant in the range of concentration of long-chain alkylamine lower than 0.1 mol/l, while in the range of concentration of the amine higher than 0.2 mol/l the interfacial rate process was assumed to be an instantaneous irreversible reaction.

These experimental results were interpreted by the diffusion model, taking account of the interfacial rate process expressed by (1, 2) order irreversible reaction with respect to the interfacial concentrations of hydrochloric acid and long-chain alkylamine.

Introduction

Liquid surfactant membranes containing mobile carriers, such as long-chain alkylamine, macrocyclic polyether or chelating agents, have attracted special interest recently, as they offer a new and effective method to separate and to concentrate heavy metal ions from waste-water¹¹). These processes are generally performed at low concentration of carriers because they are rather expensive. Long-chain alkylamine has been used to extract heavy metal ions or acids also by conventional means⁵). To investigate the extraction mechanism of acids by long-chain alkylamine the extraction rate has been measured using various equipment, such as a diffusion cell²), a laminar jet apparatus⁷), a stirred transfer cell⁶), and a single-drop method⁴). Many of these investigations were carried out at rather high concentration of long-chain alkylamine, where the rate of extraction was mostly assumed to be controlled by the diffusion near the interface. There have been few references concerned with investigation in low concentration ranges where a separation process utilizing liquid surfactant membranes is performed.

Authors indicated in the previous paper⁸) that an interfacial rate process is significant in low concentration ranges of long-chain alkylamine and hydro-

chloric acid.

This paper concerns the effects of interfacial rate process on the extraction rate of hydrochloric acid by long-chain alkylamine using a stirred transfer cell, in which the flow pattern near the interface was different from that of the horizontal rectangular channel contactor described in the previous paper.

1. Theory

Since the reaction between hydrochloric acid and long-chain alkylamine is rapid and the solubility of long-chain alkylamine in aqueous solution is very small, it follows that amine salt is likely to be formed near or at the interface between aqueous and organic phases. Furthermore, it was found from the measurement of interfacial tension³) that long-chain alkylamine and its salt behave like surface-active agent in that they may be concentrated at the interface by adsorption. As a result, the hydrochloric acid extracted encounters three separate resistances, due to diffusion through the aqueous phase, across the interface and through the organic phase, respectively. The interfacial resistance may include the adsorption of long-chain alkylamine to the interface, the reaction between hydrochloric acid and adsorbed long-chain alkylamine to form amine salt, and desorption of amine salt from the interface. Although the precise rate equation for these interfacial rate processes are quite complicated and difficult to obtain, it is considered to be expressed as

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Fig. 1 Sh as a function of T

$$R = k_r C_{Ai}^m C_{Bi}^n \quad (1)$$

where C_{Ai} and C_{Bi} are the concentrations of hydrochloric acid in the aqueous phase adjoining the interface and that of long-chain alkylamine in the organic phase adjoining the interface, m and n are the apparent orders of the interfacial reaction and k_r is the rate constant.

Since the extraction rate in a stirred transfer cell is rather slow, a pseudo-steady state will be reached in each instance; then the extraction rate of hydrochloric acid can be expressed as

$$N_A = k_A(C_A - C_{Ai}) = k_B(C_B - C_{Bi}) = k_r C_{Ai}^m C_{Bi}^n \quad (2)$$

where k_A and k_B are the mass transfer coefficients in each phase. The following equations are obtained from the mass balance in a stirred transfer cell:

$$-V_A \frac{dC_A}{dt} = k_A S(C_A - C_{Ai}) \quad (3a)$$

$$-V_B \frac{dC_B}{dt} = k_B S(C_B - C_{Bi}) \quad (3b)$$

where V_A and V_B are the volumes of each phase and S is the interfacial area. The basic equations, (2), (3a) and (3b), are numerically solved to obtain a time-course of the concentrations of hydrochloric acid and long-chain alkylamine when the apparent orders of the interfacial reaction, the reaction rate constant, mass transfer coefficients in each phase, the volumes of each phase, and the interfacial area are given.

The basic equations are rewritten using dimensionless variables to compare them with the theoretical results for the horizontal rectangular channel contactor reported in the previous paper⁸.

$$Y_A = Y_{Ai} + \alpha^{m-1} M_T Y_{Ai}^m Y_{Bi}^n \quad (4)$$

$$Y_B = Y_{Bi} + \alpha^m \beta_T M_T Y_{Ai}^m Y_{Bi}^n \quad (5)$$

$$-\frac{dY_A}{dT} = Sh^*(Y_A - Y_{Ai}) \quad (6)$$

and Y_B is also expressed as

$$Y_B = 1 - \alpha v(1 - Y_A) \quad (7)$$

where the dimensionless variables are

$$\left. \begin{aligned} Y_A &= C_A/C_{A0} & Y_{Ai} &= C_{Ai}/C_{A0} \\ Y_B &= C_B/C_{B0} & Y_{Bi} &= C_{Bi}/C_{B0} \\ \alpha &= C_{A0}/C_{B0} & \beta_T &= k_A/k_B \\ M_T &= k_r C_{B0}^{m+n-1}/k_A & T &= (S/V_A)^2 D_A t \\ Sh^* &= (V_A/S)k_A/D_A & v &= V_A/V_B \end{aligned} \right\} \quad (8)$$

As before, Eqs. (4)–(7) are numerically solved to obtain the dimensionless average extraction rate, Sh , from the following equation:

$$Sh = \frac{Sh^*}{T} \int_0^T (Y_A - Y_{Ai}) dT \quad (9)$$

When the interfacial reaction rate is assumed to be instantaneous, that is, $M_T = \infty$, Y_{Ai} can be considered negligibly smaller than Y_A in the case of $\alpha\beta_T < 1$. In this case, Eq. (6) can be analytically integrated with $Y_{Ai} = 0$, and then Eq. (9) also can be integrated to obtain the expression for Sh . When $M_T = \infty$ and $\alpha\beta_T > 1$, Y_{Bi} can be considered negligibly smaller than Y_B . Therefore, a mathematical manipulation with respect to Y_B and Y_{Bi} , in a similar manner as for Y_A and Y_{Ai} , leads to the expression for Sh . These are as follows:

$$Sh = (1/T)\{1 - \exp(-Sh^*T)\} \quad (\alpha\beta_T < 1) \quad (10)$$

$$Sh = (1/\alpha T)[1 - \exp\{-(Sh^*/\beta_T)T\}] \quad (\alpha\beta_T > 1) \quad (11)$$

It was shown in the previous paper that $m=1$, $n=2$ and $k_r = 5.4 \times 10^6 \text{ cm}^7/\text{mol}^2 \cdot \text{sec}$ for the extraction of hydrochloric acid by long-chain alkylamine in the rectangular channel contactor. The numerical analysis was done by using these values, and the results are shown as full lines in Fig. 1. The dotted lines in Fig. 1 are the calculated values from Eqs. (10) and (11), where the extraction rate is controlled only by the diffusion step in the bulk phase. Figure 1 includes the case of $\alpha\beta_T = 0.1$, where the interfacial concentration Y_{Ai} is negligibly small, and the case $\alpha\beta_T = 10$, where

Fig. 2 Effect of Sh^* on Sh_0

Fig. 3 Relationship between Sh_0 and $\alpha\beta_T$

Fig. 4 Experimental apparatus

Y_{Ai} is fairly large and cannot be disregarded. In Fig. 2, the effect of the stoichiometric parameter, $\alpha\beta_T$, on the initial extraction rate, Sh_0 , is shown for the case of $M_T = \infty$. These relationships between Sh_0 and $\alpha\beta_T$ are given for $T \rightarrow 0$ from Eqs. (10) and (11) as follows:

$$Sh_0 = Sh^* \quad (\alpha\beta_T < 1) \quad (12)$$

$$Sh_0 = Sh^* / \alpha\beta_T \quad (\alpha\beta_T > 1) \quad (13)$$

Sh_0 at $M_T = \infty$ corresponds to the maximum extraction rate at a certain Sh^* , which is specified by the hydrodynamics near the interface.

Since Sh varies gradually with T as shown in Fig. 1, the experimental results are analysed only for the initial rate of extraction. Figure 3 shows the relationship between Sh_0 and $\alpha\beta_T$, which were obtained numerically from the basic equations for various values of M_T . It is seen that Sh_0 is nearly equal to Sh^* in the case of $M_T > 10^2$, except for the range of $3 > \alpha\beta_T > 0.5$, and that Sh_0 decreases with increase of $\alpha\beta_T$, especially in the range of $\alpha\beta_T > 1$.

2. Apparatus and Method of Experiment

The stirred transfer cell used is shown in Fig. 4, and it is similar to that of Lewis⁹⁾, but is slightly modified. The inner diameter of the vessel was 70 mm and the length of the stirrer blades was 30 mm for the upper phase and 25 mm for the lower one. All metal parts in contact with reagent solutions were made of stainless steel. An electric conductivity cell was installed in the lower part of the vessel to follow the concentration change of hydrochloric acid in the aqueous phase. The transfer cell was situated within a bath through which water maintained at $30.0 \pm 0.1^\circ\text{C}$ could be circulated.

Aqueous solutions were prepared by diluting commercial GR grade hydrochloric acid with ion-exchanged water. Amberlite LA-2 (commercial name of *N*-lauryl-(trialkylmethyl) amine, shortened to amine hereinafter) was used as the long-chain alkylamine. Amine was first purified by the same method as described elsewhere¹⁰⁾, and then was diluted with commercial GR grade *n*-hexane to the required concentration.

Aqueous phase was first introduced to the transfer cell from a buret fitted with constant temperature jacket, and then the organic solution was placed carefully in such a way as not to disturb the interface. The two stirrers were driven independently with two motors, and the stirring speeds were checked with a stroboscope.

3. Results and Discussion

Provided that the interfacial rate process is approximated by (m, n) order irreversible reaction respect to the interfacial concentrations of hydrochloric acid and amine, the dimensionless coefficient of average extraction rate of hydrochloric acid $Sh (= N_A V_A / SD_A C_{A0})$ is related to the ratio of initial concentrations $\alpha (= C_{A0} / C_{B0})$, the ratio of mass transfer coefficients at each phase $\beta_T (= k_A / k_B)$ and $M_T (= k_r C_{B0}^{m+n-1} / k_A)$ which contains the interfacial reaction rate constant and the concentration of amine. Therefore, the extraction

Table 1 Experimental conditions and values of Sh_0 and M_T

Run	$C_{A0} \times 10^3$ [mol/cm ³]	$C_{B0} \times 10^3$ [mol/cm ³]	α [—]	Sh_0 [—]	M_T [—]
5	0.0200	0.0119	1.68	98	0.25
1	0.0100	"	0.84	131	"
2	"	"	"	124	"
6	0.0200	0.0170	1.18	137	0.50
10	"	"	"	"	"
11	0.0140	"	0.82	146	"
7	0.0100	"	0.59	141	"
16	"	"	"	182	"
18	0.0326	0.0300	1.09	215	1.6
17	0.0202	"	0.68	254	"
20	0.0142	"	0.47	254	"
19	0.0101	"	0.34	281	"
21	0.1009	0.0911	1.11	250	15
22	0.0571	"	0.63	333	"
25	"	"	"	346	"
29	0.0326	"	0.36	422	"
24	0.0163	"	0.179	422	"
28	0.1009	0.201	0.50	471	70
26	0.0326	"	0.162	602	"
27	0.0163	"	0.081	576	"
30	0.0790	0.344	0.24	580	194

rate in a stirred transfer cell was measured with various α and C_{B0} , as shown in Table 1. All the experiments were carried out at a stirring speed of 80 rpm.

Figure 5 shows the typical results of time-course of acid concentration. The tangents of these curves correspond to the rate of extraction. It can be seen from Fig. 5 that in the case of $C_{B0} < 0.1 \times 10^{-3}$ the extraction rate varies with either α or C_{B0} : even at equal C_{B0} the extraction rate increases with decrease of α , and even at nearly equal α the extraction rate increases with C_{B0} . In the case of $C_{B0} > 0.2 \times 10^{-3}$, however, the initial rates of extraction were scarcely affected by α and C_{B0} , as shown in Fig. 5. It was assumed that these were the upper limit of the extraction rate, which corresponds to the line with $M_T = \infty$ in Fig. 3. Therefore, Sh^* was determined from these data to be 600, and then k_A was calculated as 3.0×10^{-3} cm/sec from Eq. (8).

The values of Sh_0 obtained by experiments and the results of numerical analysis based on the above-mentioned mathematical model are superimposed in Fig. 6 with $Sh^* = 600$. Although β_T is to be obtained virtually as the ratio of the mass transfer coefficients in each phase, as defined by Eq. (8), it was calculated assuming either $\beta_T = \sqrt{D_A/D_B}$ or $\beta_T = D_A/D_B$ because k_B could not be determined experimentally. The values of D_A and D_B used were 3.87×10^{-5} cm²/sec⁽¹⁾ and 1.41×10^{-5} cm²/sec, respectively, and D_B was measured by capillary-cell method⁽²⁾. Since m , n and k_v had been obtained in a rectangular channel contactor as shown previously in this paper, the values of M_T were calculated from Eq. (8) and are shown in Table 1. From Figs. 6(a) and 6(b), the experimental results are more likely to agree with the diffusion model that takes account of the interfacial

Fig. 5 Typical results of experiment (a) $\beta_T = \sqrt{D_A/D_B}$ (b) $\beta_T = D_A/D_B$ **Fig. 6** Correlation of extraction performance

reaction with $\beta_T = \sqrt{D_A/D_B}$ than with that where $\beta_T = D_A/D_B$. Although this is likely to correspond to the surface renewal model with equal fractional rates of renewal in both phases, further consideration is required. The data of much lower C_{B0} are rather deviated from the simulated lines: this may be ascribed presumably to the effects of reversible reaction or to the variation of interfacial rate process at extremely low C_{B0} .

Conclusion

The extraction of hydrochloric acid by Amberlite LA-2 was carried out in a stirred transfer cell. It was found from the analysis of the initial rate of extraction that the interfacial rate process was significant in the range of amine concentration lower than 0.1 mol/l, while in the range higher than 0.2 mol/l the interfacial rate process was assumed to be an instantaneous irreversible reaction. These experimental results were interpreted by a diffusion model that takes account of the interfacial rate process expressed by (1, 2) order irreversible reaction respect to the interfacial concentrations of hydrochloric acid and amine.

Nomenclature

C	= concentration	[mol/cm ³]
D	= diffusion coefficient	[cm ² /sec]
k	= mass transfer coefficient	[cm/sec]
k_r	= interfacial rate constant	[mol ^{1/2} /cm ² ·sec]
M_T	= dimensionless reaction rate constant ($= k_r C_{B0}^{m+n-1}/k_A$)	[—]
N	= rate of extraction	[mol/cm ² ·sec]
S	= interfacial area	[cm ²]
Sh^*	= Sherwood number based on the aqueous-phase mass transfer coefficient	[—]
Sh_0	= Sherwood number based on the initial extraction rate	[—]
t	= extraction period	[sec]

V	= volume of liquid phase	[cm ³]
v	= ratio of liquid volume ($= V_A/V_B$)	[—]
α	= ratio of initial concentrations ($= C_{A0}/C_{B0}$)	[—]
β_T	= ratio of mass transfer coefficients ($= k_A/k_B$)	[—]

<Subscripts>

A	= hydrochloric acid or aqueous phase
B	= amine or organic phase
i	= at the interface

<Superscripts>

m	= order of reaction with respect to hydrochloric acid
n	= order of reaction with respect to amine

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